Analysis of alternatives for chloroplatinates

In co-operation with:

Dr. Martin Lok

Dr. Hubert Schmidbaur

Precious Metals and Rhenium Consortium

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Signed by: Jens Tørsløv

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Prepared for	Precious Metals and Rhenium Consortium
Represented by	France Capon

Project manager	Jens Tørsløv
Quality supervisor	Peter Christian Kortegaard

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APPENDICES

1 List of abbreviations

To be developed further

ClPts	Chloroplatinates. In this context chloroplatinates means chlorinated platinum compounds where the chlorine atom is covalently bound to a platinum atom. Examples are hexachloroplatinic acid, dipotassium and diammonium hexachloroplatinate and dipotassium tetrachloroplatinate.
CPA	Chloroplatinic acid
CVD	Chemical Vapour Deposition
DTCP	Dipotassium tetrachloroplatinate(II)
PMC	Precious Metals and Rhenium Consortium
Pt	Platinum
tpa	Tonnes per annum

2 Executive summary

Chloroplatinates are known as potent respiratory sensitisers (Resp. Sens. 1A) and for this reason within the scope of regulation under REACH, possibly under the authorisation title.

The present Analysis of Alternatives identifies alternatives to chloroplatinates in the manufacture and refining processes as well as in the main industrial uses in catalysis and plating. Where relevant, the possible substitution of chloroplatinates is analysed considering the technical and economic consequences as well as the expected human health benefits.

Chloroplatinates are central in all manufacturing and recycling of platinum. They are the product of extraction, refining and recycling processes of platinum and there are no known alternatives to the currently applied technology with hydrochloric acid and chlorine. This inevitably leads to chlorinated platinum compounds, and chloroplatinates are therefore the starting point of all platinum chemistry. Chloroplatinates are intermediates for the manufacture of other platinum and platinum compounds, including those that have been identified as alternatives in this report.

Platinum is mainly used in automotive catalysts, but also in catalysts for industrial purposes. Other industrial uses include plating and pharmaceutical uses. The main non-industrial uses are jewellery and investment.

Chloroplatinates are no longer used in the EU for manufacture of exhaust catalysts by the automotive industry. Today this production is based on alternative platinum compounds. In contrast, industrial catalysts used in refining (reforming catalysts) and chemistry (dehydrogenation catalysts) depend on chloroplatinates as precursor. Although it may be possible to develop techniques based on alternative platinum compounds this will require intensive research, development and testing. It is expected that shifting to other production techniques will require extensive investments in R&D, pilot scale testing, production equipment and training. Moreover it will require more than 10 years before an alternative is available for industrial scale production. Since the performance benefit of the possible alternative solutions are not obvious the incentive for industry to invest in this is small.

The reason for wanting to phase out the use of chloroplatinates is their classification as respiratory sensitisers and the potential risk to workers that may be exposed. It is estimated that in the EU about 120-140 workers are currently working with chloroplatinates, mainly in catalysts production.

Platinum catalysts are also used for production of organosilicon compounds, which are widely used a.o. as sealants and adhesives in the construction industry. Chloroplatinates were previously used as catalysts in hydrosilylation processes, but have in the EU been almost fully replaced by alternatives.

Platinum is used as plating material due to its resistance to heat and corrosion, e.g. in electronic equipment. Chloroplatinates were earlier commonly used as platinum source in plating processes but have been replaced by alternatives. Today, chloroplatinates are used only for specialised electroplating, where no alternative is suitable. This is, however, a niche market involving a low number of workers.

Overall, chloroplatinates are already phased out from some of the main use areas: automotive catalyst, hydrosilylation catalysts and plating. The remaining areas include industrial catalysts where no alternative solutions to use of chloroplatinates are currently available. The possible alternatives are not suitable neither from a technical, nor from an economical point of view. Moreover the benefit in terms of reduced risk to workers seems limited.

3 Introduction

The Precious Metals and Rhenium Consortium (PMC) has initiated this Analysis of Alternatives for four specific substances within the group of Chloroplatinates (ClPts): chloroplatinic acid (CPA), diammonium and dipotassium hexachloroplatinate and dipotassium tetrachloroplatinate. These substances play a key role in the refining and use of platinum in catalysts, plating and pharmacology. However, ClPts are potent respiratory sensitizers and within the scope of being possible future entries on the REACH candidate list for authorisation. For this reason, the PMC Consortium has initiated the development of this AoA with the purpose to identify and analyse possible alternatives to ClPts. The ClPt substances are used as intermediates in the production of other platinum substances. Another main use is as precursor in the production of catalysts. Moreover ClPts were earlier commonly used in plating baths, but today ClPts have been replaced by alternative platinum compounds. In general, over a 20-year period, the relative share of chloroplatinates vs. non-chlorinated platinum compounds in sales have gone down by over 75%.

The present analysis is intended to give input to the Risk Management Option Analysis developed by the PMC with the purpose to proactively identify the needs of possible future regulatory initiatives on ClPts.

The report has been prepared by a team led by DHI and with key contributions from Professor Dr. H. Schmidbaur Emeritus; Department of Chemistry, Technical University of Munich, and expert in catalyst chemistry, Dr. Martin Lok. The team has been supported by a group of experts from members of the PMC hereinafter referred to as the “PGM Work Group”.

4 Scope

The current picture of the uses of ClPts within the scope of the current report is summarised in the table below. The information on uses is based on the current knowledge from the REACH registration process supplemented with information from relevant associations and companies covering manufacturers and downstream users of ClPts. The ClPts in focus in this report are listed in Table 4.1. The uses discussed in this report include areas where ClPt are currently used as well as previous important uses where ClPt have been replaced by alternatives. This includes uses that still may be significant outside the EU.

Table 4.1 Overview of chloroplatinates that will be registered by PMC by the May 2018 deadline and are the main focus in the current report

Substance name	**CAS No.**
Hexachloroplatinic acid (IV) (and hydrate)	16941-12-1 (26023-84-7 or 18497-13-7)
Dipotassium hexachloroplatinate (IV)	16921-30-5
Dipotassium tetrachloroplatinate (II)	10025-99-7
Diammonium hexachloroplatinate (IV)	16919-58-7

Table 4.2 Overview of uses of chloroplatinates.

Chloroplatinates are used in refining and recycling of platinum as well as intermediates for all other platinum compounds. The main use is in the catalysts sector. Surface treatment was earlier an important end use.

Use	**Chloroplatinates used**	**Comments**
Platinum refining/purification, including recycling	Hexachloroplatinic acid Dipotassium hexachloroplatinate Dipotassium tetrachloroplatinate Diammonium hexachloroplatinate	ClPts are formed in the recovery, refining and purification steps of platinum. This includes recycling of platinum from waste.
Manufacturing of other platinum compounds	Hexachloroplatinic acid Dipotassium hexachloroplatinate Dipotassium tetrachloroplatinate Diammonium hexachloroplatinate	ClPts are the most important intermediates in the manufacture of other platinum-compounds. These substances are then used e.g. in catalysts production, in plating or for other purposes.
Manufacturing of catalysts and catalyst precursors	Hexachloroplatinic acid Dipotassium tetrachloroplatinate	Direct uses are as catalyst precursors for heterogeneous catalysts, including: 1) Platforming catalysts (Pt/Re) for naphtha reforming

		to produce high-octane gasoline. 2) Dehydrogenation catalysts to produce propylene and other olefins. 3) Other specialised platinum-catalysts
Surface treatment (This use is phased-out in the EU)	Diammonium hexachloroplatinate	Today other platinum compounds than chloroplatinates are used in surface treatment. The current use of ClPt in surface treatment is negligible.

5 Annual tonnage range

The world gross demand for platinum in 2015 was around 235 tons of which about 41% went into automotive catalysts, 35% was used in jewellery and 20 % in other industrial applications. The remaining 4% was used for investment. Recycling satisfies nearly 25% of the gross demand. In the EU the gross demand is 65-70 tons per annum, of which about 70% is used in automotive catalysts, 16% in other industrial applications (including catalysts), 10% in jewellery and the remaining 4% for investment.

Table 5.1 Consumption of platinum in 2015.

Automotive industry (exhaust catalysts) has the highest consumption of platinum on world basis. The economic significance of industry catalysts is much higher than indicated by the tonnage. Platinum catalysts play a key role in refining and chemical industry (Data from WPIC 2015, Johnson-Matthey 2015).

	World	**EU**
Demand 2015 (tonnes)	235	65-70
Use distribution	**%**	
Automotive	41	70
Jewellery	35	10
Industry	20	16
Investment	4	4

Due to the use of ClPts as intermediate in the production, refining and recycling of platinum the use tonnage is closely linked to the annual production of platinum.

6 Refining/ recycling/ manufacturing

Choroplatinic acid (CPA) is the main product of all leaching and refining of platinum from ores or recycled material because chlorine and hydrochloric acid are needed in the process.

Platinum is contained in minerals in low concentrations in its metallic state, but also as sulfides, selenides and oxides. In ores platinum is associated with other platinum group metals (PGM), some of which have very similar chemical and physical properties. Depending on the geology, the ores may further contain large amounts of base metals and refractory materials based on silica and alumina.

Extraction of PGM starts with grinding, flotation and extraction steps where components are separated according to their gravity, solubility and surface tension properties. The remaining concentrate is leached in hydrochloric acid using either nitric acid or chlorine gas as oxidizing agents. At this stage platinum is transformed to a hexachloroplatinate complex $[PtCl_6]^{2-}$ where it is present as its corresponding acid, $H_2[PtCl_6]$ aq. chloroplatinic acid, CPA. Neutralization of this acid yields sodium, potassium or ammonium salts.

In recycling, the processing of "secondary material" (recycling) must be adjusted to the specific composition of the spent or waste material, which may vary considerably. Organic material such as plastics is removed by incineration before inorganic material can be subjected to the usual work-up and leaching processes.

CPA is the result of the leaching and refining processes because chlorine and hydrochloric acid is needed in the process. Platinum has one of the highest redox potentials of all metals and only the strongest oxidants can extract platinum metal and its insoluble compounds from ores and recycled materials. Other halogens (fluorine, bromine, and iodine) are also strong oxidants but cannot be used for extraction of platinum and the related substances from ores and other materials (see discussion in Appendix A). In short, chlorine is necessary because of its very strong oxidation potential, the process is easy to control and leads predominantly to a single oxidation state of platinum. Moreover chlorinated platinum salts have solubility properties allowing selective precipitation and re-dissolution and thus an efficient refining.

For these reasons all currently documented protocols for the recovery and recycling of platinum yield hexachloroplatinates (Pt in +IV oxidation state) as the primary products. This substance therefore holds a key position and is the source for "all platinum chemistry" performed in industry.

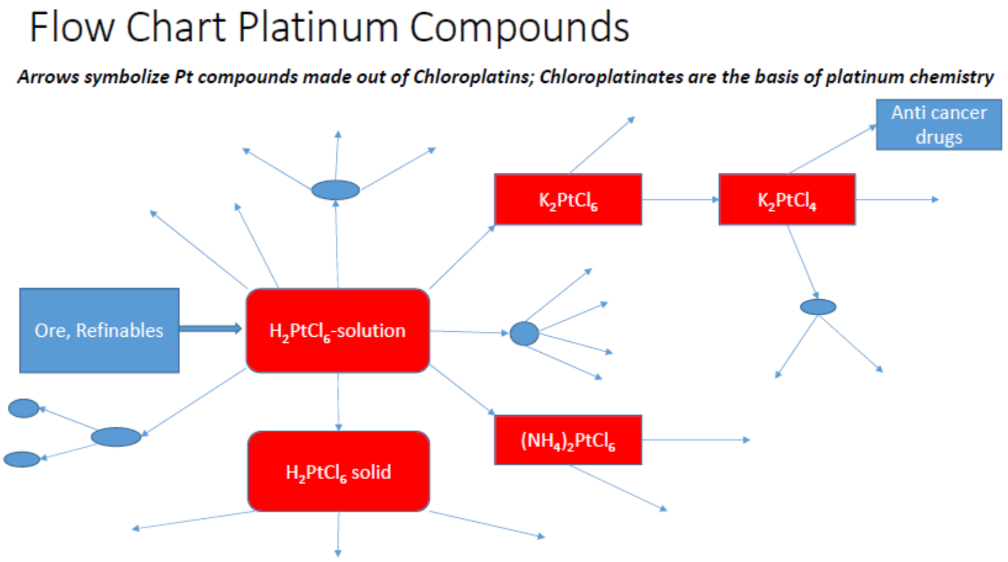


Figure 1 Chloroplatinates holds a key position in the life cycle of platinum.

7 Manufacturing of platinum compounds

Without any exception, chloroplatinates are the starting intermediate for the syntheses of any platinum chemical. The key compound is hexachloroplatinic acid and its sodium, potassium and ammonium salts. Thus, if a chloroplatinate is substituted by an alternative platinum compound to reduce risks associated with certain use it will still play a key role as intermediate in the life cycle of platinum.

Chloroplatinates are used as intermediate for manufacture of various inorganic and organic complexes with specific industrial uses, including the alternatives to chloroplatinates in downstream applications.

The platinum compounds prepared from chloroplatinates may be grouped as indicated in the table below.

Table 7.1 – The main uses of chloroplatinic compounds

Chloroplatinates are used as intermediates in manufacture of all other platinum compounds. Different sectors depend on various platinum compounds that originates from chloroplatinates.

Platinum compounds and main use	**Remarks**
Precursors for heterogeneous catalysts (mainly automotive)	Precursors for the deposition of platinum on supports for common automotive catalysts, e.g. hexahydroxyplatinic acide $H_2[Pt(OH)_6]$; hexanitrate $H_2[Pt(NO_3)_6]$; Pt- ammine complex $[(Pt(NH_3)_2(NO_2)_2]$ and $Pt(NH_3)_4Ac_2$.
Electrolytes for plating	Chloroplatinates used in electroplating has generally been replaced by non-chlorinated platinum salts: P salt $[Pt(NH_3)_2(NO_2)_2]$; Q salt $Pt(NH_3)_4](HPO_4)$ and DNS salt $H_2Pt(NO_2)_2SO_4$.
Precursors for platinum powders used in electronic industry	Platinum powder is deposited from Pt-ammonia complexes by reduction. In fuel cells the platinum source for deposition on carbon is a solution of $(NH_3)_4Pt]Cl_2$
Volatile compounds for chemical vapour deposition of platinum	Chemical vapour deposition relies mainly on volatile organoplatinum compounds, e.g. Platinum(II) acetylacetonates or tetrakis(trifluorophosphine)platinum
Platinum in pharmacology	The complex cis-$(NH_3)_2PtCl_2$ ("cis-platin") and related compounds are used in cancer chemotherapy.

8 Information sources for the current report

The discussion of alternatives to chloroplatinates in this report is based on information collected from available scientific literature, including patent literature. Industrial specialist have been consulted to retrieve information on the industrial practice regarding use of chloroplatinates. This survey included members of the Precious Metals Consortium representing the main European manufacturers of platinum and platinum compounds.

9 Chloroplatinates in catalysts

Among the chloroplatinates, only chloroplatinic acid (CPA) and potassium tetrachloroplatinate (K_2PtCl_4, DTCP) are identified as being relevant for catalyst production.

Of the total world supply of 246 tpa of platinum in 2015, about half (125 tpa) was used in catalyst production. The main application is in automotive catalysts (World: 102 tpa platinum; Europe: 49.6 tpa platinum) (WPIC, 2016). The use of platinum for chemical catalysts is much smaller: 18.5 tpa platinum while 5.0 tpa is used for petroleum refining. Because the recycling rate for these uses is very high (97-98%) the importance of these catalysts is higher than the consumption data suggest. Chemical catalysts (18.5 tpa platinum) include catalysts for hydrosilylation (ca 6 tpa platinum), for production of nitric acid and HCN, and for selective hydrogenation and dehydrogenation, a.o. The main petroleum catalyst is the so-called platforming or naphtha reforming catalyst, which is used for converting naphtha into high-octane gasoline.

Catalysts are heterogeneous catalyst, where the active catalyst is coated on a carrier material, e.g. alumina. This includes for example the reforming and dehydrogenation catalysts discussed in this report. In homogeneous catalysts the active catalyst is dissolved or dispersed in the reaction and without a bearing material, e.g. the most commonly used hydrosilylation catalysts.

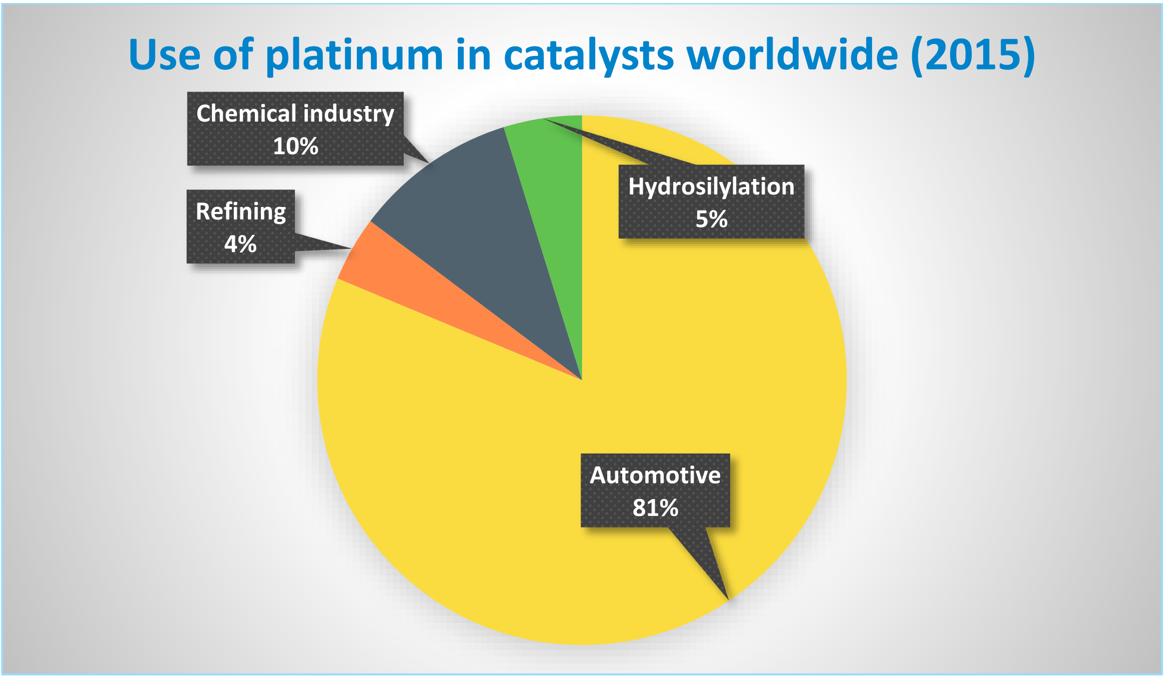


Figure 2 –Platinum is used as catalyst for various purposes but mainly in automotive industry (in exhaust catalysts). The economic importance of industrial catalysts is higher than the relative tonnage indicates and they have a very high recycling rate.

9.1 Exhaust catalysts

Exhaust catalyst account for a consumption of 102 tpa platinum worldwide and is by far the most important application of platinum in catalysis. Use of chloroplatinates in the production of exhaust catalysts has, however, been phased out by all European manufacturers.

The exhaust catalyst in cars are typically three-way catalysts that convert three pollutants, carbon monoxide, hydrocarbons and nitrogen oxides into carbon dioxide, water and nitrogen. Both platinum and palladium are able to catalyse oxidation reactions such as the conversion of carbon monoxide and hydrocarbons while rhodium is the most effective catalyst for the reduction of nitrogen oxides.

Figure 3 Automotive catalysts is the most important application of platinum as catalyst.

Table 9.1 “Three way” exhaust catalysts converts carbon monoxide, hydrocarbons and nitrogen to harmless gasses and water. This is achieved by combining the properties of platinum, palladium and rhodium. (‘+’ = high activity; ‘0’ = medium activity; ‘-‘ = low activity)

Reaction	**Platinum**	**Palladium**	**Rhodium**
CO, CH oxidation	+	+	-
NO oxidation	+	0	-
NOx reduction	-	0	+
Sulphur resistance	+	-	0

A typical exhaust catalyst composition based on the patent literature is: platinum & palladium 1.1%, rhodium 0.11%, alumina 52%, ceria 24%, zirconia 12%, lanthana 6%, baria 5%. (Bartholomew and Farrauto, 2005b). The platinum compounds that potentially could be used in manufacturing of exhaust catalysts are presented in the table below.

