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Convenient preparation of (η^4-alkadiene)dichloroplatinum(II) complexes from $[PtCl_6]^{2-}$ anions and their reduction to platinum(0) alkene complexes under phase-transfer catalysis conditions

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ABSTRACT

Convenient one-pot reduction-complexation reactions of hexachloroplatinato(IV) anions to (η^4-alkadiene)dichloroplatinum(II) complexes (η^4-alkadiene = COD, DAE, DCPD, NBD) under suitable phase-transfer catalysis conditions are reported. Reduction to zerovalent platinum alkene complexes has been obtained in the presence of an excess of alkene, potassium formate and 18-crown-6 as phase-transfer catalyst (alkene = COD, NB, dba). The crystal and molecular structure of $[Pt_{1.03}(dba)_3]\cdot CH_2Cl_2$ has been studied by X-ray diffraction methods: it can be described as a solid solution of $Pt(dba)_3$ and $Pt_2(dba)_3$, the mononuclear complex being largely prevailing.

1. Introduction

Complexes of platinum(0) find application in the field of homogeneous catalysis [1]. Among them, the so-called "ligand free" or "naked" homoleptic alkene complexes are important precursors to other species of platinum(0), coordinated olefins being easily replaced by other ligands [1e,f,2]. These complexes are usually synthesized starting from dichloro-(diene)platinum(II) complexes as precursors. The reduction of dichloro-(η^4-1,5-cyclooctadiene) platinum(II) $[PtCl_2(COD)]$ by lithium cyclooctatetraene in the presence of a strong excess of the alkene (see reaction 1) [2c,g,h,3] is commonly used.

$$PtCl_2(COD) + Li_2(C_8H_8) + x\ \text{alkene} \rightarrow Pt(\text{alkene})_x + 2LiCl + C_8H_8 + COD \qquad (1)$$

This route affords satisfactory results both for platinum derivatives {for instance tris(bicyclo[2.2.1]heptene)platinum(0), $[Pt(NB)_3]$, and bis(cycloocta-1,5-diene)platinum(0), $[Pt(COD)_2]$, can be obtained in 40–74% yields [2f,3]} and for the usually unstable palladium compounds [2h,4]. Alternatively, dicyclopentadienylcobalt(II) [5] and samarium(II) iodide [6] have been reported as reducing agents for platinum(II) complexes.

Interestingly, the reduction of $H_2PtCl_6\cdot xH_2O$ by vinylsiloxane derivatives in the presence of coordinating alkenes affords platinum(0) species [7], but the relatively high temperatures (50–70 °C) required for this route are inappropriate for the preparation of $Pt(\text{alkene})_3$ complexes with non-functionalized monoenes [7c].

As far as platinum(II) precursors are concerned, the preparation of the widely used dihalo-diene complexes, $PtX_2(\text{diene})$ is generally carried out by reacting tetrachloroplatinate(II) salts with non-conjugated dienes in a water/acetic acid mixture [8] or in alcohol [9]. Syntheses starting from $H_2PtCl_6\cdot xH_2O$ or its salts are rather interesting, as these species are primary products in platinum chemistry. Diiodo-(diene)platinum(II) complexes have been synthesized by treating potassium hexachloroplatinate(IV) with KI in the presence of the suitable diene [10]. The preparation of the analogous dichloro-derivatives from hexachloroplatinic acid, in acetic acid solution [11] requires the use of the diene both as reducing and complexing agent. The outcome of the reaction is largely dependent on the nature of the diene; when dienes other than cycloocta-1,5-diene are used, yields are low and the formation of dark by-products makes the purification step quite long and tedious [11].

Although many procedures have been reported [12] describing the use of PT catalysts for the preparation of organic compounds, only few examples are known where PT catalysis conditions are applied to the preparation of organometallic derivatives [13]. Under these conditions it is usually possible to maintain the concentration of the reagents in the organic phase low enough to be tolerated by

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List of the acronyms

COD	1,5-Cyclooctadiene
DAE	4-Oxahepta-1,6-diene (diallylether)
dba	E,E-1,5-diphenyl-3-oxopenta-1,4-diene (dibenzylidenacetone)
DCPD	Dicyclopentadiene
NB	Bicyclo[2.2.1]heptene (norbornene)
NBD	Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)
TBA	Tetrabutylammonium
DCE	1,2-Dichloroethane
DMSO	Dimethylsulfoxide
PT	Phase transfer

sensitive substrates. We thus thought that this approach could be useful for the preparation of both platinum(II) and platinum(0) species.

