

Preparation and reactivity of penta- and tetracoordinate platinum(II) hydride complexes with P(OEt)₃ and PPh(OEt)₂ phosphite ligands†

Gabriele Albertin,^{*a} Stefano Antoniutti,^a Christian Busato,^a Jesús Castro^b and Soledad García-Fontán^a

^a Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro, 2137, 30123, Venezia, Italy. E-mail: albertin@unive.it; Fax: +39 041 234 8917

^b Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310, Vigo (Galicia), Spain

Received 18th April 2005, Accepted 7th June 2005

First published as an Advance Article on the web 21st June 2005

The pentacoordinate [PtH{P(OEt)₃}₄]BF₄ (**1**) hydride complex was prepared by allowing the tetrakis(phosphite) Pt{P(OEt)₃}₄ to react with HBF₄·Et₂O at –80 °C. Depending on the nature of the acid used, however, the protonation of the related Pt{PPh(OEt)₂}₄ complex yielded the pentacoordinate [PtH{PPh(OEt)₂}₄]BF₄ (**3**) or the tetracoordinate [PtH{PPh(OEt)₂}₃]Y (**4**) [Y = BF₄[–] (**a**), CF₃SO₃[–] (**b**), Cl[–] (**c**)] derivatives. Neutral PtHCIP₂ (**7**, **8**) [P = P(OEt)₃, PPh(OEt)₂] hydride complexes were prepared by allowing PtCl₂P₂ to react with NaBH₄ in CH₃CN. The tetrakis(phosphite) [Pt{P(OEt)₃}₄](BF₄)₂ (**2**) derivative was also synthesised and then characterised spectroscopically and by an X-ray crystal structure determination. Reactivity with aryldiazonium cations of all the hydrides was investigated and found to proceed only with the PtHCIP₂ complex to yield the aryldiazene [PtCl(ArN=NH)P₂]BF₄ [P = PPh(OEt)₂] derivative. The hydrazine [PtCl(NH₂NH₂){PPh(OEt)₂]₂BPh₄ complex was also prepared by allowing PtHCIP₂ to react first with AgCF₃SO₃ and then with hydrazine.

Introduction

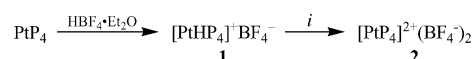
The chemistry of transition-metal hydrides continues to attract considerable interest and a large number of complexes have been reported in recent years.¹ The ancillary ligands used to stabilise this class of compounds involve mainly π-acceptor species such as carbonyl, tertiary phosphine and cyclopentadienyl. However, the use of phosphite ligands in hydride chemistry has received little attention^{1,2} when compared to tertiary phosphines, whose fundamental systematic study began in the 1950s.^{3,4} These results are somewhat surprising, in view of the easy synthesis of phosphite ligands,⁵ their good π-acceptor properties,⁶ and the relevance of some phosphite complexes as catalysts for hydrocyanation,⁷ alkene oligomerisation⁸ and isomerisation,⁹ and hydroformylation¹⁰ reactions.

We are interested in the chemistry of classical and non-classical transition-metal hydrides and have reported the synthesis and the reactivity of several complexes of manganese,¹¹ iron,¹² and cobalt¹³ triads of the MH(CO)_nP_{5–n} (M = Mn, Re; n = 1–3), ReH₃P₄, ReH₅P₃, MXHP₄, [MX(η²-H₂)P₄]⁺ (M = Fe, Ru, Os; X = H, Cl, Br, N₃), and [CoH₂P₄]⁺ [P = P(OEt)₃, PPh(OEt)₂, PPh₂OEt] type containing phosphites as supporting ligands. Now we have extended these studies to platinum(II) with the aim of testing whether hydride complexes with P(OEt)₃ and PPh(OEt)₂ ligands can be prepared for this metal as well. A glance through the literature, in fact, has shown that the Pt(II) complexes with phosphite ligands are rather few^{14–17} and the only reported hydrides are PtHCl{P(OMe)₃}₂, PtHCl{PMe(OMe)₂}₂,^{15a} the unstable^{14d} PtHCl{P(OC₆H₄OMe-2)₃}₂ and the cationic [PtH{P(OR)₃}₄]BF₄ (R = Me, Et) derivatives.^{15b} It is therefore desirable to increase the knowledge of this class of compounds, and in this paper we report the synthesis and some reactivity of new penta- and tetracoordinate platinum(II) hydride complexes containing P(OEt)₃ and PPh(OEt)₂ as supporting ligands.

Results and discussion

Preparation of the hydrides

Tetrakis(phosphite)platinum(0), Pt{P(OEt)₃}₄,¹⁶ reacts with HBF₄·Et₂O to give the pentacoordinate [PtH{P(OEt)₃}₄]BF₄ (**1**) hydride complex, which was separated as white microcrystals and characterised (Scheme 1). In the presence of an excess of HBF₄·Et₂O or by standing in solution, however, the hydride (**1**) slowly decomposes to give the tetrakis(phosphite) [Pt{P(OEt)₃}₄](BF₄)₂ (**2**) derivative.



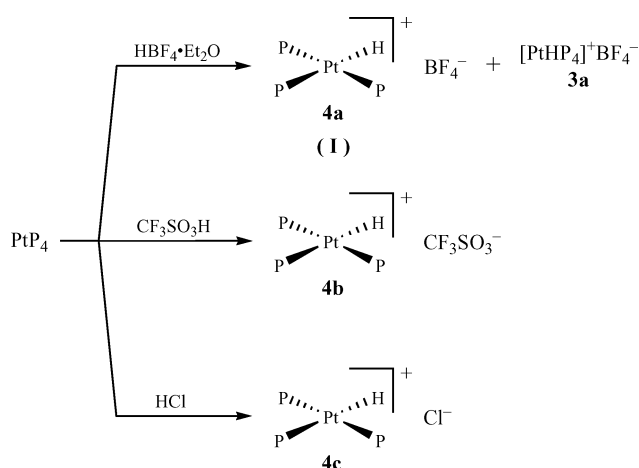
Scheme 1 P = P(OEt)₃; Reagents and conditions: (i) excess HBF₄·Et₂O or by standing in solution.

Different Brønsted acids such as CF₃SO₃H and HCl also react with Pt{P(OEt)₃}₄ to give, in each case, the pentacoordinate hydride cation **1**⁺.

On the other hand, the outcome of the protonation reaction of the related Pt(0) complex Pt{PPh(OEt)₂}₄ containing the PPh(OEt)₂ ligand depends on the nature of the acid used, as shown in Scheme 2.