Table 9.2 Examples of platinum compounds are available as catalyst precursors for use in automotive industry (ref.: Johnson Matthey web page)

Platinum(IV) nitrate: $H_2Pt(NO_3)_6$ solution.
Platinum(II) tetraammine nitrate, $Pt(NH_3)_4(NO_3)_2$ sold as a solution pH 6 – 6.5.
Platinum(II) tetraammine hydroxide, $Pt(NH_3)_4(OH)_2$, a solution of 8-11% Pt.
Platinum(II) tetraammine hydrogen carbonate, $Pt(NH_3)_4(HCO_3)_2$, a solid.
Ethanolamine hexahydroxyplatinic acid, $(HOCH_2CH_2NH_2)_2\,Pt(OH)_6$
Platinum(II) tetraammine acetate, $Pt(NH_3)_4Ac_2$, a 18-22% Pt solution
hexahydroxyplatinic acid $H_2Pt(OH)_6$, a solid

The benefits of using platinum in exhaust catalysts are a combination of its properties including a high activity in catalyzing the oxidation of carbon monoxide and hydrocarbons as well as a high temperature and poison resistance. The functional properties of platinum in exhaust catalysts are summarised in the table below.

Table 9.3 Platinum has catalyst properties that gives a high performance as exhaust catalyst. Today chloroplatinates are not used in the manufacturing of automotive catalysts.

Platinum in exhaust catalysts	**Explanation**
Activity	Both platinum and palladium are able to catalyse oxidation of carbon monoxide and hydrocarbons. Platinum further catalyses the oxidation of nitrogen monoxide.
Stability (high temperature)	Platinum (and palladium) have remarkable resistance to high-temperature operations. Palladium improves the high-temperature stability by specific platinum-palladium alloys.
Selectivity	Platinum has the important property of being able to oxidise hydrocarbons and CO completely to water and CO_2 at a range of operating temperatures without the production of dioxins.
Poison resistance	Unlike other metals platinum has a remarkable resistance towards poisons like sulphur and the presence of platinum in automotive catalysts ensures a long active life. The only poison which is irreversibly adsorbed is lead which has already been eliminated from automotive fuels some time ago.
Affinity of precursor towards the carrier material	The precursor CPA has a high affinity towards the acidic carrier material. At low pH, the positively charged alumina strongly adsorbs the negatively charged $PtCl_6^{2-}$ and Cl^- ions leading to a homogeneous distribution of the platinum. Thus, technically CPA is a very suitable platinum precursor for

	these catalysts. However, the high operating temperatures and chloride enhance the rate of metal sintering leading to a loss of active surface area. Moreover the chlorine leads to corrosion of exhaust pipes. Therefore, nowadays no chloroplatinates precursors are used.

9.2 Reforming (platforming) catalysts

Reforming (or platforming) catalysts are used in the oil refining industry to convert straight-run low octane naphtha to high-octane gasoline and to aromatic compounds. The total platinum consumption for petroleum catalysts worldwide is around 5 tpa platinum, of which the main application is for catalytic reforming.

Reforming catalysts efficiently perform dehydrogenation and hydrogenation reactions as well as complementary reactions. The support material is normally a high-purity alumina designed to have an acid functionality. The catalyst often includes rhenium as a promotor. At low pH, the positively charged alumina strongly adsorbs the negatively charged $PtCl_6^{2-}$ and Cl^- ions. Thus, technically CPA is a very suitable platinum precursor for these catalysts. The method is highly optimized and provides both a uniform distribution of highly dispersed platinum and a chlorination of the alumina surface.

The functional requirements fulfilled by platinum and CPA are summarised below.

Table 9.4 The function of CPA in reforming catalysts.

Reforming catalysts based on platinum gives a high, selective and stable activity with and a catalyst with high resistance to catalyst poisons. The precursor CPA is very suitable for as platinum source in the manufacturing of reforming catalysts.

Platinum in reforming catalysts	**Explanation**
Activity	Platinum catalysts with rhenium as promoter have a high catalyst activity. The reforming catalysts are complex composites of platinum to efficiently perform dehydrogenation and hydrogenation reactions. The catalysts convert straight-run low octane naphtha to high-octane gasoline and to aromatic compounds.
Stability	Stability of platinum against sintering is greatly enhanced by the presence of rhenium.
Reuse	Platinum reforming catalysts have the interesting property that deactivated catalysts can be regenerated by addition of chlorine which re-disperses the platinum metal thus restoring most or all of the initial activity.
Selectivity	Platinum efficiently performs dehydrogenation and hydrogenation reactions, which allows the resulting olefins to be isomerized by the acidic sites.

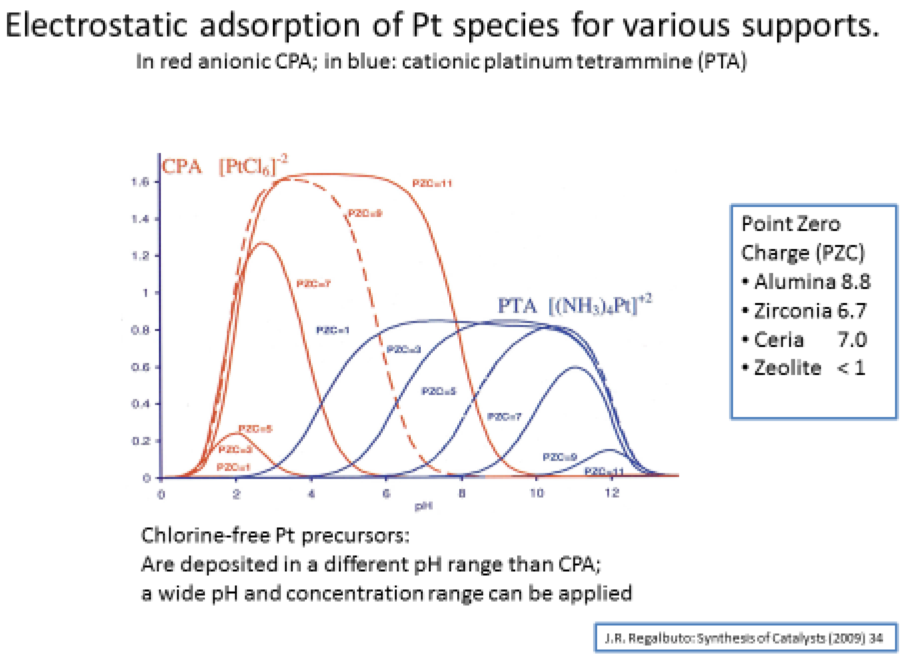
Poison resistance	Unlike other metals platinum has a remarkable resistance towards poisons.
Affinity of precursor towards the carrier material	The precursor CPA has a high affinity towards the acidic carrier material leading to a homogeneous distribution of the platinum. Thus technically CPA is a very suitable platinum precursor for these catalysts.

9.2.1 Possible alternatives to platinum catalysts and use of CPA as precursor

Considerable research has shown that using platinum catalysts with Re as promoter provides catalysts that are superior to non-platinum alternatives. Other promoters like tin (Sn), germanium (Ge) and iridium (Ir) can be used too but there does not seem to be a suitable alternative to platinum as the main metal.

Theoretically, it is possible to substitute CPA with an alternative platinum precursors. These precursors are positively charged and the carrier material thus needs to be negatively charged. In theory this is possible by raising the pH to create a negatively charged alumina support followed by chlorination of the resulting precursor. Rhenium, which is stable in the basic pH region over a wide range, could be included in the impregnation solution. The method is, however, unproven and would require lengthy development work and years of pilot plant and commercial scale testing. Moreover after manufacture, the catalyst has to be chlorinated to generate acid sites. This will entail a potential risk of some CPA formation.

An alternative carrier material is silica-alumina which is negatively charged over a wide pH range and suited for depositing positively charged non-chloride platinum(II) precursors. The use of silica-alumina as carrier has been commercialized but was later abandoned because of too strong acidity of the material.


Electrostatic adsorption of Pt species for various supports.

In red anionic CPA; in blue: cationic platinum tetrammine (PTA)

Point Zero Charge (PZC)
- Alumina 8.8
- Zirconia 6.7
- Ceria 7.0
- Zeolite < 1

Chlorine-free Pt precursors:
Are deposited in a different pH range than CPA;
a wide pH and concentration range can be applied

J.R. Regalbuto: Synthesis of Catalysts (2009) 34

Figure 4 The adsorption of platinum precursors on different carrier material. Note the high degree of adsorption of hexachloroplatinate at the lower pH range.

Table 9.5 Possible alternatives in reforming catalysts.

There are no technical suitable alternatives to platinum as reforming catalysts. Alternative platinum precursors are possible theoretically and subject to analysis in this report.

Possible alternatives	Assessment
Possible alternatives to platinum based catalysts	Other promoters like tin, germanium and iridium can be used but none of these seem to be a suitable alternative to platinum as the main metal.
Non-chloride platinum(II) precursor on a negatively charged carrier material.	Theoretically platinum(II) precursors could be deposited on a negatively charged alumina support. This method is, however unproven and would require lengthy development work and years of pilot plant and commercial scale testing. In addition, the resulting catalyst has to be chlorinated anyway to provide the required acidity with the likely formation of small quantities of CPA. Platinum(II) precursors might also be used in combination with silica-alumina as a carrier material. The use of silica-alumina has been commercialized earlier, but was abandoned because of too strong acidity of the carrier. **The alternative is further analysed below.**

Figure 5 Heterogeneous catalysts are highly important for a wide range of reaction processes in refineries and in the chemical industry. Their action is often very specific and based on the unique properties of the catalyst substances, e.g. platinum.

9.2.2 Assessment of the identified alternatives

The assessment of the suitability of alternative platinum precursors in reforming, dehydrogenation, and DTCP based catalysts, are discussed in Section 4.5.

9.3 Dehydrogenation catalysts

Out of the about 18.5 tpa of platinum used for catalysts worldwide less than 10 tonnes platinum is expected to be used solely in dehydrogenation catalysts. Platinum dehydrogenation catalysts are heterogeneous catalysts used for converting alkanes into the corresponding olefins e.g. propane into propylene and butane into butylene. Platinum is an ideal metal for dehydrogenation because of its high activity for cleaving C-H bonds combined with its low activity for C-C bond rupture. The standard preparation involves impregnating gamma alumina or zinc aluminate with a solution of CPA, HCl and promoter salts, e.g. tin salts.

At low pH, the positively charged alumina strongly adsorbs the negatively charged CPA ($PtCl_6^{2-}$) in an acid solution with HCl. After the calcination and activation processes, the platinum is in the metallic state and no traces of the CPA remain on the catalyst. The key functions of the catalyst and its precursor CPA are summarised in the table below.

Table 9.6 The function of platinum in dehydrogenation catalysts.

Platinum gives highly active, selective and stable dehydrogenation catalysts. Furthermore these catalysts have a high resistance to catalyst poisons. The precursor CPA is very suitable for alumina carrier.

Function	**Explanation**
Activity	Platinum is an ideal metal for dehydrogenation because of its high activity for cleaving C-H bonds combined with its low activity for C-C bond rupture. The preferred promoter is tin which enhances its selectivity and stability
Stability	The platinum/tin catalysts are very stable and after deactivation can be regenerated by oxidative treatment, optionally in the presence of chlorine.
Selectivity	Unlike other metals platinum does not cause rupture of the carbon bond and thus suffers less from by-product formation.
Poison resistance	Unlike other metals platinum has a remarkable resistance towards poisons. The platinum/tin combination reduces the tendency of deactivation by coke deposition.
Affinity of precursor towards the carrier material	The positively charged alumina carrier material strongly adsorbs the negatively charged $PtCl_6^{2-}$ at low pH.

9.3.1 Possible alternatives to platinum catalysts and use of CPA as precursor

Chromium (Cr) is widely used as catalyst for dehydrogenation processes but does not have the same technical applicability as platinum in catalysis. Moreover because of the toxicity of chromate (Cr^{VI}) there is an increased pressure to substitute chromium catalysts with less toxic catalysts, e.g. platinum.

Theoretically platinum could be deposited by using positively charged non-chloride platinum(II) precursors on a negatively charged alumina carrier material (at high pH). However, the preferred promoter, tin, is insoluble at high pH and eventually forms negatively charged tin-compounds, which will be repulsed by the negatively charged alumina support.

A development of alternatives by this route would be costly and require intense development work and years of pilot plant and commercial scale testing. As the performance benefits are not obvious this method is not attractive from a commercial point of view.

Table 9.7 Possible alternatives to CPA in reforming catalysts.

The platinum based catalysts are very suitable for dehydrogenation processes. Chromium can be used as well but due to the hazards of chromate not feasible from a health point of view. Theoretically, use of alternative platinum precursors is possible. This is discussed further in this report.

Possible alternatives	**Assessment**
Possible alternatives to platinum based catalysts	Chromium catalysts are also used in dehydrogenation processes but do not have the same technical applicability. Furthermore, because of the toxicity of Cr^{6+} this type of catalyst cannot be regarded as an alternative. **This alternative is not analysed further**
Non-chloride Platinum(II) precursors	Theoretically positively charged platinum(II) precursors could be deposited on a negatively charged alumina support (at high pH). Most promoter ions are however, insoluble at high pH and the preferred promotor, tin, forms negatively charged compounds, which will be repulsed by the negatively charged alumina support. **The alternative is further analysed below.**

9.4 Catalysts based on tetrachloroplatinate, DTCP

Dipotassium tetrachloroplatinate, (K_2PtCl_4), DTCP is used as precursor for homogeneous catalysts but the substance is also a catalyst on its own. It is used in functionalization processes of saturated hydrocarbons and has a very high selectivity for oxidation of the least reactive hydrocarbon positions. The products are mainly alcohols, chloroalkanes, ethers, and acids. Ethanol can be selectively converted to ethylene glycol.

The main use of DTCP is as starting material for a range of platinum(0) and platinum(II) substances used for both homogeneous and heterogeneous catalysts. Due to its very good water solubility DTCP is also used as precursor for catalysts on support. These heterogeneous catalysts are used for production of bulk as well as fine chemicals and for gas purification. DTCP itself is claimed to be a good heterogeneous catalyst for hydrosilylation.

In addition, DTCP is used as a hydrogen isotope exchange catalyst for labelling of aromatic and aliphatic compounds with deuterium (D) and/or tritium (T) in one step.

Table 9.8 The functions of DTCP in dehydrogenation catalysts.

DTCP is used as intermediate in platinum chemistry, as a precursor in for platinum catalysts and is also a catalyst on its own. DTCP is due to its properties the preferred platinum precursor for some carrier materials used in heterogeneous catalysts.

Function	**Explanation**
Activity	DTCP is mainly used as intermediate for manufacture of other platinum compounds but it is also used as catalyst precursor especially in functionalization of saturated hydrocarbons. Moreover DTCP is used as precursor for in platinum-catalysts for specialised purposes in both the bulk and fine chemicals and gas purification industry.
Stability	Platinum catalysts are more stable than most non-platinum alternatives.
Selectivity	DTCP has a very high selectivity for oxidation of the least reactive carbon positions in hydrocarbon molecules. DTCP has unique properties as a hydrogen isotope exchange catalyst for both aromatic and aliphatic compounds
Poison resistance	Platinum catalysts are more poison-resistant than all non-platinum alternatives.
Affinity of pre-curser towards the carrier material	DTCP has a good water solubility and is an essential precursor for heterogeneous catalysts where the support material is basic, e.g. MgO or hydrotalcites.

9.4.1 Possible alternatives to platinum catalysts and use of DTCP as precursor

There are several possibilities to substitute DTCP used as homogeneous catalyst e.g. platinum(II) tetraammine based catalyst. For catalysts based on supports like MgO or hydrotalcites a negatively charged platinum ion is required, which means that DTCP may be essential. The highly acidic CPA may dissolve or corrode the basic support, whereas the less acidic DTCP is a suitable precursor. It will be difficult to find alternatives. The main alternative candidate for depositing platinum compounds are the negatively-charged platinum(IV) nitrate $[Pt(NO_3)_6]^{2-}$ and hexahydroxyplatinate $[Pt(OH)_6]^{2-}$ anions.

Table 9.9 Possible alternatives to DTCP as precursor.

Iridium and palladium are possible future alternatives to platinum based catalysts. Some alternative platinum precursors have been identified as possible alternatives to DTCP as precursor.. These possibilities are discussed further in this report.

Possible alternatives	**Assessment**
Iridium and palladium	The use of these metals as catalysts in alkane functionalization is under research. DTCP has unique properties in alkane

	functionalization because of its high selectivity towards the least reactive places. So far no applications for palladium and iridium in this reaction have been commercialised. **The alternative is not analysed further.**
Platinum(II) tetraamine carbonates and nitrates	Regarding homogeneous catalysts the chloride ligands in $(PtCl_4)^{2-}$ of DTCP can be easily displaced by many other ligands. The alternative platinum precursors are less corroding as the chlorine reduces the activity of the catalysts by platinum sintering. **The alternative is further analysed below.**
Platinum(IV) nitrate $[Pt(NO_3)_6]^{2-}$ or hexahydroxyplatinate $[Pt(OH)_6]^{2-}$	Negatively-charged platinum ions are essential in depositing platinum on positively-charged basic supports. **The alternative is further analysed below.**

9.5 Assessment of the identified alternatives to CPA and DTCP in catalysts manufacture

9.5.1 Substance ID and properties

The alternatives to CPA and DTCP in the manufacture of reforming catalysts, include positively charged non-chloride platinum(II) precursors, e.g. platinum(II) tetraammine nitrate, $Pt(NH_3)_4(NO_3)_2$ or platinum(II) tetraammine hydroxide, $Pt(NH_3)_4(OH)_2$. Furthermore, negatively charged platinum precursors in acidic platinum(IV) nitrate $H_2Pt(NO_3)_6$ or $H_2Pt(OH)_6$ are mentioned as interesting candidates for dehydrogenation catalysts.

Table 9.10 Platinum substances available on the market that could be alternatives to chloroplatinates.

Substance	Formular	CAS No.	EC No.
Platinum(II) tetraammine nitrate	$Pt(NH_3)_4(NO_3)_2$	20634-12-2	243-929-9
Platinum(II) tetraammine dihydroxide	$Pt(NH_3)_4(OH)_2$	15651-37-3	239-719-1
Platinum(IV) nitrate	$H_2Pt(NO_3)_6$	-	432-400-1
Dihydrogen hexahydroxyplatinate(IV)	$H_2Pt(OH)_6$	51850-20-5	257-471-2

9.5.2 Technical feasibility

In heterogeneous catalysts CPA and DTCP are used as precursors and the platinum in the final catalyst is in the metallic state. Chloroplatinates are preferred due to very good water solubility and the ability to provide a high dispersion and low porosity of the deposited platinum layer. It will be difficult to substitute chloroplatinates with alternative precursors without reduction of yields and service life time of the catalysts. Theoretically positively charged platinum(II) compounds could be used.

The solution will require a negatively charged alumina support or silica-alumina support, which could be obtained by raising the pH in the deposition process. Non-chloride platinum(II) precursors on silica-alumina support have been commercialized earlier, but was abandoned again because of too strong acidity.

According to information from industry it will require 7.5 - 10 years of research, development, piloting testing, process optimisation, upscaling and installation before an alternative could be available for industrial production. Further the efficiency and life time of the catalysts based on alternative platinum sources are questioned, and the alternatives are not regarded as promising from a commercial point of view.

This is true also for the negatively-charged platinum(IV) nitrate $H_2Pt(NO_3)_6$ and hexahydroxyplatinate $H_2Pt(OH)_6$, which are possible alternative precursors on basic supports like MgO or hydrotalcites. The techniques are yet unproven and the performance benefits are not obvious.

DTCP used as homogeneous catalysts should be possible to replace by other platinum substances, e.g. platinum(II) tetraammine compounds.

9.5.3 Economic feasibility

In terms of investmentsit is estimated that the implementation of alternatives techniques that can replace CPA and DTCP will require extensive investments covering research and development, trial testing, investments in production equipment and training for the European production sites. Moreover it is expected that the alternative catalyst products will have lower overall efficiency and shorter life time, which reduces the market value and the profit margin.

9.5.4 Reduction of overall risk

The chlorinated platinum compounds CPA and DTCP both have harmonised classifications as respiratory sensitisers.

The hazard classification of possible alternatives substances are shown in the table below based on the harmonised classifications and classifications notified to ECHA by PMC. The hazard classification of the alternative platinum substances include allergic skin reactions, eye damage, skin corrosion and skin sensitization, but not respiratory sensitisation. For the environment the substances are classified as "harmful" to "very toxic" to aquatic life with "with long lasting effects".

Table 9.11 Classification of chloroplatinic compounds and examples of possible alternatives. CPA and DTCP both have a harmonised classification as respiratory sensitisers. The substances proposed as alternatives do not have this classification.