The reasons discussed above prompted us to search, under PT catalysis conditions, for: (a) a new and more direct route to convert hexachloroplatinate(IV) salts into dichloro-(diene)platinum(II) complexes and (b) a simple and economic way to obtain platinum (0) complexes with the composition Pt(alkene)$_n$. The results we have obtained are here presented and discussed.

2. Results and discussion

2.1. Preparation of dichloro-(diene)platinum(II) complexes from $[PtCl_6]^{2-}$

As mentioned in Section 1, the conversion of hexachloroplatinic acid into dichloro-(diene) platinum(II) complexes was claimed to occur in good yields in acetic acid solution [11]; in our hands, when dienes other than cycloocta-1,5-diene were used, low yields were always obtained. Since the metal precursor and the complexing agent have different solubility properties, it seemed interesting to investigate PT catalysis conditions in biphasic water/organic solvent systems. Tetraalkylammonium halides are often useful as liquid–liquid phase transfer catalysts, thanks to their good solubility in water as well as in many common organic solvents. Moreover, it is known that $PtCl_n^{2-}$ ($n = 4, 6$) can be extracted from aqueous solutions of H_2PtCl_n into chlorinated solvents in the presence of suitable alkylammonium salts [14]. In a preliminary experiment $H_2PtCl_6 \cdot nH_2O$ was dissolved in water and treated with a 1,2-dichloroethane solution containing an excess of cycloocta-1,5-diene (COD, Pt/COD molar ratio = 1/7) and a catalytic amount (7% mol) of tetrabutylammonium chloride. After prolonged reflux (80 °C) of the mixture platinum(II) complexes were not obtained. Since the excess diene did not afford any reduction product, in a following experiment (Table 1, entry 1) hydrazine dihydrochloride was added as reducing agent in stoichiometric amount. The resulting biphasic mixture was refluxed, till the aqueous phase completely discoloured with formation of a colourless crystalline solid, identified as the expected dichloro-(η^4-1,5-cyclooctadiene) platinum(II) ($[PtCl_2(COD)]$ **1**) by ^1H- and ^{195}Pt NMR analysis. The complex was easily obtained (75% yield), even when the COD/Pt molar ratio was lowered from 7 to 2 (Table 1, entry 2). The overall reduction/complexation process under PT conditions can be summarised as in Eq. (2).

$$2[PtCl_6]^{2-} + H_2N - NH_2 + 2\text{diene} \rightarrow 2[PtCl_2(\text{diene})] + 4Cl^- + 4HCl + N_2 \qquad (2)$$

Table 1
Preparations of $[PtCl_2(\text{diene})]$ according to Scheme 1.[a]

Entry	Diene	[Diene/Pt] molar ratio	%Yield
1	COD	7/1	75
2	COD	2/1	78
3	NBD	2/1	78
4	DCPD	2/1	61
5	DAE	2/1	75

[a] Reducing agent $H_2N{-}NH_2 \cdot 2HCl$; $[Pt/(H_2N{-}NH_2 \cdot 2HCl)]$ molar ratio = 2.

It has to be pointed out that no formation of platinum metal was observed, although the standard potential for the reduction of $[PtCl_4]^{2-}$ to Pt(0) in water is only slightly higher than the corresponding standard potential [15] for the reduction of $[PtCl_6]^{2-}$ to $[PtCl_4]^{2-}$ (0.755 and 0.680 V, respectively). This outcome is reasonable due to the presence of the complexing diene in the organic phase: as soon as tetrachloroplatinate(II) ion is produced in water, it is extracted as $[TBA]_2[PtCl_4]$ into the chlorinated solvent and converted to the slightly soluble diene complex with release of the TBACl catalyst (Scheme 1). Thus, the concentration of tetrachloroplatinate(II) ions in the aqueous phase is never high enough for their reduction to become competitive.[1]

Similar experimental conditions (Table 1, entry 2) successfully afforded platinum(II) complexes of norbornadiene **2**, dicyclopentadiene **3**, and diallylether **4**, (Table 1, entries 3–5 respectively). All products were sparingly soluble in 1,2-dichloroethane and could be easily isolated as chemically pure crystalline solids in good yields.