With both CF₃SO₃H and HCl the reaction proceeds to give exclusively the cationic tetracoordinate [PtH{PPh(OEt)₂}₃]⁺ (**4**) hydride complex, which was isolated with both the Cl[–] (**4c**) and CF₃SO₃[–] (**4b**) anions in good yield and characterised. The oxidative addition of H⁺ to the Pt(0) complex Pt{PPh(OEt)₂}₄ was followed by the dissociation of one phosphonite ligand to give the tetracoordinate hydride derivatives **4**. The reaction of Pt{PPh(OEt)₂}₄ with HBF₄·Et₂O, on the other hand, gave a mixture of the pentacoordinate [PtH{PPh(OEt)₂}₄]⁺ (**3a**) and the tetracoordinate [PtH{PPh(OEt)₂}₃]⁺ (**4a**) hydride complexes, which were not separated. Experiments, by fractional crystallisation, gave solids only enriched in the tetracoordinate species. However, comparison of the spectroscopic data of the mixture of **3a** and **4a** with those of compounds **4b**, **4c** and with those of **1** strongly supports the presence of both the tetracoordinate **4a** and pentacoordinate **3a** species in the solid obtained in

† Electronic supplementary information (ESI) available: Hydrogen bond parameters (Table S1); packing of the molecules in the cell (Fig. S1). See http://dx.doi.org/10.1039/b505453b



Scheme 2 P = PPh(OEt)₂.

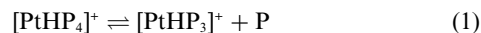
the reaction with HBF₄·Et₂O. It could also be noted that the pentacoordinate compound **3a**, once formed, is fairly stable to the loss of one phosphine and the enrichment in tetracoordinate species **4a** was observed only after several hours in solution.

The results of the protonation of the tetrakis(phosphite) PtP₄ complexes [P = P(OEt)₃, PPh(OEt)₂] giving penta- and/or tetracoordinate hydride complexes may be explained taking into account the different properties of both the phosphites and the anions of the acids used. The protonation of PtP₄ should give the pentacoordinate [PtHP₄]⁺ cation as the first formed product, which can lose one phosphite ligand to yield the tetracoordinate [PtHP₃]⁺ cation. While with P(OEt)₃ the dissociation of one phosphite is probably very slow, and the pentacoordinate **1** was obtained in each case, with PPh(OEt)₂ the influence of the anions does result. The Cl⁻ and CF₃SO₃⁻ anions, which have good coordinating properties, may be in competition with phosphite, as suggested by one referee, for the fifth coordination site and favour the tetracoordinate [PtHP₃]⁺X⁻ species (X = Cl⁻, CF₃SO₃⁻). With the poorly coordinating BF₄⁻ anion, instead, both the penta- and tetracoordination are present.

Good analytical data were obtained for the new hydride complexes **1** and **4**, which are white solids stable in air and in solutions of polar organic solvents where they behave as 1 : 1 electrolytes.¹⁹ The infrared and NMR data, reported in Table 1, support the formulation of the complexes. [PtH{P(OEt)₃}₄]BF₄ has been previously obtained^{15b} from the reaction of [Pt(1-σ,4,5-η-C₈H₁₃)(cod)]BF₄ (cod = cyclooctadiene) with P(OEt)₃ and, although the hydride signal was not detected in the proton NMR spectra, the value of the ³¹P signal is the same as that of **1**, in agreement with a correct formulation of the compounds.

The IR spectrum of [PtH{P(OEt)₃}₄]BF₄ (**1**) shows a weak band at 2110 cm⁻¹ attributed to ν(PtH) of the hydride ligand. The ¹H NMR spectra confirm the presence of the hydride and also show that the complex is fluxional. In fact, the broad signal that appears at room temperature near -13.6 ppm resolves into a sharp quintet at -30 °C with J_{PH} of 56 Hz and J_{PH} of 535 Hz due to the coupling of the hydride with four equivalent phosphite ligands. The variable-temperature ³¹P{¹H} NMR spectra, however, seem to suggest that the [PtH{P(OEt)₃}₄]BF₄ (**1**) complex undergoes two dynamic processes. At room temperature, in fact, a broad signal near 95 ppm appears, in which the coupling with the platinum nucleus is lost. Decreasing the sample temperature causes a spectra change until, at -30 °C, a sharp singlet appears at 94.1 ppm, with a platinum-phosphorus coupling of 3950 Hz. The loss of the platinum-phosphorus coupling in the temperature range between +20 and -30 °C may be interpreted on the basis of a dynamic process involving intermolecular exchange with free P(OEt)₃. A dissociative mechanism of the type of eqn. (1) may be proposed, which agrees with previous reports in the literature^{20a,b} on related pentacoordinate Pt(II) hydride species,

and also accounts for the instability of **1** observed in solution which yields the [Pt{P(OEt)₃}₄]²⁺ (**2**) species.



Decreasing the sample temperature below -30 °C does not cause changes in the ³¹P spectra, which appear as sharp singlets until -80 °C. Further lowering of the temperature causes a broadening of the signals, which approach two multiplets at the lowest attained temperature (-100 °C). These results suggest that complex **1** undergoes a second dynamic process below -30 °C involving intramolecular phosphite exchange. This exchange is fast even at -100 °C, but should show that two sets of signals are present in the low exchange limit process, in agreement with either a trigonal-bipyramidal (TBP) or a square-pyramidal (SP) geometry.

Unfortunately, these two multiplets are too broad at this temperature to give any information on the geometry. The ³¹P spectrum of the related [PtH{P(OMe)₃}₄]⁺ cation, however, shows two multiplets at -120 °C which are in a 1 : 3 ratio and are consistent with a TBP structure with the hydride in an axial position.^{15b} A similar TBP geometry probably applies also for our [PtH{P(OEt)₃}₄]⁺ (**1**) cation. The ¹H NMR spectra parallel the behaviour of the ³¹P one showing, between -30 and -80 °C, a sharp quintet for the hydride signals, which broaden below -80 °C and approach two multiplets at -100 °C.

Several examples of five-coordinate platinum(II) monohydride complexes are reported in the relevant literature^{14b,20,21} and the X-ray measurements of [PtHP₄]BPh₄ (P₄ = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane) show a distorted trigonal-bipyramidal structure in its solid state.^{21b} Variable-temperature NMR measurements of some of the other pentacoordinate hydrides were interpreted^{20,21} on the basis of the existence in solution of a distorted TBP geometry and these precedents further support the hypothesis that a similar geometry is present in solution also for our complex **1**.

The NMR spectra of the tetracoordinate [PtH{PPh(OEt)₂}₃]⁺ (**4b** and **4c**) cation indicate that also this complex is fluxional. At -70 °C, however, the ³¹P{¹H} spectra appear as a well-resolved AB₂ multiplet which can be simulated with the parameters reported in Table 1 and this indicates the presence of two magnetically equivalent phosphonites and different from the third. At the same temperature, in the proton spectra, the hydride signal appears at -4.50 ppm as a AB₂X (X = H) multiplet due to the coupling with the phosphorus nuclei of the phosphonites. A simulation, using an AB₂X model, allowed the NMR parameters to be determined. On the basis of these data,²² a square-planar geometry (**1**) of the type of Scheme 2 can reasonably be proposed for the tetracoordinate hydride complexes **4b** and **4c**.