Substance	Hazard Class	Hazard Statement
Chloroplatinic acid (CPA)[1] (CAS 16941-12-1; EC 241-010-7)	Acute Tox 2	H300 - Fatal if swallowed
	Skin Corr. 1B	H314 – Causes severe skin burns and eye damage
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Eye dam. 1	H318 - Causes serious eye damage

	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	STOT RE1	H372 - Causes damage to organs through prolonged or repeated exposure.
	Aquatic acute 1	H400 Very toxic to aquatic life (Acute M-factor 10)
	Aquatic chronic 1	H410 Very toxic to aquatic life with long lasting effects (Chronic M-factor 10)
	Met. Corr. 1	H290- May be corrosive to metals
Dipotassium Tetrachloroplatinate[1], DTCP (CAS 10025-99-7; EC 233-050-9)	Acute Tox 3	H301 – Toxic if swallowed.
	Skin irrit. 2	H315 – Causes skin irritation
	Eye Dam. 1	H318 – Causes serious eye damage.
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	Met. Corr. 1	H290 - May be corrosive to metals
Platinum(II) tetraammine nitrate (CAS 20634-12-2; EC 243-929-9)[2]	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
	Met. Corr. 1	H290 - May be corrosive to metals
Platinum(II) tetraammine hydrogen carbonate [1] (CAS 123439-82-7; EC 426-730-3)	Acute Tox. 4	H302 – Harmful if swallowed.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
Platinum(II) tetraammine dihydroxide[3] (CAS 15651-37-3; EC 239-719-1) According to the PMC strategy the classification as Skin Sens is challenged. To be updated!	Skin Sens. 1	H317 – May cause an allergic skin reaction.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Acute 1	H400 – Very toxic to aquatic life.
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects.
Platinum dinitrate [2] (CAS 18496-40-7; EC 242-383-9)	Skin Corr. 1A	H314 – Causes severe skin burns and eye damage.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)

	Aquatic chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)
	Met. Corr. 1	H290 - May be corrosive to metals
	Oxid solid 1	H271 - May cause fire or explosion; strong oxidiser
Dihydrogen hexahydroxyplatinate[2] (CAS 51850-20-5; EC 257-471-2)	Eye Irrit. 2	H319 - Causes serious eye irritation
	Aquatic Acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)

[1] Harmonised Classification; [2] Notified classification by PMC member;

In terms of human health hazards the discriminator among these platinum substances is respiratory sensitisation. As this is a hazard of concern in the work place the benefit by substituting CPA and DTCP with alternative platinum compounds is the reduction of risk of respiratory sensitisation among workers. It is estimated that in the EU 120-140 workers are currently working with chloroplatinates in production of precursors or manufacture of platinum catalysts.

9.5.5 Availability of alternative solutions

The identified alternatives to CPA and DTCP as precursor in catalysts are currently not available. As mentioned, the estimated time frame for developing time for alternative solutions is estimated to be over 10 years.

9.5.6 Conclusions on suitability

There are currently no available, technically suitable alternative to CPA and DTCP for industrial scale manufacture of reforming catalysts, dehydrogenation catalysts and DTCP based catalysts. Technically the alternatives are yet unproven at industrial scale, and the performance benefits of the suggested alternative methods are not obvious. Industry expects catalysts based on alternative platinum and solutions to provide lower yields in use and have a shorter service life.

The possible alternatives platinum precursors are generally less hazardous mainly because they are not respiratory sensitizers. A phase-out of the use of CPA and DTCP can potentially reduce the risk of respiratory sensitisation effects among workers employed with the manufacturing of chloroplatinates and their use on production of catalysts. It is estimated that about 120-140 workers are currently working with chloroplatinates, mainly in catalysts production in the EU.

If industry should phase-out the use of chloroplatinates from the current use in manufacture of catalysts, intensive research and development of alternative solutions will be needed. The European catalyst industry foresee that research, development, trial testing and installation of alternative solutions will require extensive investments and require more than 10 years before an alternative solution for industry scale production will be available.

9.6 Miscellaneous heterogeneous catalysts

9.6.1 Analysis of substance function

Platinum is used in heterogeneous catalysts used for various purposes. The carrier is carbon, alumina or calcium carbonate and the preferred precursor is CPA. The catalysts are used for hydrogenation, dehydrogenation, selective oxidation, etc.

Table 9.12 Platinum function in miscellaneous catalysts.

Platinum catalysts have different niche application, e.g. as heterogeneous catalysts on a carrier of carbon. Platinum has excellent performance properties and CPA as precursor is very suitable when carbon or alumina is the carrier material.

Function	**Explanation**
Activity	Platinum is very suitable as catalyst for hydrogenation, dehydrogenation, selective oxidation reactions.
Stability	The platinum catalysts are stable and can be regenerated by oxidative treatment after deactivation.
Selectivity	Platinum does not cause rupture of the C-C bond resulting in by-product formation in dehydrogenation processes, unlike other metals.
Poison resistance	Platinum has a high resistance to poisons.
Affinity of precursor towards the carrier material	The carbon and alumina carrier strongly adsorbs the negatively charged $PtCl_6^{2-}$.

9.6.2 Possible alternatives to platinum catalysts and use of CPA as precursor

For several applications there are alternative catalysts based on chromium, nickel, copper or palladium. Platinum, however, remains the preferred metal for certain applications, often in combination with promoters, e.g. tin. The use of the catalyst includes selective hydrogenation of halonitroaromatics to the corresponding haloaminoaromatics, the hydrogenation of unsaturated aldehydes to the unsaturated alcohols and reductive alkylations involving the reaction of an aldehyde or ketone with an amine.

The platinum catalysts belonging to this group are often made by precipitation of platinum using CPA on a carrier of carbon.

Theoretically platinum(II) compounds could be used as platinum source instead of CPA. Further research and development will, however, be needed to provide an alternative suitable for industry scale production. These catalysts are produced to a niche market, with a total platinum consumption of less than 300 kg/ year, and there is little incentive for industry to invest in development of alternative solutions.

Table 9.13 Possible alternatives to platinum and CPA as a precursor.

Platinum remains the preferred catalyst for specific applications due to the technical performance of this metal. Theoretically alternatives to chloroplatinates could be used as precursors but this will require further development and testing.

Possible alternatives	**Assessment**
Possible alternatives to platinum based catalysts	Catalysts based on chromium, nickel, copper or palladium are also used. For specific applications platinum, however, remains the preferred solution. **This alternative is not analysed further**
Non-chloride Platinum(II) precursors	Theoretically positively charged platinum(II) precursors could be deposited on the carbon support. Tin promoter ions are, however, insoluble at high pH. Because it is a niche market industry has little incentive to invest in finding alternatives to CPA as platinum source. **The alternative is not analysed further.**

9.7 Homogeneous catalysts for hydrosilylation

Hydrosilylation is an important method for preparing organosilicon compounds, which are widely used e.g. in the construction industry. In terms of market value it is the most important application of homogeneous catalysis. Although a range of catalysts are known, the platinum based Karstedt's catalyst [Pt (sym-tetramethyldivinyldisiloxane)] is by far the most common hydrosilylation catalysts. Recent observations indicate possible reprotoxic effects of Karstedt's catalyst. This introduces an incentive for substituting the Kartedts catalysts with alternative platinum complexes.

When a homogeneous hydrosilylation catalyst is used, the platinum usually remains with the reaction products. This can cause issues of cost, colour and safety. The estimated loss via silicon products is 4-6 tpa platinum worldwide corresponding to $377 million worth of metal.

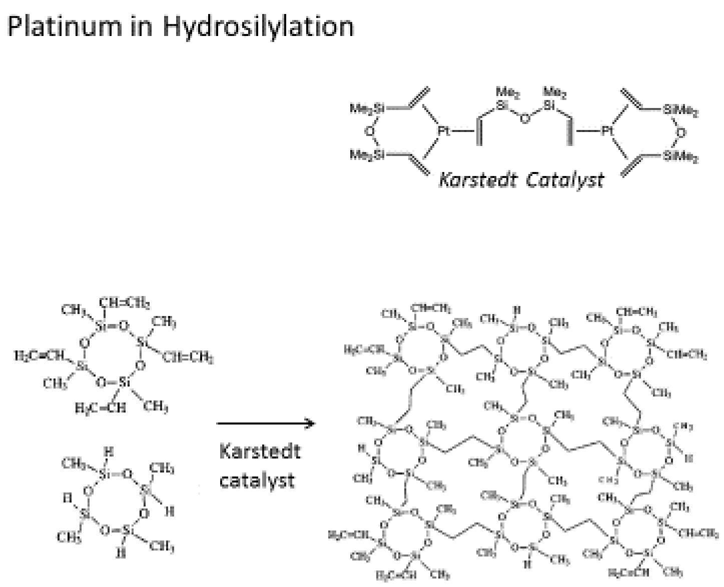


Figure 6 Production of a silicone resin by hydrosilylative cross-linking. The platinum remains in the product (a loss of 4-6 **t/y** as of 2015).

9.7.1 Analysis of substance function

Karstedt's catalyst is a non-chlorinated platinum compound and the most widely used hydrosilylation catalyst. Earlier Speier's catalyst (CPA) was used, but in Europe it has been fully replaced by Karstedt's catalysts. Other platinum-complexes are also used in hydrosilylation reactions.

Table 9.14 Platinum function in homogeneous catalysts.

Platinum is by far the most active and selective catalyst for hydrosilylation processes. The most commonly used hydrosilylation platinum catalysts is Karstedt's catalyst which is active immediately and provides quick curing at low temperatures.

Function	**Explanation**
Activity	A wide range of catalysts (e.g. iron and nickel catalysts) are known to catalyse hydrosilylation but platinum catalysts are by far the most active.
Selectivity	Platinum catalysts yield desirable cure kinetics and offer a better shape control without formation of by-product than, for example, Sn catalysed condensation.

Stability	Karstedt’s catalyst contain stabilizing ligands and does not form platinum colloids in the process.

9.7.2 Identification of possible alternatives

About 50% of the silicon crosslinking is conducted in alternative processes without platinum. A major alternative is tin (Sn) condensation. However, there are increasing concerns about the health risks of tin used as condensation catalyst. Moreover, unlike the platinum addition reaction, tin condensation produces water as a by-product, which affects the control and selectivity.

It has recently been demonstrated that base metal catalysts such as iron and nickel have good efficiency and unique chemo- and region-selectivity in hydrosilylation (Nakajima and Shimada, 2015). However, no application at commercial scale has been reported and it is too early to judge the potential to replace platinum. Because of the superior properties of platinum, viz. the two-electron redox processes catalysed so effectively by platinum and having the desirable cure kinetics, this metal is not easily replaced.

Thus, platinum has several advantages and the share of platinum processes is expected to grow. The development of hydrosilylation catalysts that do not require platinum remains, however, an important research area.

Industry also offers heterogeneous platinum catalysts (Pt/Al_2O_3) for hydrosilylation allowing the catalyst to be filtered from liquid products. Generally a higher loading of catalyst will be needed than for the corresponding homogeneous catalyst. However, the reaction may be smoother, with better exotherm control and it is often possible to re-use the catalyst. Obviously the heterogeneous catalyst can only be used for liquid products.

Karstedt’s catalyst has several advantages over CPA, i.e. Karstedt’s catalyst is active without an induction period and it provides a quick low-temperature curing. Other beneficial features of Karstedt’s catalyst are:

- A higher activity (higher platinum turnover number) and no induction period
- The reactivity can be fine-tuned by choice of catalyst loading, solvent and inhibitors.
- Cross-linking between the vinylsiloxane and silicon hydride is possible at temperatures below 50ºC with no by-product formation.
- No or less corrosive HCl or chloride containing by-products present.
- Less formation of platinum colloids

Possible human health concern related to Karstedt’s catalyst has made considerations of using other platinum catalysts relevant. Alternatives include commercially available platinum catalysts, platinum dodecene chloride and Pt-96 (platinum cyclooctadiene dichloride), which are currently used in hydrosilylation processes but at higher temperatures than for standard Karstedt’s.

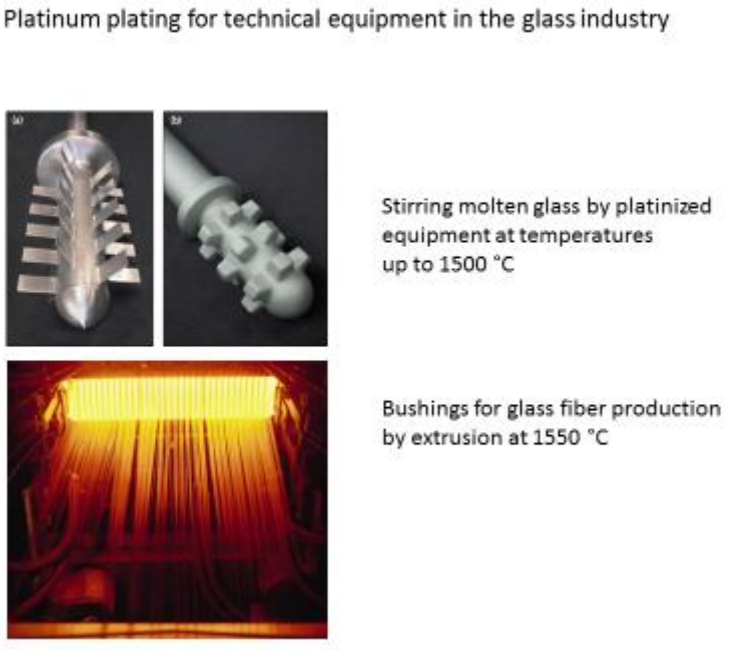
10 Chloroplatinates in surface treatment

One of the main uses of platinum is jewellery including plating of jewellery, but it is also applied as a technical coating e.g. in electronics. The use for technical coatings has been estimated at 0.4 tons in 2010 in the EU.

10.1 Analysis of substance function

In technical coatings platinum is used as cover layer or a sub-layer on different materials because of its stability to high temperature, its corrosion resistance, hardness and electrical conductivity. The range of possible applications includes electronics, such as contact materials, connectors, resistors, capacitors, sensors, computer hard discs, components of printed circuits etc., but also plating of instruments, sanitary equipment, and of jewellery.

The world demand of platinum for galvanic processes has been estimated at 1.3 tons platinum per year for 2010, broken down to 0.4, 0.3 and 0.5 tpa for Europe, the Americas and Asia, respectively.



Platinum plating for technical equipment in the glass industry

Stirring molten glass by platinized equipment at temperatures up to 1500 °C

Bushings for glass fiber production by extrusion at 1550 °C

Figure 7 Thick, wear- and temperature-resistent platinum layers are deposited on instruments and vessels for the *glass industry*, mainly by electroplating from molten salt baths (*ionic liquids*) containing $K_2[Pt(CN)_4]$ at 500 – 600 °C.

Chloroplatinates were earlier - and are still in some cases - used as platinum source for electroplating, which is the most important plating technique with platinum. Electroplating is carried out by depositing platinum from an electrolyte through applying a voltage between the substrate as the cathode and the anode.

Other less important platinum plating methods are electroless plating and chemical vapour deposition (CVD). In electroless plating platinum is deposited on the item by chemical reduction of a platinum salt in solution. In Chemical Vapour Deposition (CVD) a volatile platinum compound in a vacuum or in a low pressure gas phase is deposited directly on the item induced either thermally or by laser or UV irradiation.

Table 10.1 The function of platinum coatings in surface treatment.

Platinum coatings provide a heat and corrosion resistant layer and can be applied electroplating, by electroless plating and by chemical vapor deposition.

Electroplating	**Explanation**
Dispersion/ adhesion on base material	Electroplating by use of ammonium hexachloroplatinate as platinum-source seems to be preferred due to high current efficiencies. The technique is used to provide temperature resistance.
Corrosion resistance	Platinum layers have a high resistance to corrosion
Heat resistance	Platinum is used in alloys to increase heat resistance e.g. high performance Pt-Al alloys.
Appearance	Platinum plating is used in jewellery due to its bright and resistant surface.
Electroless plating	
Dispersion/ adhesion on base material	Electroless platinum plating generally gives a good dispersion and special surface characteristics of the plated layer.
Corrosion resistance	The corrosion resistance of electroless platinum coating is similar compared to electroplated platinum coatings.
Heat resistance	The heat resistance of a platinum coating is high.
CVD	
Dispersion/ adhesion on base material	CVD provides excellent adherence of the platinum coating and excellent dispersion. The substance used as platinum source for CVD includes chlorinated as well as non-chlorinated platinum compounds.
Corrosion resistance	The corrosion resistance of any platinum coating is high.
Heat resistance	The heat resistance of platinum coatings is generally high.
Surface alloy formation	Annealing of multilayer CVD yields highly resistant alloys

10.2 Identification of possible alternatives

For all three methods of platinum plating, alternatives to chloroplatinates are available. Moreover, in electroplating, the alternative compounds seem to be preferred solution for technical reasons.

Table 10.2 Possible alternatives to chloroplatinates as platinum source in plating.

The substances used as platinum source in different coating technologies are usually non-chlorinated. The most widely used application method is by electroplating where chloroplatinates are today replaced by alternative platinum compounds.

Possible alternatives, electroplating	**Assessment**

Hexahydroxyplatinate(IV) salt cis-Diammine(dinitrito)platinum(II) (P-salt) Dinitrito(sulfato)platinous acid (DNS-salt) Tetraammineplatinum(II) salts (Q-salts)	DNS salt (dinitrito(sulfato)platinous acid) , Q-salts (tetraammineplatinum(II) salts), P-salt and sulfito/nitrito complexes of platinum(II) are preferred as platinum source in electroplating due to their higher current efficiency, less corrosion and a better quality of the deposited platinum-layers. Corrosion of the base material is often a problem when using CPA because of the low pH and high temperature required. **The alternative is analysed further below**
Possible alternatives, electroless plating	
Hexahydroxyplatinate(IV) salt, Dinitrito(sulfato)platinous acid (DNS-salt) Potassium tetranitritoplatinate(II)	Electroless platinum-plating generally leads to less robust coatings as compared to electroplating, but the technique can be used under very mild conditions. The coatings have a higher surface area which is advantageous for heterogeneous catalysis and surface affinity (e. g. avoiding overvoltage of electrodes). Plating can be carried out on electrically non-conducting or poorly conducting surfaces. **The alternative is not analysed further**
Possible alternatives, CVD	
Volatile (organo)platinum compounds	With the only exception of $PtCl_2(CO)_2$, which is not regarded as a chloroplatinate substance, all other known platinum compounds used for CVD are non-chlorinated. **The alternative is not analysed further**

Only for specific purposes where ammonium hexachloroplatinate is used for depositing high temperature resistant Pt-Al layers, the alternatives may not provide the same functionality. This is however, a niche production accounting for less than 100 kg of platinum per year and with a limited number of workers involved (< 40).

10.3 Conclusions on suitability

The alternatives to chloroplatinates in plating are well proven and available for industrial scale use. They provide competitive solutions for most purposes and have generally replaced the use of chloroplatinates for industrial coatings in the EU.

For certain speciality coatings ammonium hexachloroplatinate is, however, still used and for technical reasons difficult to substitute. This is a niche production based on a small yearly volume of hexachloroplatinate and with a small number of workers involved. Overall the benefits of substituting hexachloroplatinate used in the surface treatment sector with alternatives will have little significance.

11 Discussion of the conclusions of alternatives to chloroplatinates

Chloroplatinates plays a central role in the manufacture and recycling of platinum because chlorine and hydrochloric acid is needed for the extraction and refinement processes. Platinum has one of the highest redox potentials of all metals and only the strongest oxidant can extract platinum from ores and recycled materials. Other oxidants, e.g. halogens, are not able to provide the same function. Currently all documented protocols for recovery and recycling of platinum yield hexachloroplatinate (Pt in +IV oxidation state) as the primary products. Chloroplatinates are therefore the common starting point of all platinum chemistry, and intermediate for manufacture of other platinum compounds.

The main use of platinum is in exhaust catalysts for the automotive industry. Chloroplatinates have, however, been replaced by alternative platinum substances and are no longer used in the EU for this purpose.

Within the area of industrial catalysts there are currently no available, technically suitable alternative to the chloroplatinic substances CPA and DTCP used in the manufacture of reforming catalysts, dehydrogenation catalysts and other platinum catalysts used for different specialised purposes. Other metals cannot replace platinum as catalyst in these processes. Industry expects that replacement of chloroplatinates with alternative platinum pre-cursors will give catalysts with lower yields in use and with a shorter service life.

If chloroplatinates should be phased out from the use as pre-cursors for platinum catalysts intense research and development will have to be carried out to identify and qualify alternatives. It is expected that substitution will entail massive investments in R&D, production equipment, training etc.

The benefits of substitution of chloroplatinates with alternative substances is a reduced risk of respiratory sensitisation among workers that are potentially exposed to the substances during manufacture or use. The number is estimated to 120-140 workers across the EU.

Platinum catalysts play a key role in hydrosilylation processes for the production of silicones. Earlier chloroplatinic acid was commonly used for this purpose but has in the EU been fully replaced by other platinum compounds. Chloroplatinates are, however, intermediates and platinum source in the production of the platinum containing catalysts currently used in hydrosilylation.