2.2. Preparation of (alkene)platinum(0) derivatives from dichloro-(diene)platinum(II) complexes

Previous outcome in the preparation of platinum(II) dichloro diene complexes prompted us to investigate if PT conditions could be also suitable to synthesize platinum(0) complexes. Experiments were carried out using potassium formate as reducing agent. Although alkali metal formates are used for the reduction of platinum salts to platinum-black [16], at the best of our knowledge their use is not reported for the synthesis of platinum(0) complexes. A suspension of $[PtCl_2(COD)]$ in 1,2-dichloroethane was treated, in the presence of COD and 18-crown-6 as PT catalyst, with an aqueous solution containing a threefold excess of potassium formate. Under these experimental conditions the platinum(II) precursor was reduced but no complexation occurred: ^1H- and ^{195}Pt-NMR spectra of the organic phase showed the absence of signals attributable to platinum(0) complexes. Platinum metal was recovered, together with some brown by-products, possibly due to base-promoted isomerisation/oligomerisation of the 1,5-diene [17]. Taking into account that crown ethers are very good PT catalysts in heterogeneous solid-liquid systems [18], a suspension of $[PtCl_2(COD)]$ in 1,2-dichloroethane was treated at room temperature with a threefold excess of potassium formate in the presence of a strong excess of COD and a catalytic amount of 18-crown-6, while no water was deliberately added (Table 2, entry 1). Long reaction times (12–24 h) were necessary for a complete conversion of the substrate into the expected bis(cycloocta-1,5-diene)platinum(0),

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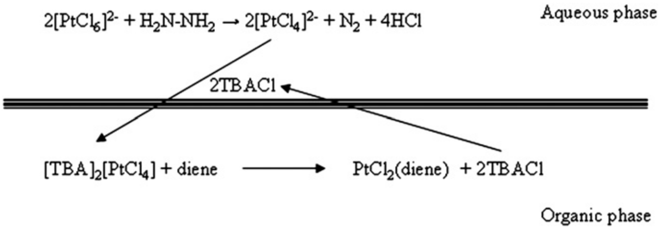
[1] This hypothesis was indirectly confirmed by the following experiment: a sample of $[TBA]_2[PtCl_6]$ was dissolved in 1,2-dichloroethane and treated with an aqueous solution containing a stoichiometric amount of hydrazine dihydrochloride ($[Pt/H_2N{-}NH_2 \cdot 2HCl]$ molar ratio = 2) under the conditions used to prepare the diene complexes of platinum(II), in the absence of the complexing agent. In this case some platinum metal formed at the interface of the biphasic system and the organic phase contained $[TBA]_2[PtCl_4]$ and unreacted $[TBA]_2[PtCl_6]$ in about 80/20 molar ratio (^{195}Pt NMR).



Scheme 1.

$[Pt(COD)_2]$ **5**, (^{1}H- and ^{195}Pt-NMR). The yield could be increased from 25% to 40% (Table 2, entry 2) by using Et_2O instead of 1,2-dichloroethane as solvent. As a matter of fact, oxidative addition of the chlorinated solvents to platinum(0) derivatives may occur to some extent over long reaction times. The experimental procedure was successfully applied in good yields also to the preparation of *tris*(bicyclo[2.2.1]heptene)platinum(0), $[Pt(NB)_3]$ **6**, (Table 2, entry 3). Furthermore, when $[PtCl_2(NBD)]$ was reacted with dibenzylidenacetone (dba), the reaction afforded the yellow-brown product of analytical composition $[Pt(dba)_2]_n$ **7**, (89% yield, Table 2, entry 4), scarcely soluble in diethyl ether. Platinum(0) complexes with dba as ligand are well known and the compositions $[Pt(dba)_2]$, $[Pt(dba)_3]$ and $[Pt_2(dba)_3]$ have been reported [19]. Structural data are available [20] only for a species with dba/Pt molar ratio of about 2, $[Pt_{1.44}(dba)_3 \cdot CH_2Cl_2]$, corresponding to a mixture of the dinuclear $[Pt_2(dba)_3]$ and the mononuclear $[Pt(dba)_3]$ species. For sake of comparison, in the course of this work we have prepared $[Pt(dba)_3]$ **8**, according to the experimental procedure described by Moseley and Maitlis [19b]: yellow crystals of this product were obtained and the crystal and molecular structure of this substance was established, as discussed in Section 2.3 of this paper.

The synthetic procedure used to prepare Pt(0) complexes is summarized in Scheme 2: the reduction–complexation process is accompanied by the formation of CO_2 and HCl, a threefold excess of potassium formate preventing HCl addition to the complexing alkene [21]. Moreover, a strong excess of alkene (alkene/Pt molar ratioes in the 7–10 range) is necessary in order to replace the diene completely and to obtain a pure product.