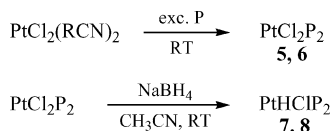
The ¹H NMR spectra of the mixture containing **4a** and **3a** show, in the hydride region at -70 °C, an AB₂X (X = H) multiplet centred to the same value of chemical shift of the tetracoordinate **4b** and **4c** (-4.50 ppm) and a quintet at -13.35 ppm (J_{PH} = 47 Hz, J_{PH} = 535 Hz). The multiplet at -4.50 ppm is simulable with the same parameters of **4b** and **4c** and is attributed to the tetracoordinate [PtH{PPh(OEt)₂}₃]⁺ (**4a**) cation, while the quintet at -13.35 ppm is attributable to the pentacoordinate tetrakis(phosphonite) [PtH{PPh(OEt)₂}₄]⁺ hydride derivative. The ³¹P{¹H} NMR spectra (Table 1) confirm the presence of the two species **3a** and **4a** showing, besides the AB₂ multiplet of the [PtHP₃]⁺ cation **4a**, a singlet at 113 ppm (J_{PP} = 3818 Hz) attributable to the pentacoordinate [PtHP₄]⁺ cationic derivative **3a**. Variable-temperature NMR spectra also show, as for the related complex **1**, that the pentacoordinate [PtH{PPh(OEt)₂}₄]⁺ undergoes two dynamic processes. Above -30 °C, an intermolecular exchange *via* a dissociative mechanism of the type of eqn. (1) is probably present. Below -30 °C, a sharp singlet with Pt-P coupling was observed, which began to broaden near -80 °C and approached to two multiplets at -100 °C suggesting that a TBP geometry may be present also for **3a** at a very low temperature.

Table 1 (Contd.)

Compound	IR ^a	Assgnt.	¹ H NMR ^{b,c} δ (J/Hz)	Assgnt.	Spin system	³¹ P{ ¹ H} NMR ^{b,d} δ (J/Hz)
<i>trans</i> -[PtCl(C ₆ H ₅ N=NH){PPh(OEt) ₂ } ₂]BF ₄ (10a)			14.5 s, br ² J _{PtH} = 84 4.20 m 4.03 m 1.30 t	NH CH ₂ CH ₃	A ₂	110.0 s J _{PtP} = 3370
<i>trans</i> -[PtCl(C ₆ H ₅ N= ¹⁵ NH){PPh(OEt) ₂ } ₂]BF ₄ (10a ₁)			14.54 d ¹ J _{15NH} = 77 ² J _{PtH} = 84 4.22 m 4.05 m 1.30 t	NH CH ₂ CH ₃	A ₂ X (X = ¹⁵ N)	δ _A 110.0 J _{AX} = 3.8 J _{PtP} = 3370
<i>trans</i> -[PtCl(4-CH ₃ C ₆ H ₄ N=NH){PPh(OEt) ₂ } ₂]BF ₄ (10b)			14.2 s, br ² J _{PtH} = 84 4.16 m 2.55 s 1.25 t	NH CH ₂ CH ₃ <i>p</i> -tol CH ₃ phos	A ₂	110.2 s J _{PtP} = 3350
<i>cis</i> -[PtCl(NH ₂ NH ₂){PPh(OEt) ₂ } ₂]BPh ₄ (11)	3217 m 3163 m	ν(NH)	5.18 br ^f 3.64 m 4.00 m 1.33 t 1.18 t	PtNH ₂ NH ₂ CH ₂ CH ₃	AB ^g	δ _A 84.7 δ _B 83.6 J _{AB} = 21.4 J _{PtPA} = 4462 J _{PtPB} = 4765

^a In KBr pellets. ^b In CD₂Cl₂ at 25 °C, unless otherwise noted. ^c Phenyl proton resonances omitted. ^d Positive shift downfield from 85% H₃PO₄. ^e At -30 °C. ^f At -70 °C.

The easy synthesis of stable cationic platinum(II) hydride complexes with P(OEt)₃ and PPh(OEt)₂ ligands prompted us to extend the studies to the synthesis of related neutral hydride complexes. The method we used for the successful synthesis is shown in Scheme 3, and involves first the preparation of dichloro PtCl₂P₂ (**5**, **6**) complexes by treatment of dinitrile PtCl₂(RCN)₂ species with an excess of phosphite.



Scheme 3 R = 4-CH₃C₆H₄; P = P(OEt)₃ (**5**, **7**), PPh(OEt)₂ (**6**, **8**).

Reaction of the dichloro complexes **5**, **6** with NaBH₄ in acetonitrile gives the final PtHClP₂ (**7**, **8**) hydride derivatives. The use of CH₃CN as a solvent, instead of the usual ethanol, is crucial to the success of the synthesis. Otherwise, only traces of hydride were observed. It can also be noted that the treatment of PtCl₂P₂ with NaBH₄ does not give, under any conditions, formation of dihydride PtH₂P₂ species, resulting the monohydride PtHClP₂ the only product obtained.

The PtHCl{PPh(OEt)₂}₂ compound was isolated as a white solid, while the related PtHCl{P(OEt)₃}₂ is an oily product at room temperature. Both species **7** and **8** are stable in air and in solutions of common organic solvents, where they behave as non-electrolytes. The analytical and spectroscopic data (Table 1) support the proposed formulation for both the chloro PtCl₂P₂ precursors and the PtHClP₂ hydride derivatives. The IR spectra of PtCl₂P₂ in the ν(PtCl) region show only one band at 298 cm⁻¹ for **5** and at 295 cm⁻¹ for **6**, suggesting that the two Cl⁻ ligands are in a mutually *trans* position. The ¹H NMR spectra show the signals of the phosphite ligands, while the ³¹P spectra between +20 and -80 °C appear as a sharp singlet, in agreement with a type **II** geometry (Chart 1).²³

The ¹H NMR spectra of the hydride complexes PtHClP₂ (**7**, **8**) show, in the high-field region, a well-resolved triplet at -16.57 (**7**) and at -16.24 (**8**) ppm, attributed to the hydride ligand coupled

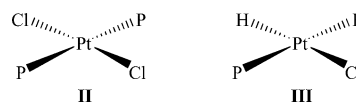
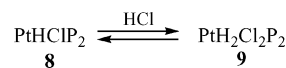


Chart 1

with two equivalent phosphite groups. In the temperature range between +20 and -80 °C, the ³¹P{¹H} NMR spectra appear as a sharp singlet, in agreement with a *trans* geometry of type **III** for the complexes. Values for ¹J_{PtH} of 1248 (**7**) and 1273 Hz (**8**) as well as for J_{PtP} of 3785 (**7**) and 3765 Hz (**8**) were also determined, and fall within the range usually observed for tetracoordinate Pt(II) hydrides.^{14,15}

Reactivity studies involving the new hydrides **1**, **3**, **4** and **7**, **8** with Brønsted acids were undertaken with the aim of testing whether either the formation of dihydrogen complexes²⁴ or the oxidative addition of H⁺ could take place. The results show that, while the cationic [PtHP₄]⁺ and [PtHP₃]⁺ complexes are unreactive in the presence of an excess of HCl or HBF₄·Et₂O, the neutral PtHCl{PPh(OEt)₂}₂ (**8**) hydride does react with an excess of HCl to give the new hydride PtH₂Cl₂P₂ (**9**) which is rather unstable and was not isolated (Scheme 4).



