Yellow crystals with a melting point of 185–190 °C were obtained. Anal. Calcd: C, 22.02; H, 2.14; S, 4.89. Found: C, 21.58; H, 2.42; S, 4.78. Proton NMR of deuteriobenzene solutions on a 60-MHz Varian 360L instrument showed the anion protons at δ 6.16 and 2.06 and the dimethyl sulfoxide at δ 2.16 with relative areas of 1:3:3, respectively.

The Me_2SO peak was identified by synthesizing the complex with Me_2SO-d_6 (which led to the disappearance of the 2.16-ppm band) and by noting that this peak would average with excess Me_2SO when it was added.

This material is a mixture of 62% cis and 38% trans compounds **1** and **2**, which is readily deduced from the ^{19}F NMR spectra of the crystals dissolved in $DCCl_3$ at low temperature. The proton spectrum is not as well resolved but is consistent with the fluorine spectrum.

At −40 °C the trans compound is static and exhibits an F spectrum of two equal size singlets at δ −75 and −75.4 (the shift being measured from internal $FCCl_3$). The cis compound is seen as a singlet near δ −75.2, shifted (shielded) slightly from the average of the trans components. On warming gradually the trans singlets are found to broaden and move toward each other without a detectable spreading of the cis singlet. At room temperature the trans compound is coalesced into a singlet seen as a pronounced shoulder on the side of the singlet corresponding to the cis compound, on the Varian 360 L spectrometer. (The shoulder is readily apparent on a 90-MHz JEOL FX-900 instrument.) The rearrangement process is roughly estimated as having an activation energy of about 5 kcal/mol from the change in peak shape with temperature (with use of the graphs of Pople, Schneider, and Bernstein).[6] This value is consistent with the more rigorous kinetics previously established for the isomerization of the hexafluoroacetylacetonate complexes.

The broadening and coalescence of the trans peak independent of the cis is the anticipated results of intramolecular base migration. If on the other hand the anions were rotating, the cis and trans absorptions would necessarily merge to a single line since every rotation would interconvert the isomers. These observations therefore indicate that base migration is the preferred process in this temperature regime for the trifluoroacetylacetonates and supports the thesis that this is also the low-energy process for the hexafluoroacetylacetonate complexes.

$UO_2[CF_3COCHCOCH_3]_2{\cdot}(CH_3)_2SO$

$UO_2(NO_3)_2{\cdot}6H_2O$ (2 mmol) was dissolved in 10 mL of H_2O. This solution was contacted with a solution of 1 mmol of Me_2SO in 5 mL of benzene in a separatory funnel. $CF_3COCH_2COCH_3$ (2 mmol) was added, and the mixture was shaken vigorously. Upon settling a yellow benzene layer separates containing the adduct and excess Me_2SO. Approximately 0.2 mmol of the Me_2SO adduct was obtained by removing the solvent and excess Me_2SO in flowing N_2.

Registry No. *cis*-$UO_2[CF_3COCHCOCH_3]_2{\cdot}(CH_3)_2SO$, isomer 1, 78280-03-2; *cis*-$UO_2[CF_3COCHCOCH_3]_2{\cdot}(CH_3)_2SO$, isomer 2, 78340-41-7; *trans*-$UO_2[CF_3COCHCOCH_3]_2{\cdot}(CH_3)_5SO$, 78340-42-8; $UO_2(NO_3)_2(H_2O)_2$, 59752-71-5; MeOH, 67-56-1; THF, 109-99-9; Me_2SO, 67-68-5; TMP, 512-56-1; pyNO, 694-59-7; Et_3PO, 597-50-2; HMPA, 680-31-9.