Chloroplatinates have in the EU a very limited use in surface treatment as they in general have been replaced by other platinum compounds for this use. Only for certain special heat resistant coatings, low volumes of ammonium hexachloroplatinic acid is still in use, and cannot be easily replaced.

APPENDICES

APPENDIX A – Platinum refining/ recycling and manufacturing

1 Refining/ recycling/ manufacturing

1.1 The standard (classical) leaching processes

Platinum is contained in minerals in low concentrations, finely divided and largely in its metallic state, but also as its sulfides, selenides and oxides. In these minerals it is also associated with other platinum group metals, some of which have very similar chemical and physical properties. Depending on the geology, the ores may further contain large amounts of base metals and refractory materials based on silica and alumina. In the recovery and refinement processes, platinum is present together with other precious metals and a careful separation of these metals is therefore required.

The process established for recovery of platinum group metals (Raub, C. J., 1986; Hagelüken, C. et al, 2005; Grehl, M., et al. 2012; Fröhlich, P. et al. 2017) from ores starts with grinding, flotation and extraction steps which facilitates separation of the components according to their gravity, solubility and surface tension properties. The resulting concentrate is roasted in electric furnaces, transforming - sulfides/selenides and elemental chalkogens into volatile sulfur or selenium dioxide. A partial segregation occurs upon slow cooling of the mattes produced in the process, and some base metals may be removed by a magnetic separation. Silica and other base metal oxides are removed as slags. An oxidative pressure leaching by sulfuric acid in air or oxygen converts another part of the material into soluble products. In the residue platinum and gold remain in their metallic state, while the other platinum group metals are present mainly as oxides.

The remaining concentrate is finally leached in hydrochloric acid (4 to 8 molar) using either nitric acid or chlorine gas as the oxidizing agents. It is at this stage that platinum becomes contained in the hexachloroplatinate complex $[PtCl_6]^{2-}$ which is first present as its corresponding acid, $H_2[PtCl_6]$ aq. Neutralization of this acid yields the salts, mainly with sodium, potassium or ammonium cations.

The classical leaching reagent is *aqua regia*, a mixture of nitric and hydrochloric acid, which is a source of elemental chlorine produced in a redox reaction between the two acids:

$$3\,HCl + HNO_3 \rightarrow Cl_2 + 2\,H_2O + NOCl;$$

$$Pt + Cl_2 \rightarrow PtCl_2; \qquad PtCl_2 + Cl_2 \rightarrow PtCl_4;$$

$$PtCl_2 + 2\,Cl^- \rightarrow [PtCl_4]^{2-}; \qquad PtCl_4 + 2\,Cl^- \rightarrow [PtCl_6]^{2-}.$$

The chlorine formally oxidizes platinum into its chlorides $PtCl_2$ and $PtCl_4$ which undergo complex formation with the excess of chloride anions to give the complexes $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$.

Chlorine can be applied directly as the gaseous element or generated *in situ* in reaction mixtures. Both principles are applied for platinum leaching through either elemental chlorine or *aqua regia*. Both processes are assisted by hydrochloric acid as a complexant.

The hydrochloric acid / chlorine leaching may be carried out in a pressure vessel or autoclave at moderate chlorine pressure, or as an extraction process with refluxing acid continuously leaching the concentrate in a chlorine atmosphere ("Soxhlet leaching").

The isolation of platinum from the leach liquor is based on the solubility and redox properties of the above chloro-complexes. Its principles have been established over many decades, but there are variants with details orientated at the specific composition and properties of the ores. In a first step, gold is reduced by sulfur dioxide, followed by iron(II) sulfate, and precipitated as elemental gold. This reduction also leads to a transformation of the chlorometalates of Ru, Ir and Os to their lower oxidation states making them susceptible to more facile substitution reactions, while platinum remains in the Pt(IV) state as $[PtCl_6]^{2-}$. The classic refining method for platinum is by precipitation by ammonia as the salt $(NH_4)_2[PtCl_6]$ which has the lowest solubility of the relevant hexachloroplatinates (Na, K). The precipitation is close to quantitative leaving << 50 ppm in solution. This salt is calcined at 700 °C to leave a sponge of still impure platinum metal (ca. 97-99 %). For further purification, this sponge is re-dissolved in *aqua regia* or HCl/Cl_2 and the solution boiled down with sodium chloride to yield $Na_2[PtCl_6]$ which is very soluble in water. It is dissolved in water and the solution treated with sodium bromate $NaBrO_3$ and sodium hydrogen carbonate $NaHCO_3$ thus providing highly oxidative conditions at a pH near 7. This leads to a precipitation of the insoluble hydroxides of the remaining platinum group metals, while $[PtCl_6]^{2-}$ remains in solution ("bromate hydrolysis"). Re-acidification and addition of ammonia give a crop of crystalline $(NH_4)_2[PtCl_6]$. Its calcination yields a sponge of metallic platinum of greatly improved purity, but the process may be repeated to approach a purity of near 100 %.

In recycling (Hagelüken, C. 2012), the processing of "secondary material" (recycling) must be adjusted to the specific composition of the spent or wasted material, which may vary considerably. A pre-treatment to remove e. g. carbon and organic material such as plastics by incineration (burn-off) will be the first move before inorganic material can be subjected to the usual work-up and leaching. In the separation process, specific metal scavengers may be used (Frankham, J. et al., 2010)

All currently documented protocols for the recovery and recycling of platinum yield hexachloroplatinates(IV) as the primary products. $[PtCl_6]^{2-}$ thus holds a key position and is the source for "all platinum chemistry" performed in industry, and this predominantly also includes the refining technology.

A.1.1 The refinement processes

Several refinement steps are needed to separate platinum from other substances present in the leach liquid. Due to the nature of the processes, all related platinum group metals are also present in the leach liquor as chloro-complexes and the separation of the metals is carried out taking advantage of their different solubility, redox, complexation, adsorption or ion exchange properties. Regarding platinum, it appears as the stable complex $[PtCl_6]^{2-}$ which may be recovered in the form of the corresponding acid or its salts. This acid and several of its salts are soluble in water and can be readily purified thus finally giving access to pure compounds and - by chemical or electrochemical reduction or by calcination - to pure platinum metal. Keeping or approaching $[PtCl_6]^{2-}$ again and again as a target chemical is the short track to high purity platinum products. It appears that detours via complexes with other ligands, while being common for metals like palladium, hold little advantage for platinum.

The currently used processes (Raub, C. J., 1986; Hagelüken, C. et al., 2005; Grehl, M., et al., 2012; Fröhlich, P. et al., 2017) rely on systems which have been optimised during more than a century of platinum mining and production, and are the most economical combination of the known variants. Recent developments have largely moved away from separation techniques by precipitation, filtration and re-dissolution of solid intermediates, and turned to selective solvent extraction (using tributylphosphate or trioctylphosphine oxide) (e. g. Pietrelli, I. et al., 2013) and absorption and desorption on suitable surfaces. This is mainly due to the increasing importance of the recycling of platinum from a wide variety of sources. Still individual solutions have to be found for specific substrates (ores, scrap, waste) with a largely constant or a strongly varying composition, respectively.

1.2 Manufacturing of Pt compounds

Without any exception, ClPts are the primary outcome of the refinement, recovery and recycling processes of platinum. Therefore, the syntheses of any platinum chemical are based on ClPts as intermediates. The key compounds are hexachloroplatinic acid $H_2[PtCl_6]$ (CPA) and its sodium, potassium and ammonium salts that are used as starting materials for all the syntheses leading to other platinum chemicals required for various applications. They are therefore the common intermediates for all platinum chemistry. In other words, each platinum atom that is put to use has at one stage been part of a hexachloroplatinate complex.

The platinum compounds prepared from CPA include inorganic and organic complexes (organoplatinum complexes) that have specific applications for the various industrial uses of platinum. This includes platinum compounds that are alternatives to chloroplatinates in downstream applications, and discussed further in the sections below.

1.2.1 Precursors for heterogeneous catalysts (mainly automotive).

For use in heterogeneous catalysts, CPA is converted into the hexahydroxide $H_2[Pt(OH)_6]$ and hexanitrate $H_2[Pt(NO_3)_6]$ maintaining the Pt(IV) oxidation state. Alternatively ammonia complexes of Pt(II) are produced by reduction: $[Pt(NH_3)_4]X_2$ with $X = NO_3$, OH, HCO_3, acetate. Reduction of CPA with nitrite and complexation with ammonia yields $[(Pt(NH_3)_2(NO_2)_2]$, and reduction by sulfite affords a soluble Pt(II) sulfito complex. All these products are the precursors for the deposition of platinum on supports for common automotive catalysts. Conversion of CPA to PtO_2 is used in production of heterogeneous catalysts for hydrogenation.

The most advanced and most widely used catalyst for hydrosilylation is produced from CPA by reduction in the presence of sym-divinyltetramethyldisiloxane (Karstedt catalyst), an organoplatinum(0) compound.

1.2.2 Soluble components of electrolytes for electroplating (mainly DNS-, P- and Q-salts).

For the production of electroplating agents, reduction of CPA with mild reagents (sulfite, hydrazine etc.) is carried out formally affording $H_2[PtCl_4]$ which is readily converted into its salts like $K_2[PtCl_4]$. Such tetrachloroplatinates(II) are transformed into the ammonia complexes $[Pt(NH_3)_4]^{2+}$ with various anions X^-, which are used as Pt sources in electroplating. Direct reduction with nitrite yields soluble $K_2[Pt(NO_2)_4]$ used for the same purpose.

1.2.3 Soluble components of electrolytes for electroless plating

The compounds used as sources of platinum for plating by electroless deposition are largely the same as those used for electroplating.

1.2.4 Precursors for particulate platinum powders for use in electrical and electronic devices (fuel cells etc.).

An important use of platinum is as powder of platinum metal used in the electronic industry and in fuel cells. Platinum powder is deposited from Pt-ammonia complexes by a reduction reaction. In fuel cell technology, the source for platinum deposition on carbon is a solution of $[(NH_3)_4Pt]Cl_2$ which is reduced on the dried support either by hydrogen at elevated temperatures or in a cold solution by agents like hydrazine. In both cases the platinum compounds used stem from CPA, which is used as intermediate in the production of the relevant platinum compounds.

1.2.5 Volatile compounds for chemical vapour deposition of platinum.

Chemical vapour deposition relies mainly on volatile organoplatinum compounds that are prepared from ClPts in the oxidation states Pt(IV), Pt(II) and Pt(0).

1.2.6 Platinum drugs for medicine (mainly anti-cancer drugs).

Following the discovery that the complex cis-$(NH_3)_2PtCl_2$ ("cis-platin") can be used successfully in cancer chemotherapy, a large number of related compounds have been prepared. "cis-Platin" is prepared from $K_2[PtCl_4]$ by treatment with ammonia, or directly from CPA and its potassium salt through reduction with sulfite followed by complexation. Prominent new developments, followed up in order to reduce side-effects of the treatment or to reach other cancer targets, have led to "Carboplatin", a dicarboxylate derivative of the formula cis-$(NH_3)_2Pt[(O_2C)_2C(CH_2)_3]$, and to "Oxaliplatin" where the ammonia molecules are replaced by a trans-1,2-diaminocyclohexane ligand and oxalate functions as the dicarboxylate ligand. In both cases, $K_2[PtCl_4]$ or $K_2[PtCl_6]$ are the starting materials of the syntheses.

1.3 Substance function

ClPts are the result of the leaching and refining processes because of the use of chlorine and hydrochloric acid in the processes. Platinum has one of the highest redox potentials of all metals and therefore the strongest oxidants (assisted by complexants) are required to extract platinum metal and its insoluble compounds from ores and recycled materials. Only in the presence of very strong complexants (like cyanide) weaker oxidants are also effective (see further below). The halogens (fluorine, chlorine, bromine, and iodine) are strong oxidants and among these, chlorine is the most suitable. Chlorine leaching of platinum has the great advantage that it leads to a single oxidation state of platinum, *viz.* Pt(IV), and does not oxidize it to the maximum oxidation states Pt(V) and Pt(VI).

The same reaction techniques are used in recycling of platinum metals, with details depending on the matrices and the amount and nature of the components. Certain wastes and scrap may contain only one or two of the platinum group metals which facilitates the separation and isolation considerably.

As described above, the functions of the ClPts are closely related to the physical-chemical properties of platinum and chlorine. The most important of these are summarised and explained in the table below.

Table 1.1 Functional requirements of chlorine and ClPts in leaching, refining and manufacturing of platinum/ platinum compounds

Leaching and refinement of platinum	**Explanation**
Very strong oxidation potential	The extreme electrochemical potential for the redox processes of Pt ($Pt \rightarrow Pt^{2+} \rightarrow Pt^{4+}$) require a strong oxidant such as chlorine to dissolve elemental platinum as one of its salts or complexes. ClPts result from leaching of Pt from ores and recycled materials by use of chlorine and hydrochloric acid.
Controllable process	Chlorine is the oxidant of choice because the processes are most easily to control and lead to a single oxidation state of platinum.
Efficiency in refining / manufacturing	ClPts salts have solubility properties allowing for selective precipitation and re-dissolution and thus an efficient refining process. In the leach liquor the platinum appears as the stable complex $[PtCl_6]^{2-}$ which may be recovered in the form of the corresponding acid or its salts. This acid and several of its salts are soluble in water and can be readily purified by crystallization thus finally giving access to pure compounds

	and - by chemical or electrochemical reduction or by calcination - to pure platinum metal Related platinum group metals are also present in the leach liquor as chloro-complexes and the separation of the metals is carried out taking advantage of their different solubility, redox, complexation, adsorption or ion exchange properties. ClPt are moreover very suitable as intermediate and platinum source in manufacturing of platinum compounds that are suitable for specialised applications in different downstream industrial sectors. This includes non-chlorinated platinum precursors for heterogeneous and homogeneous catalysts, and platinum compounds for surface treatment.

1.4 Identification of possible alternatives

1.4.1 Leaching by fluorination

Chlorine leaching of platinum presents the great advantage of leading to a single oxidation state, *viz*. Pt(IV). Chlorine does not oxidize platinum to its maximum oxidation state Pt(VI). By contrast, with elemental fluorine the metal or its compounds are oxidized not only to PtF_4 and the corresponding $[PtF_6]^{2-}$ complex, but also up to PtF_5 and PtF_6, depending on the conditions of temperature and pressure. These highly fluorinated compounds are extremely aggressive and react not only with molecular oxygen but even with xenon, a discovery which is one of the landmarks in the history of Inorganic Chemistry.

These aspects, on top of the common problems with the handling of elemental fluorine in industrial processes, have precluded so far the use of this element for platinum leaching. Any move in this direction would require an entirely new technology with great challenges in techniques and economy. For the same reasons, fluorine is not the reagent of choice in the recovery and refining of gold.

The question arises if halogen fluorides ClF or ClF_3 , which are only moderately aggressive, should be considered. However, the handling would be equally challenging, and pertinent results have not been presented.

1.4.2 Leaching by bromination

There have been several attempts to apply bromine together with hydrochloric or hydrobromic acid in platinum leaching. It has been found that bromine has a positive influence on the leaching rates and yields (recovery), but after the leaching the bromine is recycled by the reaction with chlorine, and the platinum is thereby converted into the $[PtCl_6]^{2-}$ complex for further processing (US 5542957, 1996; US 2004081602, 2004; US 7166145, 2007; RO 130166, 2015). There are no reports of successful leaching solely with bromine and bromides (in complete absence of chlorine and chlorides) and of comprehensive refinement processes based on the bromides. This does not exclude specific separation problems in special combinations of metals or in reactions with bromate etc. (above). The higher solubility of the bromo complexes and their susceptibility to substitution reactions as compared to the chloro complexes may offer advantages at certain stages of the refinement.

The combined use of chlorine and bromine may involve the interhalogen compound bromine chloride, BrCl, but the role of this mixed halogen has not been investigated. Bromine trifluoride BrF_3 or tetrafluorobromates $[BrF_4]^-$ have recently been proposed for the treatment of uranium ores and waste for the production of UF_4 and UF_6. However, there is no comparable incentive to produce platinum fluorides.

1.4.3 Leaching by polyiodides

Platinum is slowly dissolved in polyiodide solutions (mixtures of alkali iodides and iodine) assisted by an oxidant under more forcing conditions of temperature and pressure, but the process suffers i. a. from the formation of insoluble products on the surface of the substrates. Leaching rates and efficiencies are therefore unpredictable. There is no road-map for the work-up of the platinum iodo complexes in the leach liquor (Zanjani, A., et al., 2009; Jha, M. K. et al., 2013). The economics of the process have not been estimated and may be very discouraging.

1.4.4 Leaching by other oxidants

There are no reports, and there is no convincing evidence that other powerful standard oxidants have been or can be used for the recovery of platinum from minerals or other resources. Reagents like oxygen (under pressure), ozone, peroxides, hypochlorite, chlorite, chlorate or perchlorate have been tested as reported mainly in patents, but in most cases with positive results chlorine was the active ingredient of the multicomponent systems.

1.4.5 Cyanide leaching of platinum

There is no evidence that cyanide leaching is seriously considered for the recovery and recycling of platinum (Bruckard, W. J., 1992; Zhao, J. S.).

1.4.6 List of possible alternatives

The possible alternatives that are identified in the section above are listed in the table below together with a preliminary assessment of their technical suitability as alternative. Based on this it is indicated in the table whether the alternatives are subject to further analysis or not.

Table 1.2 List of alternatives and preliminary assessment

Possible alternatives to chlorine based oxidants in leaching, recovery and refining of platinum	**Assessment**
Leaching by fluorination	Use of elemental *fluorine* leads to highly fluorinated platinum compounds that are extremely aggressive. The process is very difficult to control. This has precluded the use of fluorine for platinum leaching. **The alternative is not analysed further**
Leaching by bromination	There are no reports of successful leaching solely with bromine and bromides (in complete absence of chlorine and chlorides) and of comprehensive refinement processes based on the bromides. **The alternative is not analysed further**
Leaching by polyiodides	Leaching of platinum by polyiodide solutions (mixtures of alkali iodides and iodine) leads to formation of insoluble

	products on the surface of the substrates. Leaching rates and efficiencies are therefore unpredictable. **The alternative is not analysed further**
Leaching by other oxidants	There are no reports, and no convincing evidence that other powerful standard oxidants can be used for the recovery of platinum from minerals or other resources. **The alternative is not analysed further**
Cyanide leaching of platinum	There is no evidence that cyanide leaching is seriously considered for the recovery and recycling of platinum. **The alternative is not analysed further**

It is concluded that there is currently no technically suitable alternative to the use of chlorine and hydrochloric acid (e.g. as components in *aqua regia*) in the leaching steps of refining and recycling of platinum. Thus, leaching of Pt from ores, scrap and wastes strongly depends on use of chlorine, and results in ClPts, which are therefore the common intermediates for all platinum chemistry.

APPENDIX B–Cloroplatinates in catalysts

1 Chloroplatinates in catalysts

1.1 The market for chloroplatinates in catalysts

The focus in this section on use of CPA in catalysts is exclusively on chloroplatinic acid (CPA) and potassium tetrachloroplatinate (K_2PtCl_4, DTCP) as the only two platinum compounds identified by industry as being used in catalysts manufacture. These compounds can act directly as catalysts as such or as Pt precursors in catalyst manufacture.

Of a total world supply of 246 tpa Pt in 2015, about half (125 tpa) is used for catalysts. The main application of Pt in catalysts is in automotive catalysts (World: 102 tpa Pt; Europe: 49.6 tpa Pt) (WPIC, 2016). The platinum consumption worldwide for chemical catalysts is much smaller: 18.5 tpa Pt while for petroleum 5.0 tpa is used. As in chemical and refinery catalysts recycling of Pt is almost quantitative (97-98%) the importance of these catalysts is actually much higher than these consumption data suggest. Chemical catalysts (18.5 tpa Pt) include catalysts for hydrosilylation (ca 6 tpa Pt), for production of nitric acid and HCN, for selective hydrogenation and for dehydrogenation, a.o. The main petroleum catalyst is the so-called platforming or naphtha reforming catalyst which is used for converting naphtha into high-octane gasoline.
Based on German pre-2005 consumption data the following ranking is obtained based on net input of Pt: 1) automotive exhaust 2) hydrosilylation, 3) nitric acid, 4) oil refining, 5) environmental, 6) hydrocyanic acid, 7) powder catalysts (Hagelüken et al., 2005).

Table 1.1 Platinum consumption for catalysts in Germany ranked according to net input (Hagelüken et al., 2005).

