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Platinum Hydride Cluster Complexes

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The cluster cation $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$ (**1**) is easily and reversibly protonated to give $[Pt_3(\mu_3\text{-}H)_2(\mu\text{-dppm})_3]^{2+}$ (**3**) or, in the presence of trifluoroacetate, $[Pt_3H(\mu_3\text{-}H)(\mu\text{-}O_2CCF_3)(\mu\text{-dppm})_3]^+$ (**4**). With a large excess of acid below –60 °C, the trihydride $[Pt_3(\mu_2\text{-}H)_3(\mu\text{-dppm})_3]^{3+}$ (**5**) was formed. Complex **3** reacts with CO to give H_2 and the carbonyl cluster cations $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ and $[Pt_3(\mu_3\text{-}CO)(CO)(\mu\text{-dppm})_3]^{2+}$, with phosphite ligands $P(OR)_3$ (R = Me, Et, Ph) to give $[Pt_3H(\mu_2\text{-}H)\{P(OR)_3\}(\mu\text{-dppm})_3]^{2+}$ (**6**), and with PPh_3 to give $[Pt_2H(PPh_3)(\mu\text{-dppm})_2]^+$. The new clusters are characterized by multinuclear NMR techniques. The reversible addition of protons to **1** defines a stepwise, bimolecular, electrophilic mechanism of substitution of the $Pt_3(\mu_3\text{-}H)$ ligand.

Introduction

Dissociative chemisorption of hydrogen on a platinum surface, which is a fundamental step in heterogeneous catalysis,[1] leads to PtH, $Pt_2(\mu\text{-}H)$, and $Pt_3(\mu_3\text{-}H)$ linkages.[2-5] However, the $Pt_3(\mu_3\text{-}H)$ group is rare in platinum hydride clusters,[6] although $Pt_2(\mu\text{-}H)$ groups are now familiar.[7-13] The chemistry of the coordinatively unsaturated cluster cation $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$ (**1**), dppm = $Ph_2PCH_2PPh_2$,[6] is therefore of considerable interest as a model for $Pt_3(\mu_3\text{-}H)$ groups on a platinum surface. Previous papers have reported the reactions of the 42-electron cluster **1** with acetylene to give the 46-electron vinyltriplatinum cluster $[Pt_3(\mu_3\text{-}HCCH)(CH{=}CH_2)(\mu\text{-dppm})_3]^+$ and with phosphine or phosphite ligands, PR_3, to give the 44-electron clusters $[Pt_3(\mu_3\text{-}H)(PR_3)(\mu\text{-dppm})_3]^+$.[14,15] These reactions with nucleophilic donor ligands are typical of coordinatively unsaturated clusters such as $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**2**).[16] However, unlike **2**, the cluster cation **1** is electron-rich and it also reacts with electrophilic gold complexes LAu^+, L = PMe_3 or PPh_3, to give $[Pt_3(\mu_3\text{-}H)(\mu_3\text{-}AuL)(\mu\text{-dppm})_3]^{2+}$, $[Pt_3(\mu_3\text{-}AuL)(\mu\text{-dppm})_3]^+$, and $[Pt_3(\mu_3\text{-}AuL)_2(\mu\text{-dppm})_3]^{2+}$, all of which are still 42-electron clusters.[17] Since LAu^+ and H^+ are isolobal, a study of the reactions of **1** with protic acids was a natural extension of this work, and the results are reported below. A preliminary account of parts of this work has been published.[18]

Experimental Section

NMR spectra were recorded by using Varian XL200 and XL300 spectrometers. Complexes **1** and **2** were prepared by the literature methods.[6,19]

$[Pt_3(\mu_3\text{-}H)_2(\mu\text{-dppm})_3](PF_6)_2$ (3). To a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3](PF_6)$ (40 mg) in CD_2Cl_2 (0.5 mL) in an NMR tube (5 mm) was added aqueous HPF_6 (4 μL). A series of variable-temperature ^1H, $^{31}P\{^1H\}$, and ^{31}P NMR spectra were recorded. The solvent was then removed under reduced pressure to yield a red solid residue, which was washed rapidly with *n*-pentane and dried under vacuum. Yield: 73%. Mp: 160 °C dec. NMR analysis indicated that this product contained approximately equal amounts of **1** and **3**. NMR data for **3** in CD_2Cl_2 at –40 °C (all *J* values in hertz): $\delta(^1H) = -3.68$ [sept, $^1J(PtH) = 420$, $^2J(PH) = 20$, 2H, PtH], 4.0 [s, 6H, CH_2]; $\delta(^{31}P) = -5.7$ [s, $^1J(PtP) = 3178$, $^2J(PtP) = 149$, $^2J(PH) = 20$, dppm].