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Binuclear Reductive Elimination Reactions in Diplatinum Complexes: Synthesis of Hydridoplatinum(I) Complexes

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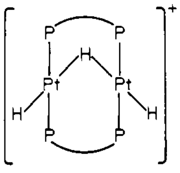
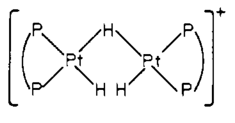
The complex $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) reacts with tertiary phosphine ligands to give H_2 and the hydridoplatinum(I) complexes $[Pt_2HL(\mu\text{-dppm})_2][PF_6]$ (**4**, L = η^1-dppm; **5**, L = PMe_2Ph; **6**, L = $PMePh_2$; **7**, L = PPh_3). Complex **4** is also obtained by the reduction of $[Pt(dppm)_2][PF_6]_2$ with sodium borohydride. Study of the ^1H and ^{31}P NMR spectra of **4**–**7** is in accord with the presence of Pt–Pt bonds and, in the case of **4**, shows that its structure in solution is similar to that previously determined in the solid state by an X-ray investigation. Methanethiol reacts reversibly with **4** to give $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. Attempts to prepare diplatinum(0) complexes by deprotonation of **4** or **7** were unsuccessful.

The many recently reported binuclear platinum hydrides now constitute a rapidly expanding and structurally diverse class of compounds, but most are platinum(II) compounds containing bridging hydrido groups. The most common type contains a $Pt_2H_3^+$ unit bound to four donor atoms which may belong to either monodentate or bidentate ligands. Where the ligands are bidentate, they may be bridging as in $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ (**1**)[2] (dppm = $Ph_2PCH_2PPh_2$) or chelating as in $[Pt_2H_2(\mu\text{-}H)(dppe)_2]^+$ (**2**)[3] (dppe = $Ph_2PCH_2CH_2PPh_2$) or $[Pt_2H_2(\mu\text{-}H)\{(Me_3C)_2P(CH_2)_3P(CMe_3)_2\}_2]^+$ (**3**).[4] In **1**, terminal and bridging hydrido groups are trans to one another, whereas in **2** or **3** they are cis. When one hydride of **1** is replaced by chloride, the latter occupies the bridging position, but when two hydrides are thus replaced, the remaining hy-



1, PP = dppm



2, PP = dppe
3, PP = $(Me_3C)_2P(CH_2)_3P(CMe_3)_2$

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(1) (a) University of Liverpool. (b) University of Western Ontario. (c) University of Oxford.

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dride is bridging. With monophosphine ligands L, a number of trihydrides[5] $[Pt_2H(\mu\text{-}H)_2L_4]^+$ and monoorganodihydrides[6] $[Pt_2R(\mu\text{-}H)_2L_4]^+$ are known which contain two unsymmetrical hydride bridges, and one of the platinum atoms is five-coordinate. An isomeric form, $[Pt_2H(\mu\text{-}H)RL_4]^+$, of the monoorganodihydrides exists which contains only one bridging hydride ligand.[6,7] The complexes $[Pt(\mu\text{-}H)(SiR_3)\{P(C_6H_{11})_3\}]_2$[8] and $[Pt(\mu\text{-}H)(GeR_3)\{P(C_6H_{11})_3\}]_2$, catalysts for the hydrosilation and hydrogermylation of olefins,[9] and $[Pt(\mu\text{-}H)\{(Me_3C)_2PC(Me)_2CH_2\}]_2$[10] have dimeric structures with two bridging hydrido groups. The unique hydridocarbonyl[11] $[Pt_2(\mu\text{-}H)(\mu\text{-}CO)(dppe)_2]^+$ is formally a platinum(I) complex and contains both bridging hydrido and bridging carbonyl groups.

We now report a new class of readily prepared and stable binuclear platinum(I) hydrides, $[Pt_2H(L)(\mu\text{-}dppm)_2]^+$ (L = dppm, Me_2PhP, $MePh_2P$, Ph_3P), containing a direct platinum–platinum bond and a terminal hydride ligand. Preliminary accounts of work on these hydrides[12] and on the related hydridocarbonyl[13] $[Pt_2H(CO)(\mu\text{-}dppm)_2]^+$ have been published. The latter and some related carbonyl chemistry will be described more fully elsewhere.

Experimental Section

Most experiments were carried out under an atmosphere of dry dinitrogen although it was probably unnecessary to take this precaution. Solvents were generally used without further purification, except for dichloromethane which was deacidified with use of alumina. The complexes $[PtX_2(cod)]$ (X = Cl, Br, and I),[14] $[PtCl_2(dppm)]$,[15] and $[Pt_2H_2(\mu\text{-}SMe)(\mu\text{-}dppm)_2][PF_6]$[16] were prepared as previously described. IR spectra were run on a PE 577 spectrometer. Mass spectroscopic determination of hydrogen was carried out on a VG Micromass 12 spectrometer using a septum inlet system. NMR spectra were recorded with use of Varian XL-100 and Bruker WH-90 spectrometers, and the convention of negative upfield and positive downfield shifts, with respect to the reference, has been adopted.

Preparation of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$. Several attempts by us to prepare the crude trihydride $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$ by the published method[2] failed although previously we had experienced no difficulty with this preparation. A modified procedure, described below, was devised and involves the use of anhydrous methanol as the medium for the $[PtCl_2(dppm)]$ suspension and ethanol as the solvent for the sodium tetrahydroborate. The methanol was dried with magnesium ethoxide (prepared in situ) and was distilled.

Sodium tetrahydroborate (2.5 g, 66.1 mmol) in ethanol (80 mL) was added over a period of 40 min to a suspension of $[PtCl_2(dppm)]$ (5.69 g, 8.75 mmol) in anhydrous methanol (120 mL) at 35 °C. During the addition and for a further period of 1 h, the reaction mixture was stirred. The resulting suspension was centrifuged, and the finely divided solid was washed with methanol to afford the crude $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$ as an orange-brown solid (4.75 g). This material was recrystallized from boiling methanol in the presence of NH_4PF_6 as previously described[2] to give pure white $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (2.88 g, 50%). Similar experiments gave yields of 47% and 49%.

Preparation of $[Pt_2H(dppm)(\mu\text{-}dppm)_2][PF_6]$. (a) From $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, and PF_6). In a typical experiment, a solution of sodium borohydride (1.0 g) in methanol (20 mL) was slowly added to a suspension of $[Pt(dppm)_2]Cl_2$ (2.16 g, 2.09 mmol) in methanol (50 mL) until a clear red solution had formed. Then ammonium hexafluorophosphate in methanol (0.50 g in 5 mL) was slowly added to give a crop of bright yellow crystals which were separately by filtration, washed with methanol, and dried under vacuum to afford the product (1.36 g, 0.81 mmol, 77%). Anal. Calcd for $[Pt_2H(dppm)(\mu\text{-}dppm)_2][PF_6]$: C, 53.32; H, 4.00; F, 6.75. Found: C, 52.77; H, 4.01; F, 6.45.

The product was washed with benzene to remove free dppm and then recrystallized from dichloromethane/methanol.

Similar preparations, giving equally good yields, have been carried out starting from $[Pt(dppm)_2]X_2$ (X = Br and I). In the case of $[Pt(dppm)_2][PF_6]_2$ it is unnecessary to add a further amount of $[PF_6]^-$ ion. In a typical preparation, sodium borohydride in methanol (1.0 g in 20 mL) was slowly added to $[Pt(dppm)_2][PF_6]_2$ suspended in methanol (3.60 g, 2.87 mmol in 80 mL) and then stirred for a further 1 h. The yellow solid was filtered off, washed with benzene, and recrystallized from dichloromethane/methanol to yield the desired product (2.20 g, 1.30 mmol, 91%). Yields from $[Pt(dppm)_2][PF_6]_2$ were superior to those from the other $[Pt(dppm)_2]^{2+}$ salts, and the hexafluorophosphate is thus the preferred starting material.

(b) From $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]X$ (X = Cl and PF_6). In one reaction, $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (0.300 g, 0.230 mmol) and dichloromethane (3 mL) were placed in a dinitrogen-filled flask (25 mL) fitted with a