Application (ranking)	**Gross input kg Pt/pa**	**Net input kg Pt/pa**
Automotive exhaust	7676	6912
Hydrosilylation	1500	1190
Nitric acid	760	45
Oil refining	830	25
Environmental	25	23
Hydrocyanic acid	180	18
Powder catalysts	350	17
Fixed-bed; fluid-bed	80	4
Total all Applications	**11401**	**8234**

A more recent ranking by a member of the PGM Working Group is as follows: 1) automotive catalysts, 2) oil refining, 3) hydrosilylation, 4) nitric acid, 5) environmental, 6) hydrocyanic acid, 7) powder catalysts.

In the following the discussion of alternatives to CPA and DTCP in catalysts is divided into a discussion of heterogeneous catalysts, where the platinum is added as a coat to an inert bearing material (e.g. in car exhaust systems), and homogeneous catalysts, where the platinum substance is the catalyst on its own, e.g. in hydrosilylation processes, in the production of silicones.

1.2 Exhaust catalysts

1.2.1 Annual tonnage range

This class of heterogeneous catalysts with a Pt consumption of 102 tpa worldwide represents by far the most important application of Pt in catalysis.

CPA has already been phased out by all manufacturers from the use as platinum precursor in the production of exhaust catalysts. One major player did so already 15-20 years ago. Since this is by volume the main use of platinum on the European market, and because CPA is probably still used for this purpose outside the EU, the discussion of alternatives is included in the report.

1.2.2 Analysis of substance function

Petrol-fuelled vehicles typically use a three-way catalyst, so-called because it converts three pollutants, carbon monoxide, hydrocarbons and nitrogen oxides into carbon dioxide, water and nitrogen. Platinum, palladium and rhodium having remarkable resistance to high-temperature operation form the active components. The standard catalytic converter on a petrol-powered vehicle is extremely durable designed to meet emission standards for 120,000 miles. Diesel catalysts too contain Pt to convert hydrocarbons by oxidation.

Table 1.2 Function and activity of platinum, palladium and rhodium in exhaust catalysts. (‘+’ = high; ‘0’ = medium; ‘-‘ = low)

Reaction	**Platinum**	**Palladium**	**Rhodium**
CO, CH oxidation	+	+	-
NO oxidation	+	0	-
NO_x reduction	-	0	+
Sulphur resistance	+	-	0

Both platinum and palladium are able to catalyse oxidation reactions such as the conversion of carbon monoxide and hydrocarbons, while rhodium is the most effective catalyst for the reduction of nitrogen oxides. Palladium has been incorporated into formulations due to a combination of price and to improvements in high-temperature stability afforded by specific Pt-Pd alloys (Morlang et al., 2005). In Pt diesel catalysts, zeolites like beta are incorporated to improve performance during the cold start (Twigg, 2011).

Today's three-way catalyst is a complex multicomponent system. For optimum use of expensive Platinum Group Metals these materials have to be deposited in a highly dispersed state. The most common carrier, a ceramic honeycomb of high-temperature fired cordierite ($2MgO.2Al_2O_3.5SiO_2$), has a too low surface area to accommodate a high metal dispersion. Therefore, this honeycomb is coated with high-surface area support material, mostly alumina stabilised with lanthana and/or baria, ceria (10-20%) and/or zirconia. This coating is called the washcoat.

Nowadays, modern catalysts have multilayered washcoats that are comprised of high-surface area, thermally-stable support materials like La-stabilised alumina in one layer and stabilized zirconia in another. Rh is usually supported on zirconia in a separate washcoat layer to avoid Rh loss due to aluminate formation (Bartholomew and Farrauto, 2005). To ensure that certain metals are fixed onto a specific carrier component sometimes the metal is first deposited on a washcoat ingredient, which then is incorporated in the total washcoat slurry to be deposited onto the cordierite brick.

A typical exhaust catalyst composition based on the patent literature is: platinum & palladium 1.1%, rhodium 0.11%, alumina 52%, ceria 24%, zirconia 12%, lanthana 6%, baria 5%. (Bartholomew and Farrauto, 2005).

Selection of Platinum Group Metal based precursors having charge compatibility with the wash coat or its ingredients greatly improves metal dispersion and stability. The pH at which the support is neutral is termed the point of zero charge (PZC). Below this pH the support becomes positively charged and the surface can adsorb anionic metal complexes such as the negatively charged hexachloroplatinate $PtCl_6^{2-}$ anion (Pt^{4+}). Above the PZC the support becomes negatively charged and cations like platinum tetraammine can be strongly adsorbed (Regalbuto, 2009). Thus depending on the precursor, platinum may adsorb onto wash coat ingredients either as a cation or as an anion. CPA readily adsorbs onto the positively charged alumina (PZC 8) but is repelled by other wash coat ingredients that are negatively charged like zeolites (PZC<1) and silicas (PZC=3).

Initially the wash coat in exhaust catalysts consisted of only lanthanum-stabilised alumina, which at the low pH of CPA was positively charged and thus attracted the negatively charged $PtCl_6^{2-}$ which was deposited in high state of dispersion. However, sintering of platinum (and palladium) during high-temperature excursions proved to be a serious problem resulting in a significant loss of active surface area. It was found that alkali metals such as Na and K accelerate the sintering of alumina and thus catalyst manufacturers exclude these elements from exhaust catalysts. In addition, chlorides in CPA and other chlorine-containing precursor salts enhance the rate of precious metal sintering. Another problem of chlorine in exhaust catalyst is corrosion of exhaust pipes (US 5489522 to Ford; M. Grehl et al., 2012). Therefore, platinum precursors used by catalyst companies are free of alkali- and halide-containing materials and thus CPA is not used anymore (Bartholomew et al. 2005, M. Grehl et al., 2012).

Table 1.3 Functional requirements of Platinum and Pt precursors in exhaust catalysts

Platinum in exhaust catalysts	**Explanation**
Activity	Both platinum and palladium are able to catalyse oxidation of carbon monoxide and hydrocarbons. Platinum further catalyses the oxidation of nitrogen monoxide.
Stability (high temperature)	Platinum (and palladium) have remarkable resistance to high-temperature operations. Palladium improves the high-temperature stability by specific platinum-palladium alloys.
Selectivity	Platinum has the important property of being able to oxidise hydrocarbons and CO completely to water and CO_2 at a range of operating temperatures without the production of dioxins.

Poison resistance	Unlike other metals Pt has a remarkable resistance towards poisons like sulphur and the presence of platinum in automotive catalysts ensures a long active life. The only poison which is irreversibly adsorbed is lead which has already been eliminated from automotive fuels some time ago.
Affinity of precursor towards the carrier material	Precursors having charge compatibility with the carrier material or its ingredients greatly improve metal dispersion and stability. CPA ($PtCl_6^{2-}$) was earlier used as precursor as it was compatible with lanthanum-stabilised alumina, which at the low pH was positively charged and thus suitable for deposition of CPA. However, the high operating temperatures and chloride enhance the rate of metal sintering leading to a loss of active surface area. Moreover the chlorine leads to corrosion of exhaust pipes. Therefore, nowadays only platinum precursors are used in which the platinum ion is positively charged. These compounds can be accommodated by adapting the pH which turns the charge of the carrier from positive to negative thus ensuring a good platinum-carrier interaction and hence a high dispersion resulting in a high catalytic activity.

1.2.3 Identification of possible alternatives

1.2.4 Possible alternatives to platinum in exhaust catalysts

Replacement of platinum by nickel and copper has been widely studied but this development was not successful because of the poor poison resistance of these metals and the fear to produce dioxins as by-products. In future, with the use of cleaner fuels, these metals may become relevant again but this will not lead to replacement of platinum in the foreseeable future.

Gold and silver are not suitable because of their limited durability and activity. Ruthenium, iridium and osmium have suitable activity profiles but they form volatile oxides ruling them out as automotive catalysts.

Full replacement of platinum by palladium-based precursors does not seem feasible either. The lower price of palladium compared to platinum has already been quite an incentive for many years and hence replacement of platinum by palladium has been widely explored and to some extent already implemented. Full replacement is not feasible because of the poor poison resistance of palladium. In addition, palladium/platinum combinations improve temperature stability (Morlang et al., 2005). Finally, platinum is superior over palladium in NO oxidation. Therefore, platinum is expected to stay as an important ingredient in exhaust catalysts.

1.2.5 Currently used alternatives to CPA

Due to the fact that chloride-free (and alkali-free) precursors have performance benefits, manufacturers of exhaust catalysts have already switched to these alternatives. Thus platinum tetra-ammine acetate or nitrate are widely used in automotive and chemical catalyst manufacturing (M. Grehl et al., 2012). There is also a trend towards greener preparation procedures. As a consequence, acetates rather than nitrates are nowadays often used to prevent the substantial emissions of NO_2 associated with calcination of nitrate salts (Bartholomew and Farrauto, 2005).

To replace CPA, several chloride-free platinum intermediates are available. Platinum tetraammine hydrogen carbonate $Pt(NH_3)_4(HCO_3)_2$, hexahydroxyplatinic acid $H_2Pt(OH)_6$ and platinum diamminedinitrite $Pt(NH_3)_2(NO_2)_2$ provide access to a range of chloride-free compounds. These insoluble intermediates are precipitated from the original chloride-containing solutions. Platinum tetraammine bicarbonate can be converted into a variety of platinum tetraammine salts by dissolving it in inorganic or organic acids.

The following chloride-free platinum compounds are listed as suitable catalyst precursors on the Johnson Matthey website, accessed May 2016

Table 1.4 - Alternative platinum compounds listed as suitable catalyst precursors (ref.: Johnson Matthey web page)

Platinum(IV) nitrate: $H_2Pt(NO_3)_6$ solution.
Platinum(II) tetraammine nitrate, $Pt(NH_3)_4(NO_3)_2$ sold as a solution pH 6 – 6.5.
Platinum(II) tetraammine hydroxide, $Pt(NH_3)_4(OH)_2$, a solution of 8-11% Pt.
Platinum(II) tetraammine hydrogen carbonate, $Pt(NH_3)_4(HCO_3)_2$, a solid.
Ethanolamine hexahydroxyplatinic acid, $(HOCH_2CH_2NH_3)_2\,Pt(OH)_6$.
Platinum(II) tetraammine acetate, $Pt(NH_3)_4Ac_2$, a 18-22% Pt solution
Hexahydroxyplatinic acid $H_2Pt(OH)_6$, a solid

Several of these compounds are also mentioned in patents by other companies e.g. ethanolamine hexahydroxyplatinic acid (US patent 5948723 to Engelhard/BASF), platinum(II) tetraammine hydroxide, $Pt(NH_3)_4(OH)_2$ (US patent 5597771 to Engelhard/BASF). In US patent 5489522 to Ford Motor Company, platinum 2-ethylhexanoate in organic solvents is claimed.

Overall it is concluded that for the production of exhaust catalysts several platinum alternatives to CPA are available. Being chlorine- and alkali-free these are even preferred over CPA because of lack of corrosion of the exhaust pipe and improved temperature stability of the final catalyst. For these reasons CPA was phased out already several years ago (Bartholomew and Farrauto, 2005, M. Grehl et al., 2012).

1.3 Reforming (platforming) catalysts

1.3.1 Annual tonnage range

As the total platinum consumption for petroleum catalysts worldwide is only 5.0 tpa platinum and catalytic reforming is the main application, the tonnage for this application alone will be close to 5.0 tpa platinum. As most of the platinum is recycled the importance of reforming catalysts is much greater than these platinum consumption data suggest. For 2005 the catalyst market for catalytic reforming was estimated to be $ 55 million (Forman, 2001). Catalyst suppliers are Criterion, Honeywell/UOP, IFP, Axens, Exxon, Sinopec, a.o. More than 800 platforming units have been installed worldwide by UOP (UOP website).

1.3.2 Analysis of substance function

Reforming catalysts are heterogeneous catalysts that convert straight-run low octane naphtha to high-octane gasoline and to aromatic compounds using a bi-functional catalyst with both metallic sites of platinum and acidic sites originating from the chlorinated alumina support. Reforming catalysts are complex composites of platinum to efficiently perform dehydrogenation and hydrogenation reactions, and an active support to do complementary reactions. The carrier is a high-purity alumina designed to have an acid functionality, which can be moderated by controlling the amount of chloride added to the support and/or by the addition of promoters like rhenium or tin. Platinum–rhenium is the most widely used.

Published preparation procedures usually involve impregnating gamma-alumina extrudates with a solution of CPA and hydrochloric acid and optionally perrhenic acid ($HReO_4$) is added (Rase et al. 2000; Bartholomew et al, 2005). At the low pH, the positively charged alumina strongly adsorbs the negatively charged $PtCl_6^{2-}$ and Cl^- ions. Thus technically CPA is a very suitable platinum precursor for these catalysts.

Apart from promoting a homogeneous distribution of the platinum the Cl^- also creates the required acidic sites. The addition of rhenium increases catalyst stability by preventing platinum sintering. After impregnation, the extrudates are air-dried, calcined at 500^{o}C and activated by converting the platinum to the metallic state in situ in flowing hydrogen yielding highly dispersed platinum crystallites of < 3.5 nm. The acid function is optimum at ca. 0.8-1.0% chlorine. Often the catalysts are pre-sulphided for controlled poisoning (Rase et al. 2000). After the main process steps of calcination and activation, the platinum is in the metallic state and no traces of the CPA remain on the catalyst. After deactivation the catalyst is regenerated by redispersing platinum using Cl_2.

Platinum levels are low and a typical catalyst composition is 0.2-0.5% platinum, 0.2-0.5% Re, 0.8-1.0% Cl and alumina (balance).

The current method of using CPA is highly optimized and provides both a uniform distribution of highly dispersed platinum and a chlorination of the alumina surface. CPA being negatively charged and chlorine containing is considered to be the ideal precursor. Even recent patents like WO2013148397 (A1) to UOP (2013) still specify this platinum precursor rather than alternative substances. No alternative methods to replace CPA seem to have been explored at commercial scale.

Table 1.5 Functional requirements of Platinum and CPA in reforming catalysts

Platinum in reforming catalysts	**Explanation**
Activity	Platinum catalysts with Re as promoter have a high catalyst activity. The reforming catalysts are complex composites of platinum to efficiently perform dehydrogenation and hydrogenation reactions. The catalysts convert straight-run low octane naphtha to high-octane gasoline and to aromatic compounds.
Stability	Stability of platinum against sintering is greatly enhanced by the presence of rhenium.
Regeneration	Platinum reforming catalysts have the interesting property that deactivated catalysts can be regenerated by addition of chlorine which re-disperses the platinum metal thus restoring most or all of the initial activity.

Selectivity	Platinum efficiently performs dehydrogenation and hydrogenation reactions which allows the resulting olefins to be isomerized by the acidic sites.
Poison resistance	Unlike other metals platinum has a remarkable resistance towards poisons.
Affinity of precursor towards the carrier material	The precursor CPA has a high affinity towards the acidic carrier material. At low pH, the positively charged alumina strongly adsorbs the negatively charged $PtCl_6^{2-}$ and Cl^- ions leading to a homogeneous distribution of the platinum. Thus technically CPA is a very suitable platinum precursor for these catalysts.

1.3.3 Identification of possible alternatives

1.3.4 Possible alternatives to platinum

Considerable research has shown that using platinum catalysts with Re as promoter coupled with pre-treatment in 10-20 ppm H_2S yields catalysts that are superior to non-platinum alternatives. Other promoters like Sn, Ge and Ir can be used too but there does not seem to be a suitable alternative to platinum as the main metal (Raseev, 2003).

1.3.5 Possible alternatives to CPA

Theoretically platinum could be depositing using positively charged non-chloride platinum(II) precursors and raising the pH to create a negatively charged alumina support followed by chlorination of the resulting precursor. Re, which is stable in the basic pH region over a wide range, could be included in the impregnation solution. This alternative method, however, is unproven and would require lengthy development work and years of pilot plant and commercial scale testing. In addition, the catalyst has to be chlorinated anyway to generated acid sites with the potential risk of some CPA formation. As the performance benefits are not obvious this method will not easily be accepted by industry.

In overviews of commercial platinum reforming catalysts gamma alumina is mentioned as the only suitable support which dictates the use of CPA as platinum precursor (Rase 2000, Table 18.1; Rasesev, 2003). Theoretically, platinum alternatives might be used in combination with silica-alumina as a support. The acidity then is provided by this support, which is negatively charged over a wide pH range and is particularly suited for depositing positively charged platinum(II) precursors (Weissermel, 1997). However, the use of silica-aluminas was commercialized but later abandoned because of too strong acidity (Raseev, 2003).

1.3.6 List of possible alternatives

It was confirmed by the PGM working group that CPA is still used because of technical and cost reasons. CPA has several technical advantages over any alternatives. Non-chloride platinum(II) precursors on silica-alumina support could be an option, but this catalyst was explored in the past and used commercially but was later rejected because of a too high acidity of the resulting catalyst.

The possible alternatives are listed in the table below together with a preliminary assessment of their technical suitability as alternative. Based on this it is indicated whether the alternatives are subject to further analysis or not.

Table 1.6 List of alternatives to CPA in reforming catalysts and preliminary assessment

Possible alternatives	**Assessment**
Possible alternatives to platinum based catalysts	Other promoters like Sn, Ge and Ir can be used too but there does not seem to be a suitable alternative to platinum as the main metal. **The alternative is not analysed further**
Non-chloride Platinum(II) precursor on negatively charged alumina	Theoretically platinum could be depositing using positively charged platinum(II) precursors and raising the pH to create a negatively charged alumina support. This alternative method, however, is unproven and would require lengthy development work and years of pilot plant and commercial scale testing. In addition, the resulting catalyst has to be chlorinated anyway to provide the required acidity with the likely formation of small quantities of CPA . **The alternative is further analysed below.**
Non-chloride platinum(II) precursors on silica-alumina support	Platinum alternatives might be used in combination with silica-alumina as a support. The use of silica-alumina has been commercialized earlier, but later abandoned because of too strong acidity. In principle acidity of silica-alumina can be tuned by adapting the silica/alumina ratio. **The alternative is further analysed below.**

1.3.7 Analysis of alternative platinum precursors to CPA

1.3.8 Substance ID and properties

The alternatives to use of CPA in the manufacture of reforming catalysts, include positively charged non-chloride platinum(II) precursors, e.g. platinum(II) tetramine nitrate, $Pt(NH_3)_4(NO_3)_2$ or platinum(II) tetramine hydroxide, $Pt(NH_3)_4(OH)_2$.

Substance	Formular	CAS No.	EC No.
Platinum(II) tetraammine nitrate	$Pt(NH_3)_4(NO_3)_2$	20634-12-2	243-929-9
Platinum(II) tetraammine dihydroxide	$Pt(NH_3)_4(OH)_2$	15651-37-3	239-719-1

1.3.9 Technical feasibility

From a theoretical point positively charged non-chloride platinum(II) precursors could be deposited by raising the pH to create a negatively charged alumina support or on silica-alumina support. Platinum(II) precursors on silica-alumina support have been commercialized earlier, but were abandoned again because of too strong acidity. According to European industry development of alternative techniques will require 7.5 to 10 years of development of testing, but without any certainty of success. Industry is concerned that the catalysts based on alternative platinum precursors may give a lower yield in use and have a shorter service life. The solution is therefore not regarded as attractive from a commercial point of view.

1.3.10 Economic feasibility

The collected information in terms of economic consequences of a legal requirement of substitution of CPA does not allow discrimination between the main groups of catalysts, i.e. reforming, dehydrogenation and DTCP based catalysts. The discussion of the economic feasibility therefore covers the three types of catalysts.

For reforming, dehydrogenation and hydrogenation catalysts there are no obvious alternatives to CPA/ DTCP as precursors, and intensive research and development programs need to be carried out before the possible alternatives identified in this report can be available for industrial scale production. Industry foresee that the required investment for developing and introducing a new techniques will require massive investments for each European production site.

1.3.11 Reduction of overall risk

CPA are known to cause respiratory sensitisation in humans and for this reason a possible candidate for being a Substance of Very High Concern under the REACH regulation.

Examples of the classification of selected alternative platinum(II) compounds are cited in the table below. The classification of human health hazards include allergic skin reactions, eye damage, skin corrosion. In the environment the substances are classified as harmful to very toxic to aquatic life with long lasting effects.

Table 1.7 – Hazard classification of CPA and examples of chlorine free platinum(II) compounds.

Substance	**Hazard Class**	**Hazard Statement**
Chloroplatinic acid (CPA)[1] (CAS 16941-12-1; EC 241-010-7)	Acute Tox 2	H300 - Fatal if swallowed
	Skin Corr. 1B	H314 – Causes severe skin burns and eye damage
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Eye dam. 1	H318 - Causes serious eye damage
	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	STOT RE1	H372 - Causes damage to organs through prolonged or repeated exposure.
	Aquatic acute 1	H400 Very toxic to aquatic life (Acute M-factor 10)
	Aquatic chronic 1	H410 Very toxic to aquatic life with long lasting effects (Chronic M-factor 10)
	Met. Corr. 1	H290- May be corrosive to metals
Platinum(II) tetraammine nitrate (CAS 20634-12-2; EC 243-929-9)[2]	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.