2.3. Crystal and molecular structure of $[Pt(dba)_3]$, **8**

Yellow single crystals of product **8** were studied by X-ray diffraction methods. In the metal complex (see Fig. 1) two positions are potentially present, both suitable to insert a platinum atom at the right distance from three C=C double bonds. One of these positions is fully occupied while in the other only a weak electron density is measured, corresponding to a calculated degree of occupancy of 0.03. According to these data, we have considered the species as a solid solution of $[Pt(dba)_3]$ and $[Pt_2(dba)_3]$, of average composition $[Pt_{1.03}(dba)_3]$. The formation of a solid solution is compatible with the expected close geometric resemblance of the two molecules. An alternative explanation could be that the sample contains only $[Pt(dba)_3]$ with about 3% of upside down molecules to give an end-for-end disorder. Due to the small fraction of misaligned molecules our X-ray experiment does not allow to exclude this possibility. We prefer however the first hypothesis by considering the results reported for the already described $[Pt_{1.44}(dba)_3] \cdot CH_2Cl_2$ [20], whose geometrical features are similar to the ones of our derivative (see Table 3).

Table 2
Synthesis of platinum(0) complexes, Pt(alkene)$_n$, according to Scheme 2.[a]

Entry	Precursor	Alkene	Solvent	n	Yield %	Product
1	$[PtCl_2(COD)]$	COD[b]	1,2-DCE	2	25	**5**
2	$[PtCl_2(COD)]$	COD[b]	Et_2O	2	40	**5**
3	$[PtCl_2(COD)]$	NB[b]	Et_2O	3	62	**6**
4	$[PtCl_2(NBD)]$	dba[c]	Et_2O	2	89	**7**

[a] HCOOK/Pt molar ratio = 3.
[b] Alkene/Pt molar ratio = 10.
[c] dba/Pt molar ratio = 7.

$$PtCl_2(\text{diene}) + HCOOK_{(s)} \xrightarrow[\text{cat. 18-crown-6, 25 °C}]{\text{solvent, alkene (excess)}} Pt(\text{alkene})_n + CO_2 + \text{diene} + KCl + HCl$$

Scheme 2.

Pt1 and the three C=C groups around it are nearly coplanar, while the C=C axes around Pt2 are approximately perpendicular to the metal coordination plane.

In olefin complexes of zerovalent platinum of the type $Pt(alkene)_3$ the three coordinated C=C groups, in the absence of geometrical constraints, are disposed on the coordination plane. Such a geometry can be observed, for instance, in *tris*(bicyclo(2.2.1)heptene) platinum (0) [2g] or in (η^2-maleic anhydride)-bis(η^2-norbornene)-platinum(0) [1e].

To discuss the geometrical features of our complex we have to consider that three conformers are possible for dba, as outlined in

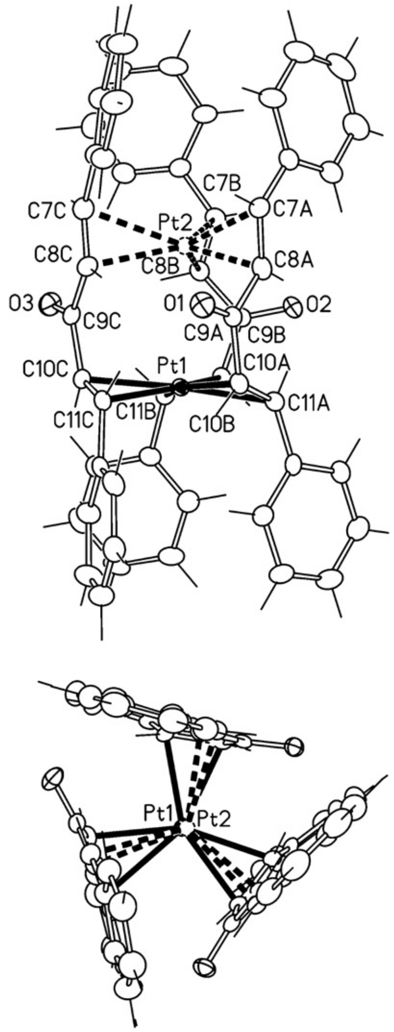


Fig. 1. Different views of the molecular model of 0.97 $Ptdba_3 \cdot 0.03Pt_2dba_3$. Thermal ellipsoids are at 30% probability.

Table 3
Bond distances (Å) and angles (°) around Pt in the crystal structure of **8**, $0.97Ptdba_3 \cdot 0.03Pt_2dba_3 \cdot CH_2Cl_2$.