$[Pt_3(\mu_3\text{-}H)H(O_2CCF_3)(\mu\text{-dppm})_3](O_2CCF_3)$ (4a). To a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3](CF_3CO_2)$ (40 mg) in CD_2Cl_2 (0.5 mL) in an NMR tube (5 mm) was added CF_3CO_2H (4 μL) by syringe. The $^{31}P\{^1H\}$ NMR spectrum indicated quantitative conversion to **4a**. NMR in CD_2Cl_2 at 20 °C: $\delta(^1H) = -3.53$ [sept, $^1J(PtH) = 415$, $^2J(PH) = 20$, 2H, PtH], 5.23 [s, 6H, CH_2P_2]; $\delta(^{31}P) = -12.3$ [s, $^1J(PtP) = 3100$, $^2J(PtP) = 235$, $^3J(PP) = 120$, dppm]; $\delta(^{195}Pt) = -2612$ [t, $^1J(PtP) = 3100$]. NMR at –90 °C: $\delta(^1H) = -3.49$ [br mult, satellites too broad to measure *J*(PtH), 2H, PtH], 4.71 [s, 2H, CH_2P_2], 5.47 [s, 2H, CH_2P_2], 5.92 [m, 1H, CH_2P_2], 6.25 [m, 1H, CH_2P_2]; $\delta(^{31}P) = -3.8$ [m, $^1J(PtP) = 2600$, $^2J(PtP) = 120$, $^3J(P^bP^{b'}) = 60$ (note: this coupling is obtained from the ^{195}Pt satellite spectra), P^b], –7.5 [m, $^1J(PtP) = 4200$, $^3J(P^aP^c) = 45$, P^a], –24.2 [m, $^1J(PtP) = 3085$, P^c].

$[Pt_3(\mu_3\text{-}H)H(O_2CCF_3)(\mu\text{-dppm})_3](PF_6)$ (4b). This was prepared in a similar way, by the reaction of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3](PF_6)$ (30 mg) with CF_3CO_2H (3 μL). NMR in CD_2Cl_2 at 20 °C: $\delta(^1H) = -3.60$ [sept, $^1J(PtH) = 420$, $^2J(PH) = 20$, 2H, PtH], 5.18 [s, $^2J(PtH) = 50$, 6H, CH_2P_2]; $\delta(^{195}Pt) = -2617$ [t, $^1J(PtP) = 3150$]. NMR at –80°C: $\delta(^1H) = -3.53$ [br mult, $^1J(PtH) = 460$, PtH], 5.48, 4.70 [s, 6H, CH_2P_2]. The ^{31}P NMR spectra at both room temperature and –80 °C were identical with those of **4a**, but with an added resonance due to PF_6^-.

The complexes $[Pt_3(D)(H)(O_2CCF_3)(\mu\text{-dppm})_3](PF_6)$ (**4b***) and $[Pt_3(\mu_3\text{-}D)D(O_2CCF_3)(\mu\text{-dppm})_3](PF_6)$ (**4b****) were prepared similarly from $[Pt_3(\mu_3\text{-}D)(\mu\text{-dppm})_3](PF_6)$ and from CF_3CO_2H and CF_3CO_2D, respectively.

$[Pt_3(\mu\text{-}H)_3(\mu\text{-dppm})_3](CF_3CO_2)_3$ (5). To a solution of $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3](PF_6)$ (40 mg) in CD_2Cl_2 (0.5 mL) at –70 °C in an NMR tube (5 mm) was added an excess of CF_3CO_2H (20 μL). The contents were mixed, and a series of low-temperature (–70 °C) multinuclear NMR

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spectra indicated that **5** was the only product in solution at this temperature. NMR in CD_2Cl_2 at −70 °C: $\delta(^1H) = -6.8$ [5, $^1J(PtH) = 604$, $^2J(PH) = 70$, 3H, PtH], 4.83 [s, 6H, CH_2P_2]; $\delta(^{31}P) = -3.28$ [s, $^1J(PtP) = 3160$, $^2J(PtP) = 151$, $J(PP) = 46$, PtP].

The above solution was allowed to warm to room temperature. A series of ^1H and $^{31}P\{^1H\}$ NMR spectra were identical to those of **3**. The solution was then evaporated to dryness. The residue was washed with diethyl ether (5 mL) and redissolved in CD_2Cl_2 (0.5 mL). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting product were identical to those of complex **1**.

Reaction of CO with Complex 3. Carbon monoxide (excess) was added to a sample of **3** (30 mg) in CD_2Cl_2 (0.5 mL) in an NMR tube (5 mm) fitted with a Teflon tap and cooled in liquid nitrogen, and the tap was closed. The color of the solution rapidly changed from red to orange. The NMR spectra of the resulting products were recorded, and the residual gas inside the NMR tube was then sampled and analyzed by GC-MS.