	Met. Corr. 1	H290 - May be corrosive to metals
Platinum(II) tetraammine hydrogen carbonate [1] (CAS 123439-82-7; EC 426-730-3)	Acute Tox. 4	H302 – Harmful if swallowed.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
Platinum(II) tetraammine dihydroxide[2] (CAS 15651-37-3; EC 239-719-1) According to the PMC classification strategy the Skin Sens classification is challenged. The classification will be updated.	Skin Sens. 1	H317 – May cause an allergic skin reaction.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Acute 1	H400 – Very toxic to aquatic life.
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects.
Platinum dinitrate [2] (CAS 18496-40-7; EC 242-383-9)	Skin Corr. 1A	H314 – Causes severe skin burns and eye damage.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)
	Aquatic chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)
	Met. Corr. 1	H290 - May be corrosive to metals
	Oxid solid 1	H271 - May cause fire or explosion; strong oxidiser

[1] Harmonised Classification; [2] Classification notified by PMC

The benefit in terms of reduced risk in the work environment of substitution CPA with alternative platinum compounds is a reduction of the risk of respiratory sensitisation among workers that are exposed to the substances in industry manufacturing the ClPt precursors and platinum catalysts. It is estimated that in the EU about 120-140 workers are currently working with chloroplatinates, mainly in production of catalyst pre-cursors or catalysts.

1.3.12 Availability of alternative solutions

The identified possible alternative solutions and techniques to the current use of CPA as precursor in reforming catalysts are currently not available for industrial scale use. As mentioned industry expects that the development time for a solution would be 7.5 to 10 years.

1.3.13 Conclusions on suitability

Based on the available information it is concluded that there are currently no available, technically suitable alternative to CPA for industrial scale manufacture of reforming catalysts. In order to develop alternative solutions investment in research and development is needed. The estimated time for development and implementation of an alternative solution is 7.5 – 10 years.

Industry estimates that research, development, trial testing, training and installation of an alternative solution will require extensive investments for each production European site.

The identified alternatives are less harmful to workers and thus easier to handle safely in the work environment mainly due to the absence of the respiratory sensitisation hazard. A phase out of CPA may reduce the risk of respiratory sensitisation effects among 120-140 workers in the EU that are currently working with manufacture of chloroplatinates or their use in catalyst production.

1.4 Dehydrogenation catalysts

1.4.1 Annual tonnage range

As the total platinum consumption of chemical catalysts is about 18.5 tpa platinum worldwide of which at least 4-6 tpa is used for hydrosilylation and the fact that chemical catalysts include a range of catalysts, the tonnage for this application alone will be well below 10 tpa platinum.

Currently two types of dehydrogenation catalysts exist: mainly platinum-tin supported on alumina and chromium supported on alumina or zirconia promoted with potassium or caesium. There are a range of processes offered by industry each using its own tailored catalyst: Houdry/ABB Lummus (Catofin, 20% Cr_2O_3-on-alumina), Snamprogetti (FBD, 10-20% Cr_2O_3-on-alumina), UOP (Oleflex, promoted 0.3% platinum-on-alumina), Phillips (Star, Sn-promoted 0.2-0.6% platinum on zinc aluminate) and Linde-BASF (Cr_2O_3-on-alumina) a.o. (Rase, 2000; Resasco, 2003, Bartholomew et al., 2005).

1.4.2 Analysis of substance function

Platinum dehydrogenation catalysts are heterogeneous catalysts used for converting alkanes into the corresponding olefins, e.g. propane into propylene and butane into butylene. Platinum is an ideal metal for dehydrogenation because of its high activity for cleaving C-H bonds combined with its low activity for C-C bond rupture (Resasco, 2003). As platinum is more active towards olefins than to alkanes, platinum levels are low and the activity of platinum has to be tempered by addition of promoters. Commercial catalysts have been reported to be 0.3% platinum-on-theta-alumina promoted with alkali, Sn, Zn or Cu. The preferred promoter is Sn. The addition of Sn has important beneficial effects. First of all, it increases the selectivity towards dehydrogenation by inhibiting hydrogenolysis. Similarly, the addition of Sn has a profound effect on the catalyst life. The Pt-Sn catalyst retains a much higher activity than the pure platinum catalyst.

The standard preparation involves impregnating gamma alumina or zinc aluminate with a solution of CPA, HCl and promoter salts, e.g. tin salts which have a good solubility. In addition, the basic nature of the supports (alkali doped alumina, zinc aluminate) requires a negatively charged platinum ion, i.e. a chloroplatinate ion. It was confirmed by the PGM Working Group that CPA is still used due to technical and cost reasons.

At the low pH, the positively charged alumina strongly adsorbs the negatively charged $PtCl_6^{2-}$. Co-impregnation, particularly when the solvent is an aqueous solution containing HCl, results in a relatively high extent of Pt-Sn interaction. By contrast, sequential impregnation results in a large fraction of unalloyed platinum and hence to a reduced performance (Resasco, 2003). After the main process steps of calcination and activation, the platinum is in the metallic state and no traces of the CPA remain on the catalyst.

Table 1.8 Functional requirements of Platinum and CPA in dehydrogenation catalysts

Function	**Explanation**
Activity	Platinum is an ideal metal for dehydrogenation because of its high activity for cleaving C-H bonds combined with its low activity for C-C bond rupture. The preferred promoter is Sn which enhances its selectivity and stability
Stability	The Pt/Sn catalysts are very stable and after deactivation can be regenerated by oxidative treatment, optionally in the presence of chlorine.
Selectivity	Unlike other metals platinum does not cause rupture of the C-C bond and thus the process suffers less from by-product formation.
Poison resistance	Unlike other metals platinum has a remarkable resistance towards poisons. The Pt/Sn combination reduces the tendency of deactivation by coke deposition.
Affinity of precursor towards the carrier material	The positively charged alumina carrier strongly adsorbs the negatively charged $PtCl_6^{2-}$ at low pH.

1.4.3 Identification of possible alternatives

1.4.4 Possible alternatives to platinum

Cr catalysts are widely used too, but are not tailored to the Star (Phillips) and Oleflex (UOP) processes. Because of the toxicity of Cr^{VI} special safety precautions are required and there is increased pressure to find substitutes for Cr with less toxic catalysts, e.g. PGM metals like platinum (Bartholomew and Farrauto, 2005).

1.4.5 Possible alternatives to CPA

Theoretically platinum could be deposited using positively charged non-chloride platinum(II) precursors and raising the pH to create a negatively charged alumina support but most promoter ions are insoluble at high pH while tin eventually forms negatively charged tin compounds, which will be repelled by the negatively charged alumina support. Alternative platinum precursors may be acidic platinum(IV) nitrate $H_2Pt(NO_3)_6$ or $H_2Pt(OH)_6$ which contain negatively charged platinum complex ions, which are commercially available. A different more speculative method might involve the platinum-catalyzed surface reduction of an organometallic tin compound, resulting in the selective deposition of Sn over the platinum surface. For example, the catalyst can be prepared from a solution of Sn in organic solvent, such as n-hexane. This solution is added onto a pre-reduced platinum/support sample, without exposure to air. The H^+ that remains adsorbed on platinum is responsible for the reduction of the Sn (causing the selective deposition over the metal). This alternative method is yet unproven at larger scale. It would be more costly and would require lengthy development work and years of pilot plant and commercial scale testing. As the performance benefits are not obvious this method will not easily be accepted by industry.

1.4.6 List of possible alternatives

The possible alternatives identified are listed in the table below together with a preliminary assessment of their technical suitability as alternative. Based on this it is indicated in the table whether the alternatives are subject to further analysis or not.

Table 1.9 List of alternatives to CPA used for manufacture of dehydrogenation catalysts and preliminary assessment

Possible alternatives	**Assessment**
Possible alternatives to platinum based catalysts	Cr catalysts are widely used. Because of the toxicity of Cr^{6+} this type of catalyst cannot be regarded as a possible alternative. **This alternative is not analysed further**
Non-chloride platinum(II) or platinum(IV) precursor	Normally platinum is co-impregnated with Sn, or other promoters. Theoretically positively charged platinum(II) precursors could be deposited on a negatively charged alumina support (at high pH). Most promoter ions are however, insoluble at high pH. Therefore, acidic platinum(IV) nitrate $H_2Pt(NO_3)_6$ or $H_2Pt(OH)_6$ which contain negatively-charged platinum complex ions and which are commercially available, may be interesting candidates. **The alternative is further analysed below.**

1.4.7 Analysis of alternative platinum precursors to ClPt

1.4.8 Substance ID and properties

The alternatives to the use of chlorinated platinum (CPA) include positively charged non-chloride platinum(II) precursors e.g. platinum(II) tetramine nitrate, $Pt(NH_3)_4(NO_3)_2$ or platinum(II) tetramine hydroxide, $Pt(NH_3)_4(OH)_2$. Negatively charged chlorine free platinum precursors include acidic platinum(IV) nitrate $H_2Pt(NO_3)_6$ or $H_2Pt(OH)_6$.

Substance	Formular	CAS No.	EC No.
Platinum(II) tetraammine nitrate	$Pt(NH_3)_4(NO_3)_2$	20634-12-2	243-929-9
Platinum(II) tetraammine dihydroxide	$Pt(NH_3)_4(OH)_2$	15651-37-3	239-719-1
Platinum(IV) nitrate	$H_2Pt(NO_3)_6$	-	432-400-1
Dihydrogen hexahydroxyplatinate (IV)	$H_2Pt(OH)_6$	51850-20-5	257-471-2

1.4.9 Technical feasibility

The method for use of chlorine free platinum(II) precursors or acidic platinum(IV) compounds is yet unproven at larger scale. Commercialisation will require lengthy development work and years of pilot plant and commercial scale testing. Moreover the performance benefits of these methods are not obvious.

1.4.10 Economic feasibility

Please refer to the discussion in section B.3.4.3.

1.4.11 Availability of alternative solutions

The identified possible alternative solutions to the current use of CPA as precursor in dehydrogenation catalysts are currently not available for industrial scale use. As mentioned industry expects that the development time for a solution would be 7.5 to 10 years.

1.4.12 Reduction of overall risk

In the section B.3.3.4. examples of the classification of non-chlorinated positively charged platinum precursors were shown. As mentioned there, negatively charged precursors may also be alternatives. The classification of these platinum(IV) nitrate, $H_2Pt(NO_3)_6$ or hexahydroxyplatinic acid, $H_2Pt(OH)_6$, is compared with CPA in the table below.

Table 1.10 – Hazard classification of CPA and examples of chlorine free platinum(II) compounds.

Substance	**Hazard Class**	**Hazard Statement**
Chloroplatinic acid (CPA)[1] (CAS 16941-12-1; EC 241-010-7)	Acute Tox 2	H300 - Fatal if swallowed
	Skin Corr. 1B	H314 – Causes severe skin burns and eye damage
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Eye dam. 1	H318 - Causes serious eye damage
	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	STOT RE1	H372 - Causes damage to organs through prolonged or repeated exposure.
	Aquatic acute 1	H400 Very toxic to aquatic life (Acute M-factor 10)
	Aquatic chronic 1	H410 Very toxic to aquatic life with long lasting effects (Chronic M-factor 10)
	Met. Corr. 1	H290- May be corrosive to metals
Platinum(II) tetraammine nitrate (CAS 20634-12-2; EC 243-929-9)[2]	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
	Met. Corr. 1	H290 - May be corrosive to metals

Platinum(II) tetraammine dihydroxide[2] (CAS 15651-37-3; EC 239-719-1) According to the PMC strategy the Skin Sens classification is challenged. To be updated!	Skin Sens. 1	H317 – May cause an allergic skin reaction.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Acute 1	H400 – Very toxic to aquatic life.
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects.
Platinum(IV) dinitrate [2] (CAS 18496-40-7; EC 432-400-1)	Skin Corr. 1A	H314 – Causes severe skin burns and eye damage.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)
	Aquatic chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)
	Met. Corr. 1	H290 - May be corrosive to metals
	Oxid solid 1	H271 - May cause fire or explosion; strong oxidiser
Dihydrogen hexahydroxyplatinate[2] (CAS 51850-20-5; EC 257-471-2)	Eye Irrit. 2	H319 - Causes serious eye irritation
	Aquatic Acute 1	H400 – Very toxic to aquatic life
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects

[1] Harmonised Classification; [2] Classification notified by PMC

The hazard classification of the alternative platinum substances include allergic skin reactions, eye damage, skin corrosion and skin sensitization, but not respiratory sensitisation. For the environment the substances are classified as “harmful” to “very toxic” to aquatic life with “with long lasting effects”.

Overall, use of the alternatives platinum(II) compounds and platinum nitrate will reduce the risk of respiratory sensitisation in the workplace. The estimated number of workers in the EU within manufacturing and use of chloroplatinates as catalyst precursor or in catalysts production is 120-140.

1.4.13 Conclusions on suitability

The available information indicates that substitution of CPA with the identified alternatives will require further development work and probably years of pilot plant and commercial scale testing. Commercially the performance benefits of the alternative solutions are not obvious.

Economically the substitution of CPA will require extensive research and development as well as investment in equipment and training. Industry estimates that research, development, trial testing, training and installation of alternative solutions will require extensive investments at each European production site.

The possible alternatives are generally less hazardous mainly because they are not respiratory sensitizers. A phase-out of the use of CPA can potentially reduce the risk of respiratory sensitisation effects among the estimated 120-140 workers currently working with chloroplatinates manufacturing or their use as catalyst precursor in catalysts production.

1.5 Miscellaneous heterogeneous catalysts

1.5.1 Analysis of substance function

A range of platinum catalysts with platinum in the zero oxidation state and supported on carbon, alumina and calcium carbonate are manufactured using CPA as a platinum precursor, sometimes only for niche applications or as proprietary catalysts. The platinum is chemically reduced. After this reduction step, the platinum is in the metallic state and no traces of the CPA remain on the catalyst. The dominant support is active carbon with a share of 98% (Hagelüken et al., 2005). These catalysts are used for hydrogenation, dehydrogenation, selective oxidation, etc.

Another use of platinum is in fuel cells. For this purpose platinum particles are precipitated on substrate surfaces such as carbon by reduction of a chlorinated platinum salt with a reductant in aqueous solution. These more particulate platinum deposits are used as heterogeneous catalysts, mainly in fuel cells based on polymer electrolyte membranes (PEMs), metalorganic frameworks (MOFs) and carbon supports.

1.5.2 Identification of possible alternatives

For several of these applications alternatives exist based on chromium, nickel, copper or palladium. For certain specific applications, platinum, however, remains the preferred metal, often in combination with specific promoters (Sn), e.g. for selective hydrogenation of halonitroaromatics to the corresponding haloaminoaromatics, the hydrogenation of unsaturated aldehydes to the unsaturated alcohols and reductive alkylations involving the reaction of an aldehyde or ketone with an amine.

Catalysts on a carbon support it is not possible to use platinum(II) ammine compounds. Theoretically, alternatives may be acidic platinum(IV) nitrate $H_2Pt(NO_3)_6$ or $H_2Pt(OH)_6$, which contain negatively-charged platinum complex ions.

These catalysts are however a niche market in the EU with a platinum consumption of less than 300 kg/year and involving only a few workers (i.e. < 10) in the production. There is little incentive for the company to research for alternatives, and in case a stricter regulation requires substitution of CPA, the most likely solution will be to allocate the production to a site outside the EU.

Based on this information the analysis of alternatives is not discussed further in this report.

1.6 Homogeneous catalysts for hydrosilylation

1.6.1 Annual tonnage range

When a homogeneous hydrosilylation catalyst is used, the platinum usually remains with the reaction products. This can cause issues of cost, colour and safety and an estimated loss of 4-6 tpa platinum worldwide corresponding to $377 million worth of metal (Friedman et al. 2012).

Based on the estimated loss of 4-6 tpa platinum worldwide remaining in the final product (Friedman et al. 2012) and a platinum loss of 79% (Hagelüken, 2005), the volume for this application will be 5-7 tpa platinum.

1.6.2 Analysis of substance function

Hydrosilylation is an important method for preparing organosilicon compounds and is the largest-cost application for homogeneous catalysis (Friedman et al., 2012). Although a wide range of catalysts are known for the hydrosilylation of C=C double bonds, Karstedt’s catalyst [Pt_2(sym-tetramethyldivinyldisiloxane)$_3$] is by far the most common hydrosilylation catalysts. Speier’s catalyst (CPA in alcohol) was used earlier but has largely been replaced by Karstedt’s catalysts. Other platinum-complexes have also been used in hydrosilylation reactions.

CPA "Speier's catalyst", was used initially in the production (Speier 1957, Lewis 1991). CPA is regarded as a precursor to the actual catalyst. CPA contains platinum in oxidation state IV which must be reduced before it becomes catalytically active. This results in an induction period. In contrast the alternative, Karstedt’s catalyst, is active straightaway. At the end of the reaction the platinum species formed by Speier's and Karstedt’s catalysts are largely identical. Importantly no chlorine containing platinum species have been reported to appear in the final product (Stein et al. 1999).

The similarity of the pathways of Speier and Karstedt suggests that Karstedt is an excellent alternative to Speier.

Table 1.11 Functional requirements of Platinum and CPA in homogeneous catalysts for hydrosilylation

Function	**Explanation**
Activity	A wide range of catalysts (e.g. base metal catalysts such as Fe and Ni catalysts) is known to catalyse hydrosilylation but platinum catalysts are by far the most active. CPA contains platinum in oxidation state +IV which must be reduced in-situ before it becomes catalytically active. This results in an induction period. Karstedt’s catalyst [Pt_2 (sym-tetramethyldivinyldisiloxane)$_3$] is by far the most common hydrosilylation catalysts, and requires no induction period.
Selectivity	Platinum catalysts show convenient cure kinetics and offer a better shape control as there is no by product formation as in, for example, Sn catalysed condensations.
Stability	CPA (Speier’s catalyst) contains no stabilizing ligands as in the case of Karstedt, and the zero-valent platinum eventually forms colloidal platinum.

1.6.3 Identification of possible alternatives

1.6.4 Possible alternatives to platinum

About 50% of the silicone crosslinking is conducted in alternative processes without platinum. A frequently used alternative is condensation by use of a tin catalyst (Sn). However, there are increasing concerns about the health risks of tin used for this purpose. Moreover, unlike the platinum addition reaction, tin condensation produces water as a by-product, which affects the control and selectivity. Thus, platinum has several advantages and the share of platinum processes is expected to grow (Hagelüken et al. 2005). The development of hydrosilylation catalysts that do not require platinum-based metals remains, however, an important research area. In recent scientific literature it has been demonstrated that base metal catalysts such as iron and nickel have good efficiency and unique chemo- and regio-selectivity (Nakajima and Shimada, 2015). However, so far no application on a commercial scale has been reported. Because of the superior properties of platinum, viz. the two-electron redox processes catalysed so effectively by platinum and having the desirable cure kinetics, this metal is not easily replaced.

1.6.5 Possible alternatives to CPA

A common alternative to CPA used in hydrosilylation is Karstedt's catalyst, which is an organoplatinum(0) compound derived from a sym-divinyl-tetraalkyl containing disiloxane. Karstedt's catalyst is generally acknowledged to have a lower hazard to humans than CPA and has replaced the use of CPA as catalyst in hydrosilylation processes in the EU. Recent observations indicate, however that Karstedt's could have reprotoxic effects and for this reason not an attractive alternative to CPA. Other compounds such as platinum(II) complexes like platinum chloride olefin complex and Pt-96 ($PtCl_2$(cyclooctadiene)), Pt-92 ($PtCl_2$(cyclohexene)$_2$ and Pt -112 ($PtCl_2$ (SEt_2)$_2$ are available as alternatives. Like Karstedt's these catalysts have the benefit of being active without an induction period, providing an advantage over CPA. Other advantages claimed are at lower catalyst loading because of the higher activity (higher platinum turnover number), absence of undesired by-products by e.g. isomerization or hydrogenation, and no formation of platinum colloids.

Industry also offers heterogeneous platinum catalysts (Pt/Al_2O_3) for hydrosilylation. These enable the catalyst to be filtered from liquid products. Generally a higher loading of catalyst will be needed than for the corresponding homogeneous catalyst. However, the reaction may be smoother, with better exotherm control and it is often possible to re-use the catalyst. (http://chemicals.matthey.com/chemicals/element/Pt). Obviously the heterogeneous catalyst can only be used for liquid products.