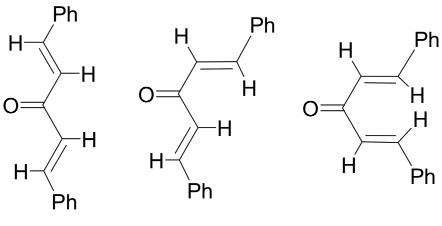
Pt1−C10A	2.181(7)	Pt2−C7A	2.514(13)
Pt1−C11A	2.217(8)	Pt2−C8A	2.292(13)
Pt1−C10B	2.190(7)	Pt2−C7B	2.488(14)
Pt1−C11B	2.225(8)	Pt2−C8B	2.273(14)
Pt1−C10C	2.201(8)	Pt2−C7C	2.441(14)
Pt1−C11C	2.209(8)	Pt2−C8C	2.343(14)
Pt1···Pt2	3.158(10)		
C10A−Pt1−C10B	118.1(3)	C8B−Pt2−C8A	117.5(5)
C10A−Pt1−C10C	120.3(3)	C8B−Pt2−C8C	115.8(5)
C10B−Pt1−C10C	119.8(3)	C8A−Pt2−C8C	112.6(5)
C10A−Pt1−C11C	85.5(3)	C8B−Pt2−C7C	115.7(5)
C10B−Pt1−C11C	156.4(3)	C8A−Pt2−C7C	126.3(6)
C10C−Pt1−C11C	37.5(3)	C8C−Pt2−C7C	31.7(3)
C10A−Pt1−C11A	36.5(3)	C8B−Pt2−C7B	31.4(3)
C10B−Pt1−C11A	84.4(3)	C8A−Pt2−C7B	116.6(5)
C10C−Pt1−C11A	155.8(3)	C8C−Pt2−C7B	130.4(6)
C11C−Pt1−C11A	118.5(3)	C7C−Pt2−C7B	112.1(5)
C10A−Pt1−C11B	153.8(3)	C8B−Pt2−C7A	130.9(5)
C10B−Pt1−C11B	37.0(3)	C8A−Pt2−C7A	31.5(3)
C10C−Pt1−C11B	85.8(3)	C8C−Pt2−C7A	112.9(5)
C11C−Pt1−C11B	119.7(3)	C7C−Pt2−C7A	108.7(5)
C11A−Pt1−C11B	117.5(3)	C7B−Pt2−C7A	111.9(5)

Fig. 2. They differ in stability because of their different H···H nonbonding interactions. Due to the presence of the terminal phenyl residues, the dba groups, independent of their conformation, have an elongated shape in a direction perpendicular to the C═O bond. Solid dba adopts the *s-cis*,*cis* conformation [22], where the H···H repulsions appear to be substantially absent. In this conformation the molecules are not planar, their two halves being twisted by 52.5°.

In $M_x(dba)_3$ complexes, the coordination to the metal imposes to three dba ligands to approach each other so that the twisted shapes will be disfavored. In fact the three dba ligands in $Pt_x(dba)_3$ or $Pd_x(dba)_3$ ($x = 1–2$) are flat. In all these coordination compounds the ligands approach each other in a trigonal prism disposition, similar to the structure of our compound.

In coordinated dba the *s-trans* conformations appear to be more stable. In $Pd(dba)_3$ [23] all the ligands show the *s-cis*,*trans* conformation, with the palladium coordinated to the *trans*-conformed olefins with formation of a planar $Pd(C{=}C)_3$ moiety. The same dba conformation is the most frequently found in $Pd_2(dba)_3$ [24] and $Pt_{1.44}(dba)_3$ [20]. Nevertheless, in the dinuclear species the two coordination sites furnished by the tern of ligands cannot offer the possibility of two planar $M(C{=}C)_3$ moieties because of the skeletal requirements of dba, independent of its conformation. For instance in $Pd_2(dba)_3 \cdot CH_2Cl_2$ [24] a *s-trans*,*trans* conformer is also found and the two Pd centres in the molecule have, at least, one C═C bond lying in its coordination plane.

The *s-cis*,*trans* conformation of the three ligands with all the C10═C11 *trans* π systems on the same side is particularly favourable for Pt1, which can efficiently bond to them at a mean Pt1−C distance of 2.204 Å. This value is comparable with the 2.183 Å distance observed in *tris*(bicyclo(2.2.1)heptene) platinum(0) [2h]. On the other hand, the three *cis* π-systems appear to form a weaker bond to the metal, although the mean Pt2−C distance of 2.392 Å cannot be directly compared being an average value derived from bonded and non-bonded olefin groups. In the species described by Lewis et al. [20] the $Pt_2(dba)_3/Pt(dba)_3$ molar ratio is 0.44, to be compared with the value of 0.03 in our derivative. The two phases are probably miscible in a large range of composition.



s-cis,cis *s-cis,trans* *s-trans,trans*

Fig. 2. The three conformers of dba.

3. Conclusions

We have described a convenient two-step process for the synthesis of platinum(0) alkene complexes under PT catalysis conditions. This method affords products in moderate to good yields (30–70%) starting from commercial hexachloroplatinic acid and with the use of easy to handle reducing agents. Furthermore, the reduction is selective so that platinum-black has never been observed and tedious purification procedures can be avoided.