Scheme 4 P = PPh(OEt)₂.

The reaction was followed by variable-temperature ¹H and ³¹P NMR spectra and showed that the addition at -80 °C of HCl to PtHCl{PPh(OEt)₂}₂ (**8**) caused the decrease of the hydride resonance near -16 ppm and the appearance of a new broad signal at -17.1 ppm (J_{PtH} = 1196 Hz) attributed to the presence of a new hydride species. T₁ measurements of this signal gave a T_{1min} value of 240 ms, which indicates the presence of a classical hydride ligand.²⁵ Therefore, the protonation of PtHClP₂ does not take place at the H⁻ giving a η²-H₂ complex of the type [PtCl(η²-H₂)P₂]⁺, but seems to proceed through an oxidative addition of HCl to the central metal to yield the PtH₂Cl₂P₂ (**9**) dihydride derivative. The progress of the protonation reaction

unreactivity is not surprising due to the positive charge present in the starting hydride complex, which makes the reaction between two cationic species, in any case, very slow.

Aryldiazene complexes of Pt(II) were reported about forty years ago,³² from the reaction of the triethylphosphine complex PtHCl(PEt₃)₂ with aryldiazonium cations. Since this pioneering result, however, no other data have been reported on diazene complexes of this metal, whose "diaz" chemistry has been scarcely developed^{32,33} compared to those of other transition metals.³⁰ Its use as a precursor of the PtHCl{PPh(OEt)₂}₂ (8) hydride complex with PPh(OEt)₂ phosphonite ligands allows new aryldiazene complexes 10 to be prepared. This result also highlights the important role of the PPh(OEt)₂ group in the stabilization of "diaz" complexes. As we have previously noted with other central metals,³¹ the introduction of PPh(OEt)₂ or P(OEt)₃ phosphites as ancillary ligands allows a rich and varied "diaz" chemistry to be observed.

The aryldiazene complexes [PtCl(ArN=NH)P₂]BF₄ (10) were isolated as yellow or orange solids, which are moderately stable in a solution of polar organic solvents, where they behave as 1 : 1 electrolytes.¹⁹ The analytical and spectroscopic data (Table 1) support the proposed formulation. The presence of the diazene ligand is confirmed by the ¹H NMR spectra which show the characteristic NH signal as a slightly broad singlet at 14.5 (10a) and at 14.2 ppm (10b) with ²J_{PtH} of 84 Hz.

Further support for this attribution comes from the proton NMR spectra of the labelled [PtCl(C₆H₅N=¹⁵NH)P₂]BF₄ (10a₁) complex, which show the diazene signal as a doublet at 14.54 ppm with ¹J_{¹⁵NH} of 77 Hz, in agreement with the proposed formulation.³⁴ In the temperature range between +20 and -80 °C the ³¹P NMR spectra of the aryldiazene complexes 10a and 10b appear as a sharp singlet, while a doublet (¹J_{¹⁵N³¹P} = 3.8 Hz) can be observed in the spectrum of the labelled complex 10a₁ due to the coupling of the phosphorus nuclei with the ¹⁵N diazenic nitrogen atom. On the basis of these data, a *trans* geometry of type IV may reasonably be proposed for the aryldiazene derivatives 10 (Chart 2).

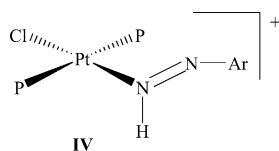
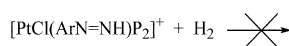


Chart 2

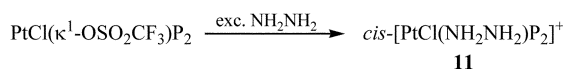
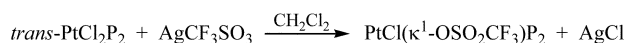
Reaction with H₂ (1 atm) of the aryldiazene derivatives 10 was extensively studied to test whether the formation of a hydrazine complex³² can take place. At room temperature, no reduction was observed (Scheme 6) and the starting complex could be recovered unchanged after 10 h of reaction. Increasing the reaction temperature or time produced only some decomposition and no evidence of the formation of hydrazine was detected.



Scheme 6 P = PPh(OEt)₂.

Hydrazine complexes of Pt(II) of the [PtCl(NH₂NH₂)P₂]BPh₄ type (11), however, were obtained following a different method (Scheme 7) involving the reaction of the PtCl₂P₂ complex with AgCF₃SO₃. The resulting triflate complex PtCl(κ¹-OSO₂CF₃)P₂ (not isolated) reacts with an excess of hydrazine to give the [PtCl(NH₂NH₂)P₂]⁺ cation, which was isolated as its BPh₄ salt and characterised.

The triflate complex PtCl(κ¹-OSO₂CF₃)P₂ was also treated with different hydrazines, such as CH₃NHNH₂ and PhNHNH₂, but in these cases only intractable mixtures of products were obtained. It seems that only with NH₂NH₂ can a pure and isolable complex be prepared.



Scheme 7 P = PPh(OEt)₂.

The platinum hydrazine complex 11 was isolated as a white solid, stable in the air and in solutions of polar organic solvents, where it behaves as a 1 : 1 electrolyte.¹⁹ The analytical and spectroscopic data (Table 1) support the proposed formulation.

The IR spectra show two slightly broad medium-intensity bands at 3217 and 3163 cm⁻¹ attributed to ν(NH) of the hydrazine ligand. The presence of the NH₂NH₂ group, however, is confirmed by the ¹H NMR spectra, which show, besides the signals of the phosphine and the BPh₄ anion, two slightly broadened multiplets at 5.18 and 3.64 ppm, due to the NH₂ group of the hydrazine. Integration of the signals, decoupling experiments, and the COSY spectrum support the proposed attribution. Furthermore, the presence of two NH₂ signals suggests also the presence of a η¹-coordination for the hydrazine ligand.

In the temperature range between +20 and -80 °C the ³¹P{¹H} NMR spectra appear as an AB multiplet which can be easily simulated with the parameters reported in Table 1. On the basis of these data a *cis* geometry like V can be reasonably proposed for the hydrazine complex 11 (Chart 3).

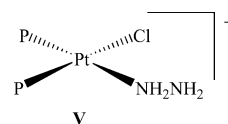


Chart 3

Conclusions

In this report we describe the synthesis of new penta- and tetra-coordinate cationic hydride complexes of Pt(II) of the [PtHP₄]⁺ and [PtHP₃]⁺ types containing the ethoxyphosphines P(OEt)₃ and PPh(OEt)₂ as ancillary ligands. The preparation and the crystal structure determination of the tetrakis(phosphite) [Pt{P(OEt)₃}₄](BF₄)₂ derivative are also reported. Neutral PtHClP₂ hydride complexes [P=PPh(OEt)₂ and P(OEt)₃] can be obtained from the dichloro PtCl₂P₂ precursors and their reaction with aryldiazonium cation allowed the new aryldiazene [PtCl(ArN=NH)P₂]BPh₄ complexes to be prepared. The hydrazine [PtCl(NH₂NH₂){PPh(OEt)₂}₂]BPh₄ derivative was, instead, obtained using the dichloro PtCl₂P₂ as a precursor.

Experimental

General information

All synthetic work was carried out in an appropriate atmosphere (Ar, N₂) using standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at -25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. K₂PtCl₄ was prepared as previously reported.³⁵ Phosphonite PPh(OEt)₂ was prepared by the method of Rabinowitz and Pellon,³⁶ while P(OEt)₃ was an Aldrich product purified by distillation under nitrogen. Diazonium salts were prepared in the usual way.³⁷ The labeled diazonium tetrafluoroborate [C₆H₅N≡¹⁵N]BF₄ was prepared from Na¹⁵NO₂ (99% enriched, CIL) and aniline. Hydrazine, NH₂NH₂, was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.³⁸ Other reagents were purchased from

commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 FT-IR or Perkin-Elmer Spectrum One spectrophotometer. NMR spectra (^1H , ^{31}P) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between -90 and $+30$ $^\circ\text{C}$, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaNMR software package³⁹ was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 $^\circ\text{C}$ were measured with a Radiometer CDM 83.

Synthesis of complexes

The nitrile complex *cis*- $\text{PtCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})_2$ was prepared following the method previously reported.⁴⁰

Pt{PPh(OEt)₂}₄ and Pt{P(OEt)₃}₄. The complexes were prepared by a modification of the method used for the P(OEt)₃ derivative.¹⁸ An excess of NaBH_4 (2 g, 53 mmol) in ethanol (35 mL) was added to a suspension of K_2PtCl_4 (2 mmol, 0.83 g) in ethanol (25 mL) containing an excess of the appropriate phosphine (10 mmol). The reaction mixture was refluxed for 4 h and then the solvent removed under reduced pressure. From the red-brown solid obtained the complex was extracted with five 10-mL portions of a mixture of benzene and petroleum ether (50–60 $^\circ\text{C}$) (ratio 1 : 1). The extracts were evaporated to dryness and the oil obtained treated with ethanol (15 mL). By slow cooling of the resulting solution, white microcrystals of the complex separated out, which were filtered off and dried under vacuum; yield about 45% for Pt{PPh(OEt)₂}₄, 55% for Pt{P(OEt)₃}₄.

Pt{PPh(OEt)₂}₄: $\text{C}_{40}\text{H}_{60}\text{O}_8\text{P}_4\text{Pt}$ (987.89): calc. C 48.63, H 6.12; found C 48.72, H 6.24%. ^1H NMR (CD_2Cl_2), δ : 7.30–7.00 m (20 H, Ph), 3.52 m, 3.27 m (16 H, CH_2), 0.95 t (24 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2), δ : 137.2 s, $J_{\text{PtP}} = 4694$.

Pt{P(OEt)₃}₄: $\text{C}_{24}\text{H}_{60}\text{O}_{12}\text{P}_4\text{Pt}$ (859.72): calc. C 33.53, H 7.03; found C 33.67, H 7.11%. ^1H NMR (C_6D_6), δ : 4.12 m (24 H, CH_2), 1.27 t (36 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6), δ : 126.6 s, $J_{\text{PtP}} = 5387$.

[PtH{P(OEt)₃}₄]BF₄ (1). Tetrafluoroboric acid (0.11 mmol, 16 μL of a 54% solution of HBF_4 in Et_2O) was added to a solution of Pt{P(OEt)₃}₄ (86 mg, 0.10 mmol) in Et_2O (5 mL) cooled to -80 $^\circ\text{C}$. The reaction mixture was brought to room temperature and stirred for about 1 h. A white solid slowly separated out which was filtered off, washed with Et_2O and dried under vacuum; yield $\geq 80\%$.

$\text{C}_{24}\text{H}_{61}\text{BF}_4\text{O}_{12}\text{P}_4\text{Pt}$ (947.53): calc. C 30.42, H 6.49; found C 30.62, H 6.53%. $A_M = 91.7$ Ω^{-1} mol^{-1} cm^2 .

[Pt{P(OEt)₃}₄](BF₄)₂ (2). A solution of the [PtH{P(OEt)₃}₄]BF₄ (1) compound (0.200 g, 0.21 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing a slight excess of NaBF_4 (0.25 mmol, 27 mg). The addition of diethyl ether (10 mL) to the resulting solution caused the separation of a white solid which was filtered off and crystallised from CH_2Cl_2 and diethyl ether; yield $\geq 35\%$.

$\text{C}_{24}\text{H}_{60}\text{B}_2\text{F}_8\text{O}_{12}\text{P}_4\text{Pt}$ (1033.32): calc. C 27.90, H 5.85; found C 28.05, H 5.91%. $A_M = 177$ Ω^{-1} mol^{-1} cm^2 .

[PtH{PPh(OEt)₂}₄]BF₄ (3a) and [PtH{PPh(OEt)₂}₃]BF₄ (4a). A slight excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.11 mmol, 16 μL of a 54% solution in Et_2O) was added to a solution of Pt{PPh(OEt)₂}₄ (0.10 g, 0.10 mmol) in Et_2O (5 mL) cooled to -80 $^\circ\text{C}$. The reaction mixture was brought to room temperature and stirred

for about 30 min. A white solid separated out, which was filtered off, washed with Et_2O and dried under vacuum. The solid resulting was a mixture of the two hydrides **3a** and **4a** (ratio about 2 : 3), which were not separated.

[PtH{PPh(OEt)₂}₃]CF₃SO₃ (4b). A slight excess of $\text{CF}_3\text{SO}_3\text{H}$ (0.11 mmol, 10 μL) was added to a solution of Pt{PPh(OEt)₂}₄ (0.10 g, 0.10 mmol) in Et_2O (5 mL) cooled to -80 $^\circ\text{C}$. The reaction mixture was brought to room temperature and stirred for 30 min. A white, gummy product separated out, which was collected and crystallised from CH_2Cl_2 (1 mL) and diethyl ether (8 mL); yield $\geq 65\%$.

$\text{C}_{31}\text{H}_{46}\text{F}_3\text{O}_9\text{P}_3\text{PtS}$ (939.77): calc. C 39.62, H 4.93, S 3.41; found C 39.55, H 5.06, S 3.28%. $A_M = 80.2$ Ω^{-1} mol^{-1} cm^2 .

[PtH{PPh(OEt)₂}₃]Cl (4c). A slight excess of HCl (1.1 mL of 0.1 M solution in Et_2O , 0.11 mmol) was added to a solution of Pt{PPh(OEt)₂}₄ (0.10 g, 0.10 mmol) in Et_2O (5 mL) cooled to -80 $^\circ\text{C}$. The reaction mixture was brought to room temperature and stirred for 1 h. A white solid separated out, which was filtered off and dried under vacuum; yield $\geq 70\%$. $\text{C}_{30}\text{H}_{46}\text{ClO}_6\text{P}_3\text{Pt}$ (826.15): calc. C 43.62, H 5.61, Cl 4.29; found C 43.55, H 5.60, Cl 4.14%. $A_M = 89.6$ Ω^{-1} mol^{-1} cm^2 .

trans-PtCl₂{P(OEt)₃}₂ (5). An excess of P(OEt)₃ (4 mmol, 0.66 mL) was added to a solution of *cis*- $\text{PtCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})_2$ (0.5 g, 1 mmol) in 40 mL of CH_2Cl_2 and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (5 mL). By cooling of the resulting solution, a gummy product was obtained, which was separated and kept at -25 $^\circ\text{C}$; yield $\geq 70\%$.

$\text{C}_{12}\text{H}_{30}\text{Cl}_2\text{O}_6\text{P}_2\text{Pt}$ (598.31): calc. C 24.09, H 5.05, Cl 11.85; found C 23.78, H 5.16, Cl 11.77%.

trans-PtCl₂{PPh(OEt)₂}₂ (6). An excess of PPh(OEt)₂ (2 mmol, 0.4 mL) was added to a solution of *cis*- $\text{PtCl}_2(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})_2$ (0.5 g, 1 mmol) in 40 mL of CH_2Cl_2 and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (5 mL). A white solid slowly separated out, which was filtered off and crystallised from CH_2Cl_2 and ethanol; yield $\geq 90\%$.

$\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{O}_4\text{P}_2\text{Pt}$ (662.40): calc. C 36.27, H 4.56, Cl 10.70; found C 36.19, H 4.60, Cl 10.49%.

trans-PtHCl{P(OEt)₃}₂ (7). To a solution of *trans*- $\text{PtCl}_2\{\text{P(OEt)}_3\}_2$ (5) (185 mg, 0.31 mmol) in 5 mL of CH_3CN cooled to -196 $^\circ\text{C}$ was added, by cannula, a solution of NaBH_4 (6 mg, 0.16 mmol) in CH_3CN (10 mL). The reaction mixture was brought to room temperature, stirred for 4 h, and then the solvent removed under reduced pressure. The hydride was extracted from the oil obtained with five 5-mL portions of a mixture of benzene and petroleum ether (bp 50–60 $^\circ\text{C}$) (ratio 1 : 1). The extracts were evaporated to dryness to give an oil which was treated with benzene (1 mL) and diethyl ether (5 mL). By cooling of the resulting solution to -25 $^\circ\text{C}$, a pale-yellow solid separated out, which was filtered off. At room temperature, however, it turns into an oil; yield $\geq 65\%$.

trans-PtHCl{PPh(OEt)₂}₂ (8). This complex was prepared exactly like the related complex **7**, but adding NaBH_4 in 1 : 1 ratio to the *trans*- $\text{PtCl}_2\{\text{PPh(OEt)}_2\}_2$ (6) precursor; yield $\geq 70\%$.

$\text{C}_{20}\text{H}_{31}\text{ClO}_4\text{P}_2\text{Pt}$ (627.95): calc. C 38.25, H 4.98, Cl 5.65; found C 38.41, H 4.94, Cl 5.80%.

trans-[PtCl(ArN=NH){PPh(OEt)₂}₂]BF₄ (10) (Ar = C_6H_5 , **a, $4\text{-CH}_3\text{C}_6\text{H}_4$, **b**).** In a 25-mL three-necked round-bottomed flask were placed equimolar amounts of $\text{PtHCl}\{\text{PPh(OEt)}_2\}_2$ (8) (200 mg, 0.32 mmol) and the appropriate aryldiazonium [$\text{ArN}\equiv\text{N}^+\text{BF}_4^-$] salt (0.32 mmol). The flask was cooled to -196 $^\circ\text{C}$ and dichloromethane (10 mL) slowly added. The reaction mixture was brought to 5 $^\circ\text{C}$ and stirred at this temperature for 30 min. The solvent was removed under reduced

pressure to give a brown oil which was triturated with Et₂O (5 mL). A yellow–orange solid slowly separated out which was filtered off and dried under vacuum; yield ≥70%.

10a: C₂₆H₃₆BClF₄N₂O₄P₂Pt (819.88); calc. C 38.09, H 4.43, N 3.42, Cl 4.32; found C 37.86, H 4.47, N 3.55, Cl 4.15%. $A_M = 90.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

10b: C₂₇H₃₈BClF₄N₂O₄P₂Pt (833.90); calc. C 38.89, H 4.59, N 3.36, Cl 4.25; found C 39.04, H 4.67, N 3.20, Cl 4.38%. $A_M = 88.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

trans-[PtCl(C₆H₅N≡¹⁵NH){PPh(OEt)₂]₂BF₄ (10a₁). This complex was prepared in exactly the same way as the related unlabelled compound **10a** using [C₆H₅N≡¹⁵N]⁺BF₄⁻ as a reagent; ≥65%.

cis-[PtCl(NH₂NH₂){PPh(OEt)₂]₂BPh₄ (11). In a 25-mL three-necked round-bottomed flask were placed equimolar amounts of PtCl₂{PPh(OEt)₂}₂ (**6**) (200 mg, 0.30 mmol) and silver triflate AgCF₃SO₃ (77 mg, 0.30 mmol). Dichloromethane (15 mL) was added into the flask and the reaction mixture was stirred in the dark for 24 h. After filtration to remove the AgCl, the solution was cooled to –196 °C and then an excess of NH₂NH₂ (16 μL, 0.50 mmol) added. The reaction mixture was brought to room temperature and stirred for 8 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (3 mL) containing an excess of NaBPh₄ (0.151 g, 0.44 mmol). A white solid slowly separated out which was filtered off and crystallised from CH₂Cl₂ and ethanol; yield ≥70%.

C₄₄H₅₄BClN₂O₄P₂Pt (978.22); calc. C 54.02, H 5.56, N 2.86, Cl 3.62; found C 53.88, H 5.64, N 2.93, Cl 3.50%. $A_M = 53.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

Protonation reactions

The protonation reactions of PtHClP₂ complexes was studied by ¹H and ³¹P NMR measurements at variable temperatures between –80 and +20 °C. A typical experiment involved the addition of 30–40 mg of the appropriate hydride PtHClP₂ in a screw-cap NMR tube placed in a Vacuum Atmosphere dry-box. CD₂Cl₂ (0.5 mL) was added, the solid was dissolved, and the tube sealed by a screw cap. Incremental amounts of HCl (2 M solution in Et₂O) or HBF₄·Et₂O were added by microsyringe to the NMR tube cooled to –80 °C, which was then transferred into the probe pre-cooled to –80 °C.

Crystal structure determination of [Pt{P(OEt)₃]₄(BF₄)₂ (2)

The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo-*K*_α radiation at –100 °C. Absorption correction was carried out using SADABS.⁴¹

The structure of [Pt{P(OEt)₃]₄(BF₄)₂ was solved by direct methods and refined by full-matrix least-squares based on F^2 , using the SHELX-97 package program.⁴² Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined using a constrained model. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.⁴³

Crystal data and structure refinement for **2**: empirical formula, C₂₄H₆₀B₂F₈O₁₂P₄Pt; formula weight, 1033.31; temperature, 173(2) K; wavelength, 0.71073 Å; crystal system, tetragonal; space group, *I4/m*; unit cell dimensions: $a = 10.6494(16)$, $b = 10.6494(16)$, $c = 18.205(4)$ Å; $Z = 2$; absorption coefficient, 3.639 mm⁻¹; reflections collected, 6872; independent reflections, 1287 ($R_{\text{int}} = 0.0500$); reflections observed ($>2\sigma$), 1282; final R indices [$I > 2\sigma(I)$], $R_1 = 0.0342$, $wR_2 = 0.0838$; R indices (all data), $R_1 = 0.0344$, $wR_2 = 0.0839$.

CCDC reference number 269224.

See <http://dx.doi.org/10.1039/b505453b> for crystallographic data in CIF or other electronic format.

Acknowledgements

The financial support of MIUR (Rome), PRIN 2004, is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

References

- (a) A. Dedieu, *Transition Metal Hydrides*, Wiley-VCH, New York, 1992; (b) M. Peruzzini and R. Poli, *Recent Advances in Hydride Chemistry*, Elsevier, Amsterdam, 2001.
- (a) S. Sabo-Etienne and B. Chaudret, *Chem. Rev.*, 1998, **98**, 2077–2091; (b) M. A. Esteruelas and L. A. Oro, *Chem. Rev.*, 1998, **98**, 577–588.
- C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of Transition Elements*, Elsevier, Amsterdam, 1979.
- (a) F. R. Hatley, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982; (b) R. M. Roundhill, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson and J. A. McCleverty, Pergamon, Oxford, 1987.
- W. Gerrard and H. R. Hudson, *Organophosphorus Compounds*, ed. G. M. Kosolapoff and L. Maier, Wiley, New York, 1973.
- (a) C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313–348; (b) M. M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W. P. Giering, *Organometallics*, 1989, **8**, 1–7.
- (a) C. A. Tolman, R. J. McKinney, W. C. Seidal, J. D. Druline and W. R. Stevens, *Adv. Catal.*, 1985, **33**, 1; (b) R. J. McKinney and D. C. Roe, *J. Am. Chem. Soc.*, 1986, **108**, 5167–5173; (c) J. E. Bäckvall and O. S. Andell, *Organometallics*, 1986, **5**, 2350–2355; (d) I. Mamalis, A. F. Noels, E. Puentes, R. Warin, P. Teyssié, A. J. Hubert, J. Grandjean, R. Hubin and D. Y. Waddan, *J. Catal.*, 1986, **102**, 357; (e) M. Hodgson, D. Parker, R. J. Taylor and G. Ferguson, *Organometallics*, 1988, **7**, 1761–1766; (f) G. D. Fallon, N. J. Fitzmaurice, W. R. Jackson and P. Perlmutter, *J. Chem. Soc., Chem. Commun.*, 1985, 4–5.
- (a) R. Taube and J. P. Gehrke, *J. Organomet. Chem.*, 1987, **327**, 419–427; (b) R. Taube and J. P. Gehrke, *J. Organomet. Chem.*, 1987, **328**, 393–401; (c) P. Benn, P. W. Jolly, R. Mynott, B. Raspe, G. Schenker, K. P. Schick and G. Schroth, *Organometallics*, 1985, **4**, 1945–1953; (d) R. Benn, B. Büssemeier, S. Holle, P. W. Jolly, R. Mynott, I. Tkatchenko and G. Wilke, *J. Organomet. Chem.*, 1985, **279**, 63–86.
- (a) R. B. King and S. Ikai, *Inorg. Chem.*, 1979, **18**, 949–954; (b) A. Vassilian and J. C. Bailar, Jr., *J. Catal.*, 1980, **62**, 389–395.
- (a) M. Cattelani, G. P. Chiusoli, G. Salerno and F. Dellatomasina, *J. Organomet. Chem.*, 1978, **146**, C19–C22; (b) H. Takaya, M. Yamakawa and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 582; (c) H. Kurosawa and M. Emoto, *Chem. Lett.*, 1985, 1161; (d) B. Åkermark, K. Zetterberg, S. Hansson, B. Krakenberger and A. Vitagliano, *J. Organomet. Chem.*, 1987, **335**, 133–142.
- (a) S. Garcia-Fontán, A. Marchi, L. Marvelli, R. Rossi, S. Antoniutti and G. Albertin, *J. Chem. Soc., Dalton Trans.*, 1996, 2779–2785; (b) G. Albertin, S. Antoniutti, M. Bettioli, E. Bordignon and F. Busatto, *Organometallics*, 1997, **16**, 4959–4969; (c) G. Albertin, S. Antoniutti, S. Garcia-Fontán, R. Carballo and F. Padoan, *J. Chem. Soc., Dalton Trans.*, 1998, 2071–2081; (d) G. Albertin, S. Antoniutti, A. Bacchi and B. Fregolent, *Eur. J. Inorg. Chem.*, 2004, 1922–1938.
- (a) G. Albertin, S. Antoniutti, E. Bordignon and M. Pegoraro, *J. Chem. Soc., Dalton Trans.*, 2000, 3575–3584; (b) G. Albertin, S. Antoniutti and M. Bortoluzzi, *Inorg. Chem.*, 2004, **43**, 1328–1335; (c) G. Albertin, S. Antoniutti, A. Bacchi, C. D’Este and G. Pelizzi, *Inorg. Chem.*, 2004, **43**, 1336–1349; (d) G. Albertin, S. Antoniutti and S. Pizzol, *J. Organomet. Chem.*, 2004, **689**, 1639–1647.
- (a) G. Albertin, S. Antoniutti, P. Amendola and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1990, 2979–2984; (b) G. Albertin, S. Antoniutti, E. Bordignon and F. Menegazzo, *J. Chem. Soc., Dalton Trans.*, 2000, 1181–1189.
- (a) N. Ahmad, E. Ainscough, T. A. Janas and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1148–1150; (b) A. Albinati, P. S. Pregosin and H. Rügger, *Inorg. Chem.*, 1984, **23**, 3223–3229; (c) M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle and G. Shaw, *J. Chem. Soc., Dalton Trans.*, 1992, 2607–2614; (d) A. Crispini, K. N. Harrison, A. G. Orpen, P. G. Pringle and J. R. Wheatcroft, *J. Chem. Soc., Dalton Trans.*, 1996, 1069–1076, and references therein.
- (a) W. R. Meyer and L. M. Venanzi, *Angew. Chem., Int. Ed.*, 1984, **23**, 529–530; (b) M. Green, D. M. Grove, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 2228–2234.
- Q.-B. Bao, S. J. Geib, A. L. Rheingold and T. B. Brill, *Inorg. Chem.*, 1987, **26**, 3453–3458.

- 17 J. M. Solar, R. D. Rogers and W. R. Mason, *Inorg. Chem.*, 1984, **23**, 373–377.
- 18 (a) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323; (b) M. Meier and F. Basolo, *Inorg. Synth.*, 1972, **13**, 112.
- 19 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81–122.
- 20 (a) A. D. English, P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, 1976, **98**, 422–436; (b) J. W. Ellis, K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *Inorg. Chem.*, 1992, **31**, 3026–3033; (c) A. Handler, P. Peringer and E. P. Müller, *J. Organomet. Chem.*, 1991, **412**, 451–456; (d) V. De Felice, M. L. Ferrara, A. Panunzi and F. Ruffo, *J. Organomet. Chem.*, 1992, **439**, C49–C51.
- 21 (a) P. Brüggeller, *Inorg. Chem.*, 1990, **29**, 1742–1750; (b) W. Lin, S. R. Wilson and G. S. Girolami, *Inorg. Chem.*, 1997, **36**, 2662–2669.
- 22 The NMR data of the complexes **4b** and **4c** are very similar, indicating that the influence of the anion is negligible.
- 23 The related $\text{PtCl}_2\{\text{P}(\text{OPh})_3\}_2$ complex shows *trans* geometry (see ref. 14a).
- 24 (a) G. J. Kubas, *Metal Dihydrogen and σ -Bonded Complexes*, Kluwer, New York, 2001; (b) P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155–284; (c) D. M. Heinekey and W. J. Oldham, Jr., *Chem. Rev.*, 1993, **93**, 913–926; (d) R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789–805.
- 25 (a) D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126–4136; (b) M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031–7036; (c) P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.*, 1991, **113**, 4173–4184.
- 26 (a) D. G. Gusev, J. U. Notheis, J. R. Rambo, B. E. Hauger, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1994, **116**, 7409–7410; (b) M. D. Butts, B. L. Scott and G. J. Kubas, *J. Am. Chem. Soc.*, 1996, **118**, 11831–11843; (c) A. Vigalok, Y. Ben-David and D. Milstein, *Organometallics*, 1996, **15**, 1839–1844.
- 27 Value estimated as an average of the Pt–P distance of 40 complexes. They were retrieved from the Cambridge Crystallographic Data Center data base on the basis of square-planar mononuclear Pt(II) complexes with four P donor ligands (core PtP_4).
- 28 T. Mizuta, A. Okano, T. Sasaki, H. Nakazawa and K. Miyoshi, *Inorg. Chem.*, 1997, **36**, 200–203.
- 29 K. A. Bunten, L. Chen, A. L. Fernández and A. J. Poë, *Coord. Chem. Rev.*, 2002, **233–234**, 41–51.
- 30 (a) For diazo complexes, see: D. Sutton, *Chem. Rev.*, 1993, **93**, 995–1022; (b) H. Kisch and P. Holzmeier, *Adv. Organomet. Chem.*, 1992, **34**, 67–109; (c) H. Zollinger, *Diazo Chemistry II*, VCH, Weinheim, Germany, 1995.
- 31 (a) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, G. Pelizzi and P. Ugo, *Inorg. Chem.*, 1996, **35**, 6245–6253; (b) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, F. Busatto and G. Pelizzi, *Inorg. Chem.*, 1997, **36**, 1296–1305; (c) G. Albertin, S. Antoniutti, E. Bordignon and S. Pattaro, *J. Chem. Soc., Dalton Trans.*, 1997, **36**, 4445–4453; (d) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P. M. Dolcetti and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1997, **36**, 4435–4444; (e) G. Albertin, S. Antoniutti, A. Bacchi, G. B. Ballico, E. Bordignon, G. Pelizzi, M. Ranieri and P. Ugo, *Inorg. Chem.*, 2000, **39**, 3265–3279; (f) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, M. T. Giorgi and G. Pelizzi, *Angew. Chem., Int. Ed.*, 2002, **41**, 2192–2194; (g) G. Albertin, S. Antoniutti, A. Bacchi, M. Boato and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 2002, **41**, 3313–3320; (h) G. Albertin, S. Antoniutti, M. Bortoluzzi, J. Castro-Fojo and S. Garcia-Fontán, *Inorg. Chem.*, 2004, **43**, 4511–4522.
- 32 (a) G. W. Parshall, *J. Am. Chem. Soc.*, 1965, **87**, 2133–2136; G. W. Parshall, *J. Am. Chem. Soc.*, 1967, **89**, 1826; (b) S. D. Ittel and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 4804–4809; (c) S. Krogsrud and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2298–2300.
- 33 (a) S. Cenini, R. Ugo and G. La Monica, *J. Chem. Soc. A*, 1971, 3441–3446; (b) U. Croatto, L. Toniolo, A. Immirzi and G. Bombieri, *J. Organomet. Chem.*, 1975, **102**, C31–C33; (c) R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1985, 2067–2077; (d) V. L. Frost and R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1985, 2059–2065.
- 34 (a) K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 2713–2722; (b) J. A. Carrol, D. Sutton and Z. Xiaoheng, *J. Organomet. Chem.*, 1983, **244**, 73–86.
- 35 G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 240–241.
- 36 R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623–4626.
- 37 A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green and Co, New York, 3rd edn., 1956.
- 38 E. Nachbaur and G. Leiseder, *Monatsh. Chem.*, 1971, **102**, 1718–1723.
- 39 G. Balacco, *J. Chem. Inf. Comput. Sci.*, 1994, **34**, 1235–1241.
- 40 D. Fraccarollo, R. Bertani, M. Mozzon, U. Belluco and R. A. Michelin, *Inorg. Chim. Acta*, 1992, **201**, 15–22.
- 41 G. M. Sheldrick, *SADABS. An empirical absorption correction program for area detector data*, University of Göttingen, Germany, 1996.
- 42 G. M. Sheldrick, *SHELX-97. Program for the solution and refinement of crystal structures*, University of Göttingen, Germany, 1997.
- 43 *International Tables for X-ray Crystallography*, Kluwer, Dordrecht, 1992, Vol. C.