Karstedt's catalyst has several advantages. It is active without an induction period and it provides a quick low-temperature curing. Other beneficial features of Karstedt's catalyst are:

- A higher activity (higher platinum turnover number).No induction period
- The reactivity can be fine-tuned by choice of catalyst loading, solvent and inhibitors.
- Cross-linking between the vinylsiloxane and silicon hydrides is possible at temperatures below 50 ^{o}C with no by-product formation.
- No or less corrosive HCl or chloride containing by-products present.
- Less formation of platinum colloids

In case operation at higher temperatures is essential, platinum (dodecene)$_2$ dichloride or platinum (cyclooctadiene) dichloride can be used.

Overall, there are sufficient alternatives to CPA to cover a wide range of operations, and as far as known no technical reasons seem to exist why Karlstedt's catalyst cannot fully replace CPA. However, it is not easy to make a direct comparison on catalytic activities based on information in the public domain since reaction conditions such as the mole ratio of reactants, the amount of catalyst, the temperature and the solvent are mostly not consistent.

The Karstedt's catalysts are manufactured from CPA by the addition of an appropriate siloxane and reducing agent resulting in platinum in zero-valent oxidation state (Johnson Matthey, 2009). According to Umicore (M. Grehl et al., 2012b) over the last years Karstedt's catalysts have almost completely replaced CPA in hydrosilylation catalysis.

1.6.6 List of possible alternatives

The possible alternatives that are identified in the section above are listed in the table below together with a preliminary assessment of their technical suitability as alternative.

Table 1.12 List of alternatives and preliminary assessment

Possible alternatives	Assessment
Possible alternatives to platinum based catalysts	Fe and Ni catalysts are theoretically possible alternatives. However, on an industrial scale has not been reported. Recent scientific literature has demonstrated that base metal catalysts such as iron and nickel have good efficiency and unique chemo- and region-selectivity in hydrosilylation (Nakajima and Shimada, 2015). However, so far no application at commercial scale has been reported and it is too early to judge whether this work has the potential to replace Pt. Because of the superior properties of platinum, viz. the two-electron redox processes catalysed so effectively by platinum and having the desirable cure kinetics, this metal is not easily replaced. **The alternative is not analysed further**
Non-chloride platinum(II) precursor	Karstedt's catalyst, platinum(II) complexes and heterogeneous catalysts (Pt/Al_2O_3) are alternatives to CPA as catalysts for hydrosilylation. Of these the Karstedt's catalyst is the most commonly used. Platinum(II) catalysts like Karstedt's are active without an induction period, providing an advantage over CPA. Karstedt's catalyst has replaced the direct use of CPA as catalysts in hydrosilylation in the EU. **The alternative is not analysed further**
Platinum dodecene chloride and platinum cyclooctadiene dichloride	These Pt catalysts offered commercially for use in hydrosilylation but require higher temperatures than Karstedt. The alternatives are currently not competitive compared and a replacement will probably entail lower performance. **The alternative is not analysed further**

1.7 Catalysts based on dipotassiumtetrachloroplatinate(II), DTCP

1.7.1 Annual tonnage range

1.7.2 Analysis of substance function

Dipotassium Tetrachloroplatinate, DTCP (K_2PtCl_4) is a versatile precursor for homogeneous catalysts but has also interesting properties in its own right, especially in functionalization of saturated hydrocarbons. Unusual and often very high selectivity is observed for oxidation at what are more commonly the least reactive positions. The products from oxidation of alkanes are mainly alcohols together with chloroalkanes, ethers, and acids. Ethanol can be selectively converted to ethylene glycol.

DTCP is used as starting material for a range of platinum(0) and platinum(II) materials that can be used for both homogeneous and heterogeneous catalysts. Thus platinum(II) tetra-amine carbonates and nitrates are prepared by treating solutions of DTCP with ammonium carbonate to precipitate corresponding tetra-amine hydrocarbonates. These precipitates are dissolved in water, neutralized with nitric acid to attain pH values suitable to obtain platinum tetra-amine nitrate solution.

Although DTCP is mainly used as an intermediate for other platinum compounds, and due to its very good water solubility, it is also used as a precursor for catalysts on support. These heterogeneous catalysts are used for production of bulk as well as fine chemicals and for gas purification.

DTCP has been used as a precursor for catalysts for specialised purposes in both the bulk and fine chemicals and gas purification industry. In most, but not all, applications DTCP is used as precursor and the platinum in the final catalyst is in the metallic state. An exception to this is supported DTCP catalyst, which is claimed to be a good catalyst for hydrosilylation.

DTCP is a precursor for heterogeneous catalysts where the support material is basic. This is the case for MgO or hydrotalcites that are positively charged over a wide pH range. Using positively charged platinum cations on a positively charged support will not work and here anionic precursors like DTCP are essential.

In addition, DTCP has unique properties as a hydrogen isotope exchange catalyst for both aromatic and aliphatic compounds. It is valuable for labelling compounds with deuterium (D) and/or tritium (T) in one step and constitutes the homogeneous equivalent of the well-known heterogeneous platinum technique. A wide range of compounds, including benzene and substituted benzenes, polyphenyls, and some steroids undergo D and/or T exchange.

The main technical reasons to avoid chlorine-containing platinum precursors are corrosion and the fact that chlorine affects the activity of the catalysts by platinum sintering.

Table 1.13 Functional requirements of DTCP as a precursor or as a catalyst itself

Function	**Explanation**
Activity	DTCP is mainly used as an intermediate for manufacture of other platinum compounds but it is also used directly as catalyst especially in functionalization of saturated hydrocarbons. Moreover DTCP is used as a precursor in platinum-catalysts for specialised purposes in both the bulk and fine chemicals and gas purification industry.

Stability	Platinum catalysts are more stable than most non-platinum alternatives.
Selectivity	Very high selectivity is observed for oxidation at what are more commonly the least reactive positions Unique properties as a hydrogen isotope exchange catalyst for both aromatic and aliphatic compounds
Poison resistance	Platinum catalysts are more poison-resistant than all non-platinum alternatives.
Affinity of pre-curser towards the carrier material	In addition to its good water solubility, DTCP is an essential precursor for heterogeneous catalysts where the support material is basic, e.g. MgO or hydrotalcites.

1.7.3 Identification of possible alternatives

1.7.4 DTCP as a precursor and as a homogeneous catalysts

The chloride ligands in $(PtCl_4)^{2-}$ of DTCP can be easily replaced by other ligands, to give e.g. platinum(II) tetraammine compounds and providing a range of homogeneous catalysts.

For catalysts based on supports like MgO or hydrotalcites a negatively charged platinum complex ion is required, which means that chloroplatinates may be essential. The highly acidic CPA may dissolve or corrode the basic support, whereas the less acidic DTCP can be the precursor of choice and it may be difficult to find alternatives. The main candidate for depositing platinum compounds are the negatively-charged platinum(IV) nitrate $H_2Pt(NO_3)_6$ and hexahydroxyplatinate $H_2Pt(OH)_6$.

1.7.5 List of possible alternatives

The possible alternatives that are identified in the section above are listed in the table below together with a preliminary assessment of their technical suitability as alternative. Based on this it is indicated in the table whether the alternatives are subject to further analysis or not.

Table 1.14 List of alternatives and preliminary assessment

Possible alternatives	**Assessment**
Iridium and palladium	The use of these metals as catalysts in alkane functionalization is under research. DTCP has unique properties in alkane functionalization because of its high selectivity towards the least reactive places. So far no applications for Palladium and Iridium in this reaction have been commercialised. **The alternative is not analysed further.**
Platinum(II) tetra-amine carbonates and nitrates	The chloride ligands in $(PtCl_4)^{2-}$ of DTCP can be easily displaced by many other ligands to produce a range of homogeneous catalysts.

	The benefit of chlorine free platinum precursors is that corrosion can be avoided and that chlorine reduces the activity of the catalysts by platinum sintering. **The alternative is further analysed below.**
Platinum(IV) nitrate $H_2Pt(NO_3)_6$ or tetrahydroxyplatinate $H_2Pt(OH)_6$	Negatively charged platinum complex ions are essential in depositing platinum on positively-charged basic supports. **The alternative is further analysed below.**

1.7.6 Analysis of alternative platinum precursors to ClPt

1.7.7 Substance ID and properties

The homogeneous catalyst alternatives to DTCP include positively charged non-chloride platinum(II) precursors e.g. platinum(II) tetramine nitrate, $Pt(NH_3)_4(NO_3)_2$ or platinum(II) tetramine hydroxide, $Pt(NH_3)_4(OH)_2$.

Where negatively charged platinum complex precursors are needed alternatives include the platinum(IV) nitrate $H_2Pt(NO_3)_6$ and hexahydroxyplatinate $H_2Pt(OH)_6$.

Substance	**Formular**	**CAS No.**	**EC No.**
Platinum(II) tetraammine nitrate	$Pt(NH_3)_4(NO_3)_2$	20634-12-2	243-929-9
Platinum(II) tetraammine dihydroxide	$Pt(NH_3)_4(OH)_2$	15651-37-3	239-719-1
Platinum(IV) nitrate	$H_2Pt(NO_3)_6$	-	432-400-1
Dihydrogen hexahydroxyplatinate	$H_2Pt(OH)_6$	51850-20-5	257-471-2

1.7.8 Technical feasibility

Technically DTCP used as a homogeneous catalyst can be replaced by other platinum substances, e.g. platinum(II) tetraammine compounds.

In heterogeneous catalysts, DTCP is used in most applications as a precursor, and the platinum in the final catalyst is in the metallic state. DTCP is often the preferred starting material due to its very good water solubility. Due to these properties and the ability to provide a high dispersion and low porosity of the deposited platinum layer, it will be difficult to substitute DTCP with the alternatives mentioned above, i.e. platinum(II) tetraamine carbonate or nitrate.

Basic supports like MgO or hydrotalcites requires a negatively charged platinum complex ion. The main alternative candidates for depositing platinum compounds are platinum(IV) nitrate $H_2Pt(NO_3)_6$ and hexahydroxyplatinate $H_2Pt(OH)_6$. These solutions are, however, not proven on an industrial scale and currently not available.

1.7.9 Economic feasibility

Please refer to the discussion in section B.3.4.3.

1.7.10 Availability of alternative solutions

The identified possible alternative solutions to the current use of DTCP as precursor in catalysts are currently not available. It will require intensive R&D efforts and investments in production facilities to provide industrial scale solutions.

1.7.11 Reduction of overall risk

The overall reduction of risks by substituting DTCP with non-chlorinated platinum compound is related to the classification of DTCP as a respiratory sensitiser. One of the alternative compounds, dihydrogen hexahydroxyplatinate, has also been notified with a classification as a respiratory sensitiser. The documentation for this self-classification is not studied but substitution with an alternative with a similar classification will not reduce the overall risk.

The other alternatives to DTCP are not classified as respiratory sensitisers but have classifications for eye damage, some are skin sensitisers or irritating the skin upon exposure. DTCP bears a harmonised classification not including the aquatic environment.

The overall picture is that a substitution of DTCP with the non-chlorinated alternatives will reduce the risk of sensibilisation of workers that are potentially exposed in the work environment.

Table 1.15 – Hazard profiles for DTCP and the identified alternatives.

Substance	**Hazard Class**	**Hazard Statement**
Dipotassium Tetrachloroplatinate[1], DTCP (CAS 10025-99-7; EC 233-050-9)	Acute Tox 3	H301 – Toxic if swallowed.
	Skin irrit. 2	H315 – Causes skin irritation
	Eye Dam. 1	H318 – Causes serious eye damage.
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	Met. Corr. 1	H290 - May be corrosive to metals
Platinum(II) tetraammine nitrate (CAS 20634-12-2; EC 243-929-9)[2]	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
	Met. Corr. 1	H290 - May be corrosive to metals
Platinum(II) tetraammine hydrogen carbonate [1] (CAS 123439-82-7; EC 426-730-3)	Acute Tox. 4	H302 – Harmful if swallowed.

	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic Chronic 3	H412 – Harmful to aquatic life with long lasting effects.
Platinum(IV) dinitrate [1] (CAS 18496-40-7; EC 432-400-1)	Skin Corr. 1A	H314 – Causes severe skin burns and eye damage.
	Eye Dam. 1	H318 – Causes serious eye damage.
	Aquatic acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)
	Aquatic chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)
	Met. Corr. 1	H290 - May be corrosive to metals
	Oxid solid 1	H271 - May cause fire or explosion; strong oxidiser
Dihydrogen hexahydroxyplatinate[2] (CAS 51850-20-5; EC 257-471-2)	Eye Irrit. 2	H319 - Causes serious eye irritation
	Aquatic Acute 1	H400 – Very toxic to aquatic life (Acute M-factor 1)
	Aquatic Chronic 1	H410 – Very toxic to aquatic life with long lasting effects (Chronic M-factor 1)

[1] Harmonised Classification; [2] Classification notified by PMC

1.7.12 Conclusions on suitability

Based on the available information it is concluded that there are currently no available, technically suitable alternative to DTCP for industrial scale manufacture of catalysts.

Massive investments in research and development of alternative solutions as well as production equipment and training are, however, required to before alternatives can replace CPA and DTCP. Moreover it is foreseen that it will take over 10 years of development before an alternative solution operating at an industrial scale will be available.

A phase-out of the use of CPA and DTCP may potentially reduce the risk of respiratory sensitisation effects among workers employed with the manufacturing of chloroplatinates and catalysts. It is estimated that in the EU about 120-140 workers are working with CPA or DTCP in production of precursors or manufacture of platinum catalysts.

APPENDIX C–Chloroplatinates in surface treatment

1 Chloroplatinates in surface treatment

1.1 Annual tonnage range

The amount of platinum used for electroplating in Germany (in 2001) was estimated at 300 kg/y. Most of the plating was carried out in alkali cyanide salt melts, where no ClPts are involved.

The demand of platinum for galvanic processes has recently been estimated at 1.3 t for the World, broken down to 0.4, 0.3 and 0.5 t for Europe, the Americas and Asia, respectively.

1.2 Analysis of substance function

Platinum is applied as a cover layer or a sub-layer on different materials because of its stability to high temperature (owing to its high melting point), its corrosion resistance, hardness, electrical conductivity, and decorative colour. The range of possible applications includes electronics, such as contact materials, connectors, resistors, capacitors, sensors, computer hard discs, components of printed circuits etc., but also plating of instruments, sanitary equipment, and of jewellery.

ClPts can be used in the following surface treatment processes:

a) *Electroplating* of objects is carried out by depositing platinum from an electrolyte through applying a voltage between the substrate as the cathode and the anode anode (Baumgärtner, M. E. et al. 1988; Rao, C. R. K. et al., 2005; van Holme, J. H, 2009; Schlesinger, M. et al, 2010; Grehl, M. et al. 2012). The electrolyte may be an aqueous or non-aqueous solution of a platinum salt, but also a molten salt system (Hagelüken, C. et al., 2005). The platinum anode may also be used as the source of platinum. Electroplating of an electrically non-conductive substrate (e. g. "plating on plastics") is possible after suitable surface treatment generating a conductive surface under-layer.

Two potential alternative methods of platinum plating are currently of more limited importance:

b) *Electroless plating* by depositing platinum from an aqueous or non-aqueous solution of a platinum salt by a suitable reductant. Electroplating generally gives better results regarding the structure and adhesion and thus the quality of the layers.

c) Chemical vapour deposition (CVD) or co-deposition of platinum from a volatile platinum compound in a vacuum or in a low pressure gas phase. Sputtering is the preferred routine gas phase process: ClPts are not used in platinum sputtering. The method is dedicated mainly to uses requiring deposition of a few atomic layers of platinum and thicknesses up to a few micro-meters.

1.2.1 Electroplating with hexachloroplatinates (IV)

Direct use of ClPts in electroplating is only practiced for specific purposes and has in terms of volume of platinum no great significance in the EU, i.e. < 1 tonne per year. The electroplating process involves cathodical reduction of choroplatinates(IV) via chloroplatinate(II) to elemental platinum: $Pt^{IV} \rightarrow Pt^{II} \rightarrow Pt^{0}$ (Baumgärtner, M. E. et al., 1988).

CPA (H_2PtCl_6) was previously used in electroplating baths operated at low pH (strong acid) and high temperature (50 - 95 °C). However, the performance was not satisfactory for most applications (low current efficiency, corrosion of the base material, short lifetime of the baths etc.). Moreover only very small thicknesses can be built because thicker deposits become brittle and show cracks.

Another platinum-source in electroplating is ammonium hexachloroplatinate, $(NH_4)_2[PtCl_6]$, which is reported used in special cases. The platinum-salt has a low solubility, which however can be improved with citrate and ammonium chloride as supporting electrolytes. The current efficiencies are higher than for CPA, but the corrosive nature is the same and substrates must be protected by noble metal under-layers. This system is used for plating of metallic objects used under extreme temperatures (>1600 °C) such as turbine blades. Platinum is deposited as a sublayer in a multilayer construction, which upon annealing result in high-performance Pt-Al alloys. Ammonium hexachloroplatinate $(NH_4)_2[PtCl_6]$ is mentioned as the preferred platinum source in an electrolyte operated at ca. pH 6-7 and 85°C, but other platinum salts are not excluded. (Patent: WO 2013/156737 A1; WO 2015/007983 A2; EP 2 582 859 B1, all by SNECMA, Paris).

For a modification of the surface of a platinum device (such as an electrode), these devices are further "platinized" in an electrolyte (pH 1 adjusted by HCl) which is 0.027 M CPA and $1.3 \cdot 10^{-4}$ M in lead(II) acetate. This "platinizing" improves the conductivity performance of the electrodes. Good adhesion of electrodeposited platinum from solutions of CPA was observed on substrates previously exposed to platinum sputtering (d). The products show improved performance also as implantable arrays in medicine (Feltham, A. M. et al. 1971; de Haro, C. et al., 2002).

1.2.2 Electroless Platinum Plating

Electroless platinum plating is based on the same platinum sources as the electroplating techniques discussed above (Review: Okinaka, Y. et al., 1990; Rao, C. R. K. et al., 2005; Ohno, I., 2010; Holton O. T. et al. 2013). The deposition is achieved by chemical reduction using hydrazine, hydroxylamine or other reducing agents. Among the chlorinated platinum salts used for this purpose is potassium hexachloroplatinate(IV). Electroless plating with CPA includes use of hydrazine hydrate as a reductant at pH 0.5 - 1.0 (maintained by hydrochloric acid) and at 60-70 °C. Several additives are essential.

1.2.3 Plating by Chemical Vapour Deposition (CVD)

Volatile platinum complexes have been used successfully for CVD. These include di(carbonyl)dichloroplatinum(II), $(CO)_2PtCl_2$ as the only chlorinated platinum source.

The deposition is generally carried out in a vacuum or in a low pressure hydrogen atmosphere and induced either thermally or by laser or UV irradiation. Plasma or ion beam and electron beam techniques are also used (Choy, K. L., 2003; Thurier, C. et al., 2008; Kodas, T. T. et al., 2008).

CVD with platinum is, however, extremely expensive and used only for surface coating of high performance materials.

Table 1.1 Functional requirements of Pt and ClPts in surface treatment

Electroplating	**Explanation**
Dispersion/ adhesion on base material	Electroplating by use of ammonium hexachloroplatinate as platinum-source seem to be preferred due to high current efficiencies. The techniques is used to provide temperature resistance.
Corrosion resistance	Platinum layers have a high resistance to corrosion
Heat resistance	Platinum is used in alloys to increase heat resistance e.g. high performance Pt-Al alloys.

Appearance	Platinum plating is used in jewellery due to its bright and resistant surface.
Electroless plating	
Dispersion/ adhesion on base material	Electroless platinum plating generally gives a good dispersion and special surface characteristics of the plated layer.
Corrosion resistance	The corrosion resistance of electroless platinum platinum coating is similar compared to electroplated platinum coatings.
Heat resistance	The heat resistance of a platinum coating is high.
CVD	
Dispersion/ adhesion on base material	CVD provides improved adherence of the platinum coating and excellent dispersion. Chlorinated as well as non-chlorinated platinum compounds can be used but there is no specific advantage of using a chlorinated platinum compound, such as $PtCl_2(CO)_2$.
Corrosion resistance	The corrosion resistance of any platinum coating is high.
Heat resistance	The heat resistance of platinum coatings are generally high.
Surface alloy formation	Annealing of multilayer CVD yields highly resistant alloys

A.1.2 Identification of possible alternatives

1.2.4 Electroplating with non-chlorinated platinum salts

Today platinum electroplating is mostly based on the non-chlorinated platinum-compounds that from a technical point are excellent alternatives to ClPts. This includes Pt salts such as hexahydroxyplatinates(IV), *cis*-diammine(dinitrito)platinum(II) ("P-salt"), dinitrito(sulfato)platinous acid ("DNS Salt"), tetranitritoplatinum(II) salts, Pt(II) sulfito complexes, and tetraammineplatinum(II) salts ("Pt-Q-Salts") "). (Hopkin, N. et al, 1960; Baumgärtner, M. E. et al., 1988; Skinner, P. E., 1989; Gregory, A. J. et al. 1993; basirun, W. J. et al., 1995; Levason, V. L. et al., 1998, Thompson, S. D. et al. 2001.).