Among the platinum(0) complexes, we have obtained crystals of $[Pt_{1.03}(dba)_3] \cdot CH_2Cl_2$, which can be considered as a solid solution of $Pt(dba)_3$ and $Pt_2(dba)_3$, with the mononuclear complex being largely prevailing. In view of their similar geometrical features, it is reasonable to conclude that the two complexes are in equilibrium in solution, Eq. (3), solid solution of various composition precipitating out depending on the dba concentration.

$$2\ Pt(dba)_3 \rightleftharpoons Pt_2(dba)_3 + 3dba \qquad (3)$$

4. Experimental

4.1. General procedures

All manipulations were performed under a dinitrogen atmosphere. Hexachloroplatinic acid (aqueous solution, Chimet S.p.A., I-52041 Badia al Pino, Arezzo), bicyclo[2.2.1]hepta-2,5-diene (NBD, Aldrich), dicyclopentadiene (DCPD, Aldrich), 4-oxahepta-1,6-diene (DAE, Aldrich), [2.2.1]bicycloheptene (NB, Aldrich), tetrabutylammonium chloride ([TBA]Cl, Fluka) were commercial products used without further purification. 1,5-cyclooctadiene (COD, Aldrich) was distilled before use. (E,E)-1,5-Diphenyl-3-oxopenta-1,4-diene (dba) was prepared according to literature.[25] 1,2-Dichloroethane (DCE) was distilled from P_4O_{10}. Diethyl ether was distilled from $LiAlH_4$. CD_2Cl_2 (99.5%, Aldrich) was treated with P_4O_{10} and distilled before use. C_6D_6 (99.6%, Aldrich) was deoxygenated before use. Potassium formate (Aldrich) and 18-crown-6 were dried *in vacuo* before use.

^1H-, ^{13}C- and ^{195}Pt-NMR spectra were recorded with a Varian Gemini 200BB spectrometer. Chemical shifts were measured in ppm (δ) from TMS by residual solvent peaks for ^1H and ^{13}C and from aqueous (D_2O) hexachloroplatinic acid for ^{195}Pt. A sealed capillary containing C_6D_6 was introduced in the NMR tube to lock the spectrometer to the deuterium signal when non-deuterated solvents were used. Elemental analyses (C, H) were performed by Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, Università di Pisa, with a C. Erba mod. 1106 elemental analyser.

4.2. Synthesis of dichloro(diene)platinum(II) complexes

A 250 ml round bottomed flask equipped with a magnetic stirrer was charged with 5.0 ml of aqueous H_2PtCl_6 (7.7 mmol Pt), 30 ml of 1,2-dichloroethane, 30 ml of H_2O, 150 mg of tetrabutylammonium chloride (0.54 mmol) and 15.4 mmol of the diene (diene/[Pt] molar ratio = 2). A solution of 1.0 M NaOH was added in portions until the final pH of the aqueous layer turned basic. A solution of 398 mg (3.8 mmol) of hydrazine dihydrochloride in 10 ml of H_2O was added under stirring at room temperature (25 °C). The colour of the aqueous layer turned from orange to red in a few minutes; when gas evolution ceased, the biphasic mixture was refluxed until the aqueous layer was colourless (6 h). After discarding the aqueous layer, the product was washed with portions of heptane (2 × 10 ml) and dried in vacuum. The recovered complexes are reported below.

Dichloro-(η^4-1,5-cyclooctadiene)platinum(II), [PtCl$_2$(COD)] **1**: (78% yield). Anal. Calcd. for $C_8H_{12}Cl_2Pt$: C, 25.7; H, 3.2. Found: C, 25.5; H, 2.9%. IR (cm^{-1}): 3008, 2962, 1475, 1450, 1424, 1339, 1179, 1008, 910, 871, 831, 780, 694. NMR (ppm): ^{1}H: 5.63 (m, 4H, $^2J_{H-Pt} = 68$ Hz); 2.73 (m, 4H); 2.28 (m, 4H); ^{195}Pt: −3337.

Dichloro-(η^4-bicyclo[2.2.1]hepta-2,5-diene)platinum(II), [PtCl$_2$(NBD)] **2**: (78% yield). Anal. Calcd. for $C_7H_8Cl_2Pt$: C, 23.5; H, 2.3. Found: C, 23.6; H, 1.6%. IR (cm^{-1}): 3051, 1435, 1388, 1309, 1226, 1180, 980, 848, 831, 799, 774. NMR (ppm): ^{1}H: 5.34 (dd, 4H, $J = J' = 2.5$ Hz, $^2J_{H-Pt} = 69$ Hz), 4.35 (m, 2H), 1.75 (dd, 2H, $J = J' = 1.5$ Hz); ^{195}Pt (d$_6$-DMSO): −3113.

Dichloro-(η^4-dicyclopentadiene)platinum(II), [PtCl$_2$(DCPD)] **3**: (61% yield). Anal. Calcd. for $C_{10}H_{12}Cl_2Pt$: C, 30.2; H, 3.0. Found: C, 31.3; H, 3.0%. IR (cm^{-1}): 3038, 3018, 2985, 2884, 1421, 1332, 1297, 1266, 1239, 1182, 993, 960, 918, 860, 811, 804, 724. NMR (ppm): ^{1}H: 6.90 (m, 1H, $^2J_{H-Pt} = 80$ Hz), 6.51 (m, 1H, $^2J_{H-Pt} = 71$ Hz), 6.11 (m, 1H, $^2J_{H-Pt} = 80$ Hz), 5.83 (m, 1H, $^2J_{H-Pt} = 71$ Hz), 3.71 (m, 2H), 2.90 (m, 2H), 2.4–1.6 (m, 4H); ^{13}C: 116.1 ($^1J_{C-Pt} = 143$ Hz), 105.3 ($^1J_{C-Pt} = 119$ Hz), 100.3 ($^1J_{C-Pt} = 142$ Hz), 97.4 ($^1J_{C-Pt} = 152$ Hz); 60.0 ($^2J_{C-Pt} = 84$ Hz), 56.1, 55.4, 43.6, 43.4, 33.7; ^{195}Pt: −3236.

Dichloro-(η^4-[4-oxahepta-1,6-diene])platinum(II), [PtCl$_2$(DAE)] **4**: (75% yield). Anal. Calcd. for $C_6H_{10}Cl_2OPt$: C, 19.8; H, 2.8. Found: C, 19.5; H, 2.6%. IR (cm^{-1}): 3100, 3087, 3021, 2982, 2905, 2860, 1513, 1455, 1403, 1381, 1301, 1263, 1225, 1126, 1101, 1052, 1018, 979, 939, 876, 778. NMR (ppm): ^{1}H (CD_2Cl_2): 5.72 (m, 1H); 5.00 (d, 1H, $J = 8.8$ Hz, $^2J_{H-Pt} = 66$ Hz); 4.54 (d, 1H, $J = 13.9$ Hz, $^2J_{H-Pt} = 49$ Hz); 3.83 (m, 2H); ^{195}Pt (d$_6$-DMSO): −3444.

4.3. Synthesis of platinum(0) complexes

4.3.1. Bis(cycloocta-1,5-diene)platinum(0) [Pt(COD)$_2$] **5**

A 100 ml Schlenk tube equipped with a magnetic stirrer was charged with 765 mg of finely divided [PtCl$_2$(COD)] (2.04 mmol), 2.20 g of cycloocta-1,5-diene (20.4 mmol), 90 mg of 18-crown-6 (0.35 mmol) and 30 ml of dry diethyl ether. The colourless suspension was cooled (0 °C) and 580 mg of potassium formate (6.9 mmol) were added under stirring. The suspension, stirred at 0 °C (4 h) and then at room temperature (25 °C, 20 h), turned dark brown. Solid components were eliminated by filtration under dinitrogen and washed with diethyl ether (20 ml) and heptane (20 ml). The brown solution was concentrated (10 ml) and filtered on a short package (5 cm) of aluminum oxide. Elimination of solvents afforded 335.3 mg (40% yield) of bis(cycloocta-1,5-diene) platinum(0). Anal. Calcd. for $C_{16}H_{24}Pt$: C, 46.7; H, 5.9. Found: C, 46.3; H, 5.8%. ^{1}H-NMR (C_6D_6, ppm): 4.19 (s, 8 H, $^2J_{H-Pt} = 56$ Hz); 2.20 (m, 16 H).

4.3.2. Tris(bicyclo[2.2.1]heptene)platinum(0), [Pt(NB)$_3$] **6**

A 100 ml Schlenk tube equipped with a magnetic stirrer was charged with 591 mg of finely divided [PtCl$_2$(COD)] (1.58 mmol), 1.509 g of [2.2.1]bicycloheptene (16.1 mmol), 63 mg of 18-crown-6 (0.23 mmol) and 30 ml of dry diethyl ether. The colourless suspension was cooled (0 °C) and 420 mg of potassium formate (5.0 mmol) were added under stirring. The suspension, stirred at 0 °C (4 h) and then at room temperature (25 °C, 20 h), turned pale grey. Solid components were eliminated by filtration under dinitrogen and washed with diethyl ether (20 ml) and heptane (20 ml). Elimination of solvents *in vacuo* from the combined pale yellow filtrates afforded 469 mg (62% yield) of pale grey tris(bicyclo[2.2.1] heptene)platinum(0). Anal. Calcd. for $C_{21}H_{30}Pt$: C, 52.8; H, 6.3. Found: C, 52.5; H, 6.6%. ^{1}H-NMR (C_6D_6, ppm): 3.25 (s, 6 H, $^2J_{H-Pt} = 63$ Hz); 2.84 (m, 12 H); 1.60 (m, 12 H); 1.29 (m, 12 H); 0.25 (m, 6 H); 0.22 (m, 6 H).

4.3.3. Bis[(E,E)-1,5-diphenyl-3-oxopenta-1,4-diene]platinum(0) [Pt(dba)$_2$] **7**

A 100 ml Schlenk tube equipped with a magnetic stirrer was charged with 380 mg of finely divided [PtCl$_2$(NBD)] (1.06 mmol), 1.640 g of (E,E)-1,5-diphenyl-3-oxopenta-1,4-diene (dba, 7.0 mmol), 14 mg of 18-crown-6 (0.05 mmol) and 30 ml of dry diethyl ether. The suspension was stirred at room temperature and 252 mg of potassium formate (3.0 mmol) were added. Stirring was continued at room temperature (25 °C, 20 h) and a yellow-brown solid formed. The mixture was filtered and the recovered solid was washed with diethyl ether (10 ml), petroleum ether (10 ml), dried, washed with water (2 × 25 ml) and finally dried under vacuum (10^{-1} mmHg, 20 h). The yellow-brown [Pt(dba)$_2$] was obtained (0.592 g, 89% yield). Anal. Calcd. for $C_{34}H_{28}O_2Pt$: C, 61.5; H, 4.2. Found: C, 60.2; H, 4.0%.

4.3.4. X-ray crystallography

The X-ray diffraction experiment was carried out at room temperature ($T = 293$ K) by means of a Bruker P4 four-circle diffractometer equipped with graphite-monochromated Mo-K_α radiation. The more relevant crystal parameters are listed in Table 4. The intensity data were collected until a maximum 2θ of 50° with the $\omega/2\theta$ scan mode, collecting a redundant set of data. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of an integration method based on the crystal shape [26]. The structure solution was obtained by means of the automatic direct methods contained in the SHELXS97 program [27]. The refinement, based on full-matrix least-squares on F^2, was done by means of the SHELXL97 [27] program. Some other utilities contained in the WINGX suite [28] were also used. The asymmetric unit contains a dichloromethane molecule and a molecule of the metal complex formed by three dibenzylideneacetone ligands, each connected through one of its double bonds to a platinum atom. In the difference Fourier map a low electron density peak was observed in the region surrounded by the remaining three double

Table 4
Crystal data and structure refinement of **8**.

Empirical formula	$C_{52}H_{44}Cl_2O_3Pt_{1.03}$
Formula weight	988.13
Crystal system	triclinic
Space group	$P\overline{1}$ (no. 2)
a [Å]	12.433(3)
b [Å]	13.212(1)
c [Å]	14.941(2)
α (°)	114.88(1)
β (°)	97.34(1)
γ (°)	95.79(1)
V [Å^3]	2175.4(6)
Z	2
D_{calc} [g cm^{-3}]	1.509
μ [mm^{-1}]	3.477
F(000)	988
Collected reflections	8152
Independent reflections	7035
No. of parameters	455
GOF on F^2	1.017
R_1 ($I > 2\sigma_I$/all data)	0.0470/0.0682
wR_2 (all data)	0.1158
Largest diff. peak/hole [e Å^{-3}]	1.787/−1.563

bonds, at a distance compatible with the presence of a second platinum atom. Nevertheless, the height of this peak is only about $4\,e\,\text{Å}^{-3}$. This feature has been inferred as the result of the presence in the structure, together with molecules of composition $Pt(dba)_3$, of a small number of molecules of composition $Pt_2(dba)_3$ in a sort of solid solution. Both platinum atoms were introduced in the model, fixing to 1.0 the population parameter of the first one and tentatively adjusting the second in order to obtain about the same thermal parameters in the refinement. As the adjusted population parameter for the "lighter" platinum is only about 0.03, this atom has been refined with isotropic thermal parameters. All the other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions with isotropic constrained thermal parameters and let to move following the "riding" convention. Final reliability factors are listed in Table 4.

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Appendix A. Supplementary material

CCDC No. 798262 contains crystallographic data for the structural analysis of compound **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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