Similar experiments were conducted with complexes **4a**, **4b**, **4b***, and **4b**** and equimolar quantities of **4b** and **4b****. In all cases, the FAB mass spectra showed the peak due to H_2, $m/e = 2$, as the major peak. The above experiment was repeated using ^{13}CO as reagent. In each case the platinum-containing products were **2** and $[Pt_3(CO)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, the adduct of **2** with CO.

$[Pt_3H(\mu\text{-}H)(\mu\text{-}dppm)_3\{P(OPh)_3\}](PF_6)(CF_3CO_2)$ (6c). To a solution of **4b** (30 mg) in CH_2Cl_2 (5 mL) was added $P(OPh)_3$ (4.3 μL). The contents were stirred for 10 min. During this period the solution became deep red. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether (10 mL) followed by *n*-pentane (5 mL) and dried under vacuum. Yield: 70%. Anal. Calcd for $C_{95}H_{83}F_9O_5P_8Pt_3$: C, 49.4; H, 3.6. Found: C, 49.1; H, 3.4.

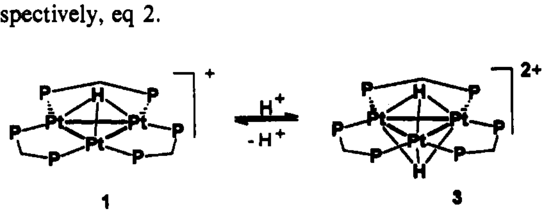
$[Pt_3H(\mu\text{-}H)(\mu\text{-}dppm)_3\{P(OPh)_3\}](PF_6)_2$ (6c′). A solution of complex **6c** (25 mg) in a minimum of acetone (3 mL) was added dropwise to a stirred solution of NH_4PF_6 (100 mg) in methanol (5 mL). After 15 min, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (5 mL), the solution was filtered to remove excess NH_4PF_6, and the product was precipitated as a red solid by using pentane. Yield: 85%. Anal. Calcd for $C_{93}H_{83}F_{12}O_3P_9Pt_3$: C, 47.7; H, 3.6. Found: C, 47.5; H, 3.5.

Complexes **6a** and **6b** were prepared similarly. Anal. Calcd for $[Pt_3H(\mu\text{-}H)(\mu\text{-}dppm)_3\{P(OMe)_3\}](PF_6)(CF_3CO_2)$ (**6a**), $C_{80}H_{77}F_9O_5P_8Pt_3$: C, 45.3; H, 3.7. Found: C, 45.1; H, 3.6. Anal. Calcd for $[Pt_3H(\mu\text{-}H)(\mu\text{-}dppm)_3\{P(OEt)_3\}](PF_6)(CF_3CO_2)$ (**6b**), $C_{83}H_{83}F_9O_5P_8Pt_3$: C, 46.1; H, 3.9. Found: C, 45.9; H, 3.7.

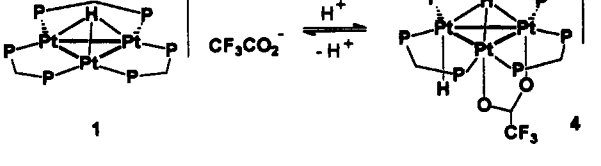
Reaction of Complex 4b with PPh₃. To a solution of **4b** (30 mg) in CD_2Cl_2 (0.5 mL) in an NMR tube, cooled to −78 °C, was added PPh_3 (4 mg). The contents were mixed, and the NMR spectra were recorded at −40 °C. The solution was then warmed to room temperature for 0.5 h, and the solvent was removed under reduced pressure. The red-brown solid residue was washed with ether (10 mL) and dried under vacuum. The NMR spectra of the resulting product were identical with those of $[Pt_2H(PPh_3)(\mu\text{-}dppm)_2]^+$.

Results and Discussion

Synthesis of New Hydridotriplatinum Clusters by Proton Addition. The dihydrido complex $[Pt_3(\mu_3\text{-}H)_2(\mu\text{-}dppm)_3](PF_6)_2$ (**3**) was synthesized by the reaction of $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3](PF_6)$ (**1**(PF_6))[6] with an equimolar quantity of HPF_6, eq 1. Similarly, complexes **4a** and **4b** were formed by reaction of $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3](CF_3CO_2)$ (**1**(CF_3CO_2)) with CF_3CO_2H and HPF_6, respectively, eq 2.



(1)



(2)

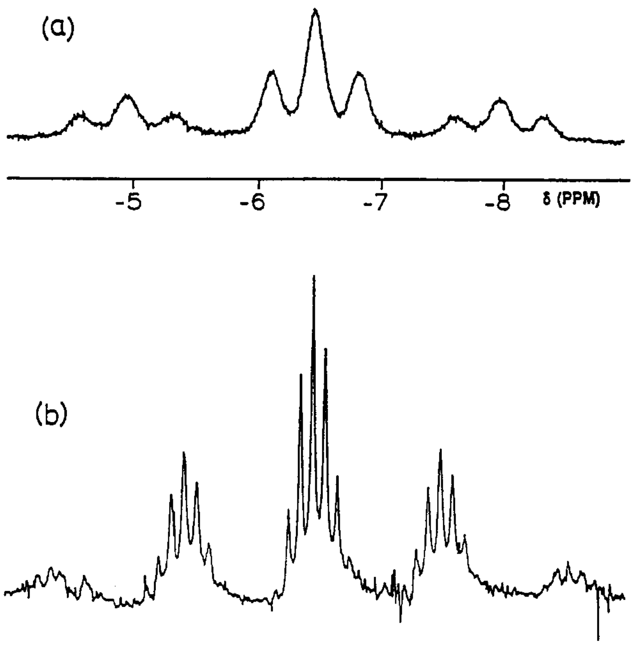
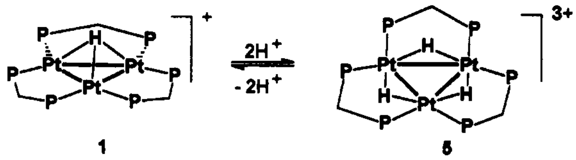


Figure 1. ^1H NMR spectra (200 MHz) in the hydride region of (a) the cluster cation **5**, in which the central triplet is due to coupling of each hydride with two equivalent phosphorus atoms and the relative intensities of the three triplets are 8:18:8, and (b) the cluster cation **3**, in which the central septet is due to coupling to six equivalent phosphorus atoms and the relative intensities of the five septets are 1:4:7:4:1.

The trihydrido complex **5** was prepared by the reaction of **1** with an excess of CF_3CO_2H or HPF_6 at −70 °C, eq 3. Complex



(3)

5 was not thermally stable above −60 °C; it could not be isolated but was characterized in solution by multinuclear NMR spectroscopy.

It is likely that the three μ-dppm ligands serve to maintain the integrity of the clusters in these reactions.[16] Thus, cluster fragmentation occurs on reaction of the triplatinum complex $[Pt_3(\mu\text{-}CO)_3(PBu_2Ph)_3]$ with HCl at −50 °C to yield the mononuclear hydridoplatinum(II) complex $[PtHCl(CO)(PBu_2Ph)]$.[20]

Spectroscopic Characterization and Fluxionality of Complexes 3–5. Complex **3** was readily characterized by elemental analysis and multinuclear NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum of **3** at room temperature or at −80 °C, the resonance due to the dppm phosphorus atoms appeared as a singlet at $\delta = -5.7$, with satellites due to coupling to ^{195}Pt [$^1J(PtP) = 3178$ Hz, $^2J(PtP) = 149$ Hz], indicating that the six dppm phosphorus atoms are equivalent. The presence of two hydride ligands was confirmed by the observation of an extra triplet splitting due to $^2J(PH) = 20$ Hz in the proton-coupled spectrum. The hydride signal in the ^1H NMR spectrum of **3** is shown in Figure 1; it appeared as a septet due to coupling to six equivalent phosphorus atoms, $^2J(PH) = 20$ Hz, with satellites due to coupling to ^{195}Pt [$^1J(PtH) = 420$ Hz] having intensities expected for a $Pt_3(\mu_3\text{-}H)$ group [the inner five lines of the expected 1:12:52:84:52:12:1 septet].[6] The resonance due to the methylene protons, CH_2P_2, appeared as a broad singlet, as expected for the proposed structure

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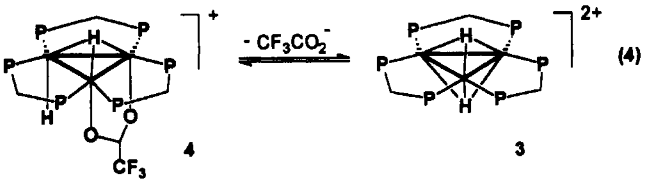
3, which has a plane of symmetry containing the $Pt_3(\mu\text{-}PCP)_3$ unit. We note that the NMR data do not preclude less symmetrical but fluxional structures for 3, such as a structure with a $Pt_3(\mu_3\text{-}H)H$ unit. However, the NMR data were unchanged at -80 °C, and no terminal Pt–H stretch was observed in the IR spectrum, so such structures are considered improbable.

The NMR spectra of **4a** and **4b** at room temperature were essentially identical and similar to those of 3. However, the ^{31}P NMR spectra of both **4a** and **4b** at -90 °C contained three resonances, two doublets and a singlet, indicating a structure with 2-fold symmetry only. In the ^1H NMR spectrum of 4 at -90 °C, the hydride resonance was observed at $\delta = -3.5$, with intensity due to two hydrogen atoms, as a very broad multiplet. The signal due to the CH_2P_2 protons, which appeared as a singlet at room temperature, split into four resonances at -90 °C, with relative intensities 2:2:1:1, as expected for the proposed structure. The NMR data are consistent with a fluxional process for 4, as shown in eq 4, involving rapid and reversible dissociation of a weakly bonded trifluoroacetate ligand to form 3; addition of trifluoroacetate to 3 to regenerate 4 can occur by coordination to any two of the three platinum atoms. Clearly, clusters **4a** and **4b** contain identical cations, each having lower symmetry than 3, but a fluxional process leads to effective 3-fold symmetry at room temperature. These data strongly suggest that coordination of a single trifluoroacetate occurs in 4. Similar coordination of trifluoroacetate has been observed in the analogous carbonyl clusters $[M_3(\mu_3\text{-}CO)(\mu\text{-}CF_3CO_2)(\mu\text{-dppm})_3]^+$ (M = Pd, Pt) and confirmed by X-ray structure determination when M = Pd.[16,21,22]



4 3 (4)

Complex 5 was characterized in solution by low-temperature NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum at -70 °C, Figure 2, contained a singlet at $\delta = -3.28$, with satellites due to coupling to ^{195}Pt [$^1J(PtP) = 3160$ Hz, $^2J(PtP) = 151$ Hz]. The corresponding proton-coupled ^{31}P NMR spectrum contained an extra doublet splitting due to $^2J(PH) = 70$ Hz, as shown in Figure 2. In the ^1H NMR spectrum of 5 at -70 °C, a single hydride resonance was observed at $\delta = -6.8$, as a 1:2:1 triplet with $^2J(PH) = 70$ Hz (Figure 1), with satellites due to coupling to ^{195}Pt [$^1J(PtH) = 604$ Hz] having the intensities expected for a $Pt_2(\mu\text{-}H)$ group (only the inner three lines of the theoretical 1:8:18:8:1 quintet were observed, but the intensities are characteristic[23]). The resonance due to the CH_2P_2 protons appeared as a single resonance, indicating a plane of symmetry containing the $Pt_3(\mu\text{-}PCP)_3$ framework. Integration of the PtH and CH_2P_2 resonances confirmed the presence of three equivalent hydride ligands in complex 5. All these observations support the proposed structure of 5, with three hydride ligands bridging the edges of the Pt_3 triangle. The spectra indicate that the hydrides and μ-dppm ligands are coplanar. However, such an arrangement will lead to some steric interaction between the hydride and dppm ligands, and it is probable that they are offset above or below the Pt_3 plane but fluxional. The structure of complex 5 is analogous to that of $[Pt_3H_3(\mu\text{-}H)_3(PBu_3)_3]$, which has terminal hydrides in place of three of the phosphorus donors in 5.[8]

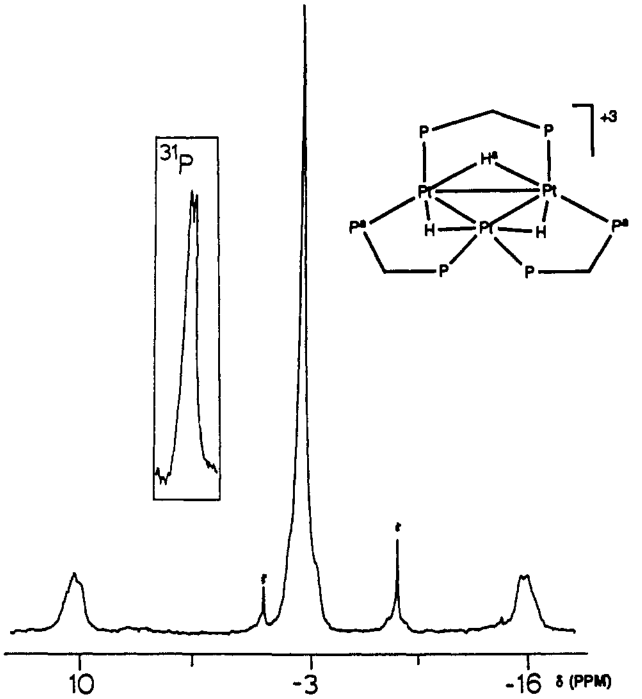
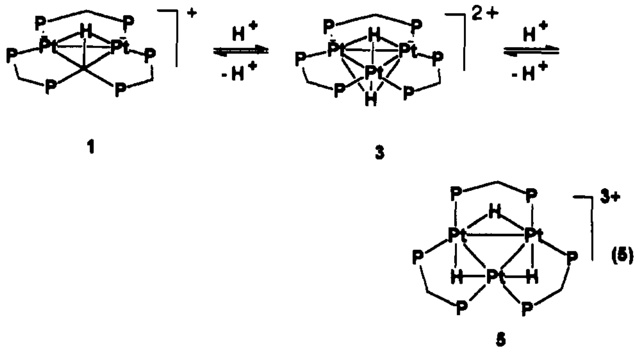


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (121 MHz) of complex 5 at -70 °C. The inset shows the extra doublet splitting of the central peak in the ^1H-coupled ^{31}P NMR spectrum due to $^2J(P^aH^a) = 70$ Hz. The peaks labeled * are due to impurities.

Reactions of Clusters 3–5. The trihydride complex, 5, is stable in solution only at temperatures below -60 °C. When it is warmed to room temperature, the NMR spectra show a quantitative conversion of 5 to 3. Upon evaporation of the solution of 3 to dryness and washing with diethyl ether, 3 is deprotonated to yield the monohydride complex 1. This sequence of reversible protonation and deprotonation reactions is shown in (5).



1 3 5 (5)

When the dihydride complex, 3, was treated with CO, quantitative elimination of hydrogen was observed and the carbonyl clusters $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**2**) and its carbonyl adduct $[Pt_3(CO)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ were formed.[24] Attempts were made to study whether the process of elimination of hydrogen from 3 was an intramolecular or intermolecular process, by use of deuterium-labeled derivatives of 3. However, these were unsuccessful, probably due to scrambling of the ^2H label between PtH and CH_2P_2 sites (indicated by loss of intensity of CH_2 signal in the ^1H NMR spectrum). The CO-induced elimination of hydrogen from 3 is reminiscent of the reaction of ligands L = CO and PR_3 with $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ to give hydrogen and $[Pt_2H(L)(\mu\text{-dppm})_2]^+$.[25]

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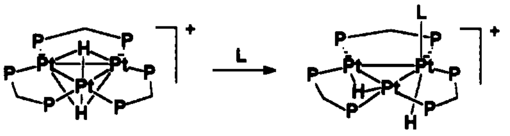
Table I. NMR Data for Cluster Cations **6** in DC_2Cl_2[a]

complex	**6a**[b]	**6b**[c]	**6c**
$\delta(H^1)$	–4.52	–4.83	–3.74
$^1J(Pt^1H^1)$	730	720	732
$^2J(Pt^2H^1)$	90	90	101
$^2J(P^dH^1)$	268	267	292
$^2J(P^aH^1)$	10.5	10.0	14.0
$\delta(H^2)$	–2.91	–2.92	–2.65
$^1J(Pt^2H^2)$	662	650	660
$^2J(P^bH^2)$	80	76	80
$\delta(CH^aH^b)$	4.42, 4.56	4.65, 4.76	4.30, 4.77
$^2J(H^aH^b)$	16	14	14
$\delta(H^cH^d)$	3.39, 3.78	3.02, 4.41	6.09, 6.22
$^2J(H^cH^d)$	9	9	9
$\delta(P^a)$	–27.1	–25.3	–24.6
$^1J(Pt^1P^a)$	1715	1670	1750
$^2J(Pt^1P^a)$	490	610	475
$^3J(P^aP^c)$	230	223	213
$\delta(P^b)$	–7.4	–6.8	–6.5
$^1J(Pt^2P^b)$	3745	3750	3750
$\delta(P^c)$	–15.1	–14.8	–12.9
$^1J(Pt^2P^c)$	2485	2490	2550
$\delta(P^d)$	102.2	96.4	81.6
$^1J(Pt^1P^d)$	3550	3550	3875

[a] For notation, see Figure 3. [b] $\delta(MeO) = 3.68$ [d, $^3J(PH) = 11.5$ Hz]. [c] $\delta(OCH_2) = 3.99$ [quint, $^3J(PH) = {}^3J(HH) = 7$ Hz]; $\delta(Me) = 1.25$ [t, $^3J(HH) = 7$ Hz].

Reaction of **4b** with the phosphite ligands $P(OMe)_3$, $P(OEt)_3$, and $P(OPh)_3$, eq 6, resulted in the formation of $[Pt_3H(\mu\text{-}H)(\mu\text{-}dppm)_3\{P(OR)_3\}]^+$ (**6a–c**), which were thermally stable and could be isolated in analytically pure form. However, reaction of the triplatinum complex, **4b**, with PPh_3 at room temperature resulted in cluster fragmentation with the formation of the diplatinum complex, $[Pt_2H(PPh_3)(\mu\text{-dppm})_2]^+$, in essentially quantitative yield.[25] An intermediate complex, $[Pt_3H(\mu\text{-}H)(\mu\text{-dppm})_3(PPh_3)]^+$ (**6d**), was observed by NMR when the reaction of **4b** with PPh_3 was carried out at –20 °C. When the solution is allowed to warm to room temperature, **6d** is converted to the diplatinum(I) complex, $[Pt_2H(PPh_3)(\mu\text{-dppm})_2]^+$. Complexes **6a–c** did not undergo this type of fragmentation reaction; they could be stored in solution at room temperature for several weeks without significant decomposition.



(6)

3

6a, L = $P(OMe)_3$
6b, L = $P(OEt)_3$
6c, L = $P(OPh)_3$

Spectroscopic Characterization of 6a–d. Complexes **6a–d** were characterized unambiguously in solution by multinuclear NMR spectroscopy. The NMR data are given in Table I. Both the ^1H and ^{31}P NMR spectra are consistent with the proposed structure **6**, which has a plane of symmetry passing through the atoms H^1, P^d, Pt^1, and H^2. The ^{31}P NMR spectrum of **6b**, Figure 3, will be discussed as a typical example. The spectrum contains four ^{31}P resonances in a 1:2:2:2 intensity ratio, that with intensity 1 being due to P^d. The resonance due to P^b appears as a singlet with $^1J(PtP) = 3750$ Hz. It should be noted that long-range couplings $^3J(P^bP^{b'})$ and $^2J(Pt^2P^b)$, which are usually observed in triplatinum clusters, are absent, suggesting that there is no Pt–Pt bond or only weak Pt–Pt bonding between the two platinum atoms, Pt^2. The phosphorus atoms, P^a and P^c, couple to each other and appear as an AB multiplet with $^3J(P^aP^c) = 223$ Hz. The resonance due to the $P(OEt)_3$ ligand, P^d, appears as a 1:4:1 triplet with $^1J(PtP^d) = 3550$ Hz. In the ^1H-coupled ^{31}P NMR spectrum, an extra doublet splitting due to $^2J(P^dH) = 267$ Hz is observed (Figure 3), indicating the presence of a single hydride ligand trans to P^d. The magnitude of $^1J(PtP^d)$ of 3550 Hz is much lower than the corresponding values for $[Pt_3(\mu_3\text{-CO})\{P(OEt)_3\}(\mu\text{-dppm})_3]^{2+}$ and $[Pt_3(\mu_3\text{-H})\{P(OEt)_3\}(\mu\text{-dppm})_3]^+$ of 4990 and 4960 Hz respectively, due to the high trans influence of the terminal hydride ligand in **6**.[26] The ^1H-coupled ^{31}P NMR spectrum also shows an extra doublet splitting in the resonance due to P^b, due to coupling to the bridging hydride, $^2J(P^bH) = 76$ Hz.

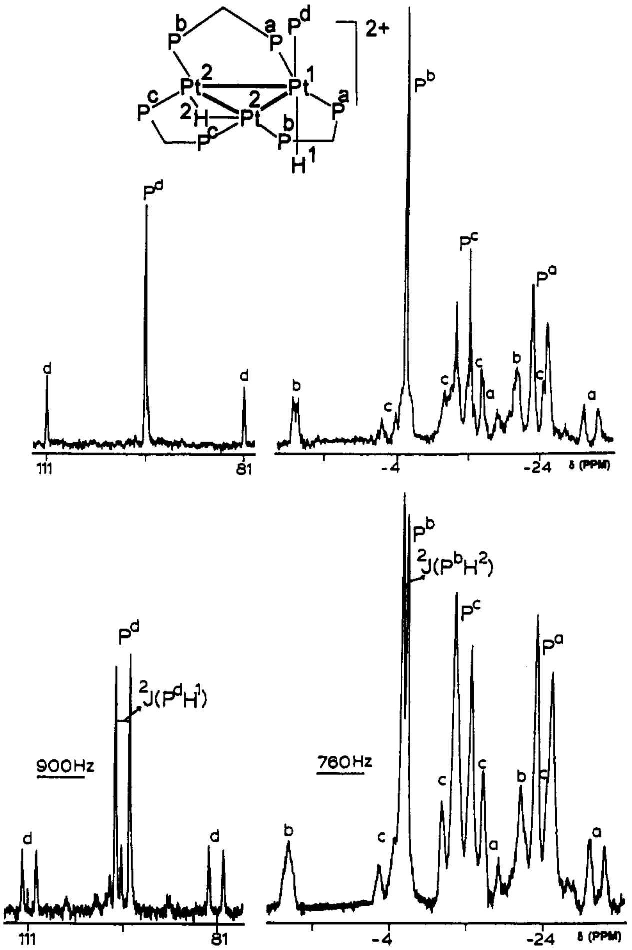


Figure 3. Above, the $^{31}P\{^1H\}$ NMR spectrum and, below, the ^1H-coupled ^{31}P NMR spectrum of complex **6b**. Assignments are given including, in the lower spectrum, the couplings $^2J(P^dH^1)$ and $^2J(P^bH^2)$ which are absent in the proton-decoupled spectrum.

The ^1H NMR spectrum of **6b** at room temperature contains four resonances in the CH_2P_2 region with relative intensities 2:2:1:1 as expected for the proposed structure **6** (Table I). The resonance due to the hydride, H^1, appears at $\delta = -4.8$ as a doublet of triplets, with $^2J(P^dH^1) = 267$ Hz and $^2J(P^aH^1) = 10$ Hz and with quarter intensity satellites due to coupling to ^{195}Pt [$^1J(PtH) = 720$ Hz]. The hydride resonance due to H^2 is observed at $\delta = -2.9$ as a triplet due to coupling to P^b and $P^{b'}$, $^2J(P^bH^2) = 76$ Hz, and with 1:8:18:8:1 satellites due to coupling to ^{195}Pt [$^1J(PtH) = 650$ Hz], indicating that the hydride H^2 is present as a $Pt_2(\mu\text{-}H)$ group. Clearly, the combined NMR data support the proposed structure of the 44-electron complexes, **6**.

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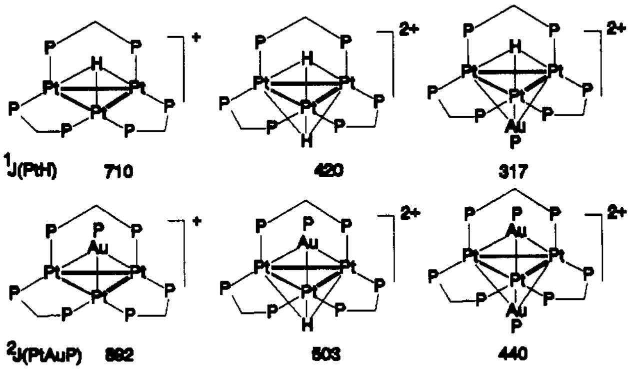
Discussion

The cluster complex $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$ (**1**) is coordinatively unsaturated and, like $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$,[15,16] can add nucleophiles, but it is also electron rich and, unlike $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, can add electrophiles.[17,18] Thus, it can be protonated rapidly and reversibly to give $[Pt_3(\mu_3\text{-}H)_2(\mu\text{-dppm})_3]^{2+}$ (**3**). The reversible addition of a proton to **1** to form **3**, in which the two hydrides are equivalent, clearly shows how electrophilic ligand substitution at the cluster can occur by a bimolecular stepwise mechanism, S_E2 in the organic nomenclature. Of course, protonation does not change the electron count and both **1** and **3** are coordinatively unsaturated 42-electron clusters. In practice, the ligand exchange of **1** with D^+ also leads to H,D exchange in the CH_2P_2 groups.

It is noteworthy that the magnitude of $^1J(PtH)$ for **3** is much lower than for **1**. If these clusters are considered to be formed by consecutive additions of a proton to the a_1 HOMO of the unknown cluster $[Pt_3(\mu\text{-dppm})_3]$,[27] the degree of Pt 6s character in each PtH bond of **3** should be about half the value in **1**, and this is reflected in the lower coupling constant (see Chart I, which shows the generality of this effect for the isolobal H^+ and Ph_3PAu^+ additions).

The coordinative unsaturation of **3** allows it to react easily with donor ligands. The adducts with trifluoroacetate, **4**, and phosphite ligands, **6**, are 46-electron and 44-electron complexes, respectively. In contrast, the reaction of **3** with CO leads to reductive elimination of hydrogen and formation of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$. It is likely that the π-acceptor ability of CO destabilizes the intermediate $[Pt_3H_2(CO)(\mu\text{-dppm})_3]^{2+}$ to loss of hydrogen, since the phosphite adducts **6** are thermally stable. A third reaction type was found with triphenylphosphine, which caused cluster fragmentation; presumably in this case, it is the greater steric bulk of PPh_3 which is responsible for difference in reactivity compared to $P(OPh)_3$.

Chart I. Coupling Constants for Related Clusters



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