Plating with hexahydroxyplatinates(IV)

Treatment of alkali or ammonium hexachloroplatinates, or of hexachloroplatinic acid, with alkali hydroxides affords precipitates of platinum oxide hydroxides, which can be dissolved in strong alkali hydroxide solution to yield the chloride-free hexahydroxy complexes $M_2[Pt^{IV}(OH)_6]$ with M = Na, K. The sodium salt forms a dihydrate $Na_2[Pt(OH)_6]\cdot 2H_2O$. Both sodium and potassium hexahydroxyplatinates(IV) can be applied for platinum plating in *alkaline solution* (pH 13) at 75 °C. The current efficiencies are high (80 - 100 %), but the baths are unstable. Additives like sodium oxalate and sulfate improve the stability, but the high pH leads to absorption of carbon dioxide producing a load of carbonate and precipitates. Plating in alkaline solution allows for thicker layers than plating in acidic solution.

Plating with cis-diammine(dinitrito)platinum(II) $(NH_3)_2Pt^{II}(NO_2)_2$*, ("Pt-P-Salt")*

This compound is produced from hexachloroplatinic acid hexahydrate $H_2[PtCl_6]\cdot 6H_2O$ by reduction with potassium nitrite. This reaction produces potassium tetranitritoplatinate(II) $K_2[Pt(NO_2)_4]$ which is then treated with ammonia in aqueous solution to give a precipitate of the Pt-P-salt.

Pt-P-Salt is used for platinum plating in a number of variants, of which the classical one employs baths containing ammonium and alkali nitrates and nitrites and ammonia. In other forms, hydrofluoric, phosphoric, sulfuric or sulphamic acid are employed. The current efficiency is strongly dependent on the temperature and shows a dramatic increase above 60 °C reaching a maximum near 95 °C. Current efficiencies reach 40 %. Replenishing with Pt-P-Salt allows to maintain the desired platinum concentrations, but an increasing load of salts is building up.

Plating with Dinitrito(sulfato)platinous acid $H_2[Pt^{II}(NO_2)_2SO_4]$ ("DNS Salt") ("DNS Salt")

The preparation of "DNS-Salt" is also based on potassium tetranitritoplatinate(II) $K_2[Pt^{II}(NO_2)_4]$ which is converted into the sulfato complex with sulfuric acid. The electrolytes based on this platinum source are operated at low pH (pH 2) by addition of sulfuric acid. Current efficiencies are low at 10-15 % at temperatures in the range 30 - 70 °C. The baths are stable producing constant results.

Plating with tetranitritoplatinum(II) salts $[Pt(NO_2)_4]^{2-}$

The potassium salt $K_2[Pt(NO_2)_4]$ dissolved in methanesulfonic acid was applied for platinum plating at 65 °C with low current efficiency. It can be used for plating from acidic solutions.

Plating with platinum(II) sulfito complexes

Electrolytes based on sulfito complexes of the tentative formulae $Na_6Pt(SO_3)_4$ and $H_3Pt(SO_3)_2OH$ were employed for the deposition of platinum mainly on glassy carbon substrates. The compounds are prepared from hexachloroplatinic acids by reduction with sulfite in the presence of sodium carbonate.

Plating with tetraammineplatinum(II) salts, based on $[Pt(NH_3)_4]^{2+}$ cations ("Pt-Q-Salts")

These electrolytes represent one of the most recent developments in platinum plating. The baths containing hydrogenphosphate HPO42- as the anion are most widely applied. The plating is only efficient at temperatures above 88 °C, and therefore carried out at 95 °C. With the pH 10 maintained by a phosphate buffer and with regular replenishment, the baths are stable up to high turnover numbers. The $[Pt(NH_3)_4]^{2+}$ X-salts are prepared from alkali hexachloroplatinates(IV) by reduction to alkali tetrachloroplatinates(II) and complexation with concentrated ammonia solution to afford $[Pt(NH_3)_4]^{2+}$ 2 Cl^-. Anion exchange yields the final products.

Electroplating using $[Pt(H_2O)_4](ClO_4)_2$ has also been carried out successfully, but it is difficult to obtain a clean electrolyte, because the preparation requires the use of silver salts.

The color of electroplated platinum is darker than that of electroplated rhodium, which for some time was the favorite for decoration of silver-white jewelry. The price of the two metals has an influence on the usage of the two metal candidates for plating.

The preference for solid and plated platinum jewelry in countries like Japan is currently less pronounced as compared to the post-World War II decades, but still exceeds that for gold.

1.2.5 Electroless plating with non-chlorinated platinum salts

There are several non-chlorinated alternative platinum sources for electroless plating:

- Sodium hexahydroxyplatinate(IV): This variant uses hydrazine as a reductant, but the process is carried out in the alkaline region (pH 10, established with NaOH) with $Na_2[Pt(OH)_6]$ at slightly elevated temperature (35 °C). In combination with $(NH_4)_3[RhCl_6]$, alloys Pt/Rh can be deposited.

- Cis-diammine(dinitrito)platinum(II) (P-salt): cis-$(NH_3)_2Pt^{II}(NO_2)_2$ is reduced by hydrazine in a medium adjusted to pH 3 by acetic acid at 50 °C. Combined with metal complexes like $(NH_4)_2Na[Rh(NO_2)_6]$ alloys Pt/Rh can be deposited.

- Potassium tetranitritoplatinate(II): The complex $K_2[Pt(NO_2)_4]$ was used together with $K_2[Pd(NO_2)_4]$ mainly for deposing Pt/Pd alloys with both hydroxyamine and hydrazine as reductants (pH 12, 60 °C).

1.2.6 Chemical Vapour Deposition (CVD) with non-chlorinated platinum salts

Several types of *volatile* platinum chlorine free complexes have been used successfully for CVD of the metal (Hue, Z. et al., 1992; Hierso, J.-C., et al. 1998; Delmas, M. et al., 2004; Delmas, M.., 2005):

- Platinum(II) acetylacetonates, Pt(acac)2 and Pt(hfa)2, where acac stands for acetylacetonate [CH3-C(O)-CH-C(O)-CH3]- and hfa for hexafluoroacetylacetonate [CF3-C(O)CHC(O)-CF3] .

- Tetrakis(trifluorophosphine)platinum(0), $Pt(PF_3)_4$, and tris(ethene)platinum(0), $(C_2H_4)_3Pt$.

- Bis(methylisocyanide)dimethylplatinum(II), $(CH_3)_2Pt(CNCH_3)_2$, (cyclooctatetraene-1,5)-dimethylplatinum(II), $(CH_3)_2Pt(COD)$, and bis(pent-4-en-1-yl)platinum(II), $[CH_2{=}CH(CH_2)_3]_2Pt$.

- (Cyclopentadienyl)trimethylplatinum(IV), $(C_5H_4R)Pt(CH_3)_3$ with R = H, methyl, ethyl.

Several of these precursors have been employed also for the deposition of alloys, such as Pt/Al, using e. g. $(C_5H_4R)Pt(CH_3)_3$ together with trialkylaluminium compounds R_3Al as the second component. This process leads to Pt-Al alloys in the same way as by electroplating of several metal layers which upon annealing yield phases like Pt_3Al on a titanium support.

1.2.7 List of possible alternatives

Table 1.2 List of possible alternatives and preliminary assessment

Possible alternatives, electroplating	**Assessment**
Hexahydroxyplatinate (IV) salt cis-Diammine(dinitrito)platinum(II) (P-salt) Dinitrito(sulfato)platinous acid (DNS-salt) Tetraammineplatinum(II) salts (Q-salts)	DNS salt (Dinitrito(sulfato)platinous acid) , Q-salts (tetraammineplatinum(II) salts), P-salt and sulfito/nitrito complexes of platinum(II) are preferred as platinum source in electroplating due to their higher current efficiency, less corrosion and a better quality of the deposited platinum-layers. Corrosion of the base material is often a problem when using CPA because of the low pH and high temperature required. Only for specific purposes, e. g. where ammonium hexachloroplatinate is used for depositing high temperature resistant Pt-Al layers, the alternative platinum sources may not provide the same functionality. **The alternative is analysed further below**
Possible alternatives, electroless plating	
Hexahydroxyplatinate(IV) salt, Dinitrito(sulfato)platinous acid (DNS-salt)	Electroless platinum-plating generally leads to less robust coatings as compared to electroplating, but the technique can be used under very mild conditions.

Potassium tetranitritoplatinate(II)	The coatings have a higher surface area which is advantageous for heterogeneous catalysis and surface affinity (e. g. avoiding overvoltage of electrodes). Plating can be carried out on electrically non-conducting or poorly conducting surfaces. **The alternative is not analysed further**
Possible alternatives, CVD	
Volatile (organo)platinum compounds	With the only exception of $PtCl_2(CO)_2$, which is not regarded as a chloroplatinate substance, all known CVD candidates are chlorine-free. **The alternative is not analysed further**

A.1.3 Analysis of alternatives to ClPt in electroplating.

1.2.8 Substance ID and properties

Substance	Formular	CAS No.	EC No.
Dihydrogen dinitrosulphatoplatinum(II) (DNS salt)	$H_2Pt(NO_2)_2(SO_4)$	12033-81-7	234-794-7
Diammineplatinum(II) nitrite (P-salt)	$Pt(NH_3)_2(NO_2)_2$	14286-02-3	238-203-3
Tetraammineplatinum(II) hydrogenphosphate (Q-salt)	$[Pt(NH_3)_4](HPO_4)$	127733-98-6	677-394-1

1.2.9 Technical feasibility

The identified alternatives are well known platinum sources used in electroplating globally. They provide excellent alternatives to CPA for a strongly adherent platinum deposits of low stress and low porosity. These alternatives have generally replaced the use of CPA in electroplating.

For specific speciality platinum coatings CPA is, however, still the preferred solution, and it is according to industry not possible to achieve the same high quality resistance by using the alternative DNS, P or Q-salts.

1.2.10 Economic feasibility

The economic importance of the use of CPA for speciality coatings is insignificant and in terms of volume of platinum less than 100 kg per year in the EU.

1.2.11 Reduction of overall risk

Compared to the classification of CPA as a respiratory sensitiser, a skin sensitiser and as skin and eye corrosive, the alternative substances DNS-, P- and Q-salts are less hazardous. They are not classified as respiratory sensitisers. Since respiratory sensitisation is of specific concern in the work environment the conclusion is that use of alternatives to CPA can reduce the overall risk of respiratory sensitisation.

The number of workers employed with supply of, and speciality electroplating with CPA, is however very low (probably < 20).

Table 1.3 – Hazard profiles for CPA and the identified alternatives

Substance	**Hazard Class**	**Hazard Statement**
Chloroplatinic acid (CPA)[1] (CAS 16941-12-1; EC 241-010-7)	Acute Tox 2	H300 - Fatal if swallowed
	Skin Corr. 1B	H314 – Causes severe skin burns and eye damage
	Skin Sens. 1B	H317 – May cause an allergic skin reaction
	Eye dam. 1	H318 - Causes serious eye damage
	Resp. Sens. 1A	H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled
	STOT RE1	H372 - Causes damage to organs through prolonged or repeated exposure.
	Aquatic acute 1	H400 Very toxic to aquatic life (Acute M-factor 10)
	Aquatic chronic 1	H410 Very toxic to aquatic life with long lasting effects (Chronic M-factor 10)
	Met. Corr. 1	H290- May be corrosive to metals
Dihydrogen dinitrosulphatoplatinum(II) (DNS salt)[2] (CAS 12033-81-7; EC 234-794-7) Does PMC have any classification suggestions to this substances?		
Diammineplatinum(II) nitrite (P-salt)[2] (CAS 14286-02-3 EC 238-203-3) Does PMC have any classification suggestions to this substances?	Eye dam. 1	H318 - Causes serious eye damage
		H001: Explosive when dry

Tetraammineplatinum(II) hydrogenphosphate (Q-salt) [2]		

[1] Harmonised Classification; [2] Classification notified by PMC;

1.2.12 Conclusions on suitability

The alternatives to CPA in electroplating are well proven and available for industrial scale use. They provide competitive solutions for most purposes and have generally replaced the use of CPA for industrial coatings in the EU.

For certain speciality coating CPA is, however, still used and for technical reasons difficult to substitute. This is a niche production based on a small yearly volume of CPA and with a small number of workers involved and overall the benefits of substituting CPA with alternative substances has only little significance.

APPENDIX D - References

Basirun, W. J., Pletcher, D., Saraby-Reintjes, A. Studies of Platinum Electroplating Baths: Deposits on Copper from Q Bath. J. Appl. Electrochem. 1996, 26, 873.

Baumgärtner, M. E., Raub, C. R. The Electrodeposition of Platinum and Platinum Alloys. Platinum Metal Rev. 1988, 32, 188.

Bruckard, W. J., K. J. McDonald, C. M. McInnes, G. J. Sparrow, J. T. Woodcock: Platinum, palladium, and gold extraction from Coronation Hill ore by cyanidation at elevated temperatures. Hydrometallurgy 1992, 30, 211-217.

C. H. Bartholomew and R.J. Farrauto (2005), Fundamentals of Industrial Catalytic Processes. 2nd edition.

Choy, K. L. Chemical Vapour Deposition of Coatings. Progr. Mater. Sci. 2003, 48, 57

de Haro, C., Mas, R., Abadal, G., Munoz, J., Perez-Murano, F., Dominguez, C. Electrochemical Platinum Coatings for Improving Performance of Implantable Microelectrode Arrays. Biomaterials 2002, 23, 4515.

Delmas, M., Poquillon, D., Khin, Y., Vahlas, C. Al-Pt MOCVD Coatings for the Protection of Ti6242 Alloy. Surface & Coatings Technology 2005, 200, 1413.

Delmas, M., Ucar, M., Ressier, L., Pons,M., Vahlas, C. MOCVD Processed Platinum-aluminium Coatings on Titanium Alloys. Surface & Coatings Technology 2004, 188-189, 49.

Feltham, A. M., Spiro M. Platinized Platinum Electrodes. Chem. Rev. 1971, 71, 177.

Frankham, J., Kauppinen, P. The Use of Metal Scavengers for Recovery of Precious, Base and Heavy Metals from Waste Streams. Platinum Metals Rev. 2010,54, 200.

Friedman D., T. Masciangioli, and S. Olson (2012): The Role of the Chemical Sciences in Finding Alternatives to Critical Resources: A Workshop Summary. The National Academies Press, Washington, D.C. p. 13-19.

Fröhlich, P., Lorenz, T., Martin, G., Brett, B., Bertan, M., Angew. Valuable Metals - Recovery Processes, Current Trends and Recycling Strategies. Chem. Int. Ed. 2017, 56, 2544.

Gregory, A. J., Levason, W., Pletcher, D. Studies of Platinum Electroplating Baths. J. Electroanal. Chem. 1993, 348, 211.

Grehl M. et al. (2012). Precious Materials Handbook. Umicore, Hanau.

Grehl, M., Van den Broeck, K., Drieselmann, R., Graedel, T. E., Hegelüken, C. in Precious Materials Handbook, published by Umicore AG & Co. KG, Hanau, Germany; ISBN 978-3-8343-3259-2, 2012.

Grehl, M., Van den Broeck, K., Drieselmann, R., Graedel, T. E., Hagelüken, C. in Precious Materials Handbook, published by Umicore AG & Co. KG, Hanau, Germany; ISBN 978-3-8343-3259-2, 2012.

Hagelüken C. Recycling of Platinum Group Metals. A European Perspective, Platinum Metals Rev. 2012, 56, 29.

Hagelüken, C. M. Buchert, H. Stahl, (2005). Materials Flow of Platinum Group Metals in Germany.

Hagelüken, C., Buchert, M., Stahl, H., Materials Flow of Platinum Group Metals, published by Umicore, Öko Institut, GFMS, ISBN: 0-9543293-7-6, 2005.

Hierso, J.-C., Feurer, R., Kalck, P. Platinum, Palladium and Rhodium Complexes as Volatile Precursors for Depositing Materials. Coord. Chem. Rev. 1998, 178-180, 1811.

Holton, O. T., Stevenson, J. W. The Role of Platinum in Proton Exchange Membrane Fuel Cells. Platinum Metal Rev. 2013, 57, 259.

Hopkin, N, Wilson, L. F. Bright Platinum Plating. Platinum Metals Rev. 1960, 4, 56.

Hue, Z., Thridandam, H., Kaesz, H. D., Hicks, R. F. Organometallic Chemical Vapour Deposition of Platinum. Chem. Mater. 1992, 4, 162.

Jha, M. K., Lee, J.-C., Kim, M. S., Jeong, J., Kim, B.-S., Kumar, V. Hydrometallurgical Recovery and Recycling of Platinum by the Leaching of Spent Catalysts. Hydrometallurgy 2013, 133, 23.

Johnson Matthey (2009). The Catalyst Technical Handbook.

Kodas, T. T., Hampden-Smith, M. J. The Chemistry of Metal CVD. Wiley & Sons, 2008.

Levason, V. L., Pletcher, D., Smith, A. M., Berzins, A. R. Studies of Electroplating Baths. J. Appl. Electrochem. 1998, 28, 18.

Lewis, L. N; K. G. Sy, G. L. Bryant and P. E. Donahue (1991): "Platinum-catalyzed hydrosilylation of alkynes". Organometallics 10: 3750.

Mallory, G. O., Hajdu, J. B., eds. Electroless plating. Fundamentals and Applications, Cambridge Univ. Press 1990, chapter 16 by Okinaka, Y., Wolowodiuk, C.

Miao, Q. J.; Z.-P. Fang, G. P. Cai (2003). Silica-supported Karstedt-type catalyst for hydrosilylation reactions. Catalysis Communications 4: 637.

Modern Electroplating, van Horne, J. H., Publisher J. van House, 2009.

Morlang, A., U. Neuhausen, K.V. Klementiev, F.-W. Schütze, G. Miehe, H. Fuess, E.S. Lox (2005). Appl. Catal. B 60: 191.

Nakajima, Y., S. Shimada (2015) Hydrosilylation reaction of olefins: recent advances and perspectives. RSC Advances 5: 20603.

Pietrelli, I., Fontana, D., Int. J. Environment & Waste Management, 2013, 11, 222.

Rao, C. R. K., Trivedi, D. C., Coord. Chemical and Electrochemical Deposition of Platinum Group Metals and their Application. Chem. Rev. 2005, 249, 613.

Rase, H. R. (2000). Handbook of Commercial Catalysts/Heterogeneous Catalysts. CRC Press p. 305.

Raseev, S. (2003). Thermal and Catalytic Processes in Petroleum refining. Marcel Dekker.

Raub, C. J. in Gmelin Handbook of Inorganic Chemistry, Pt Suppl. Vol. A1, Springer Verlag, Berlin 1986.

Regalbuto, J. R. (2009), Electrostatic Adsorption. In: Synthesis of Solid Catalysts, edited by K.P. de Jong. Wiley-VCH Verlag, Weinheim. p. 33.

Resasco, D. (2003), Dehydrogenation-Heterogeneous, in Encyclopedia of Catalysis, ed. I. T. Horvath, Wiley, New Jersey p. 49.

Schlesinger, M., Paunovic, M., eds. Modern Electroplating. J. Wiley& Sons 2010, chapter 20 by Ohno, I.

Shannon, M. D., C. M. Lok, J. L. Casci (2007) J. Catal. 249: 41.

Skinner, P. E. Improvements in Platinum Plating. Platinum Group Metals 1989, 33, 102.

Speier, J.L., J. A. Webster, G. H. Barnes (1957). "The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts". J. Am. Chem. Soc. 79: 974.

Thompson, S. D., Jordean, L. R., Shukla, A. K., Forsyth, M. Platinum Electrodeposition from H3Pt(SO3)2OH Solution. J. Electroanal. Chem. 2001, 515, 61.

Thurier, C., Doppelt, P., Coord. Platinum OMCVD processes and precursor chemistry. Chem. Rev. 2008, 252, 155.

Twigg, M.V. (2011), Catalysis Today 163: 33.

Weissermel, K. , H.–J. Arpe, Industrial; Organic chemistry (1997) p. 314.

World Platinum Investment Council (2016): Platinum Quarterly Q1 2016.

Zanjani, A., Baghalha, M., Factors affecting platinum extraction from used reforming catalysts in iodine solution up to 95°C. Hydrometallurgy 2009, 97, 119.

Zhao, J. S., J. H. Dai: Kinetics and Mechanism of Platinum Pressure-Cyanide Dissolution. Appl. Mechan. Mater. 2014, 522-524, 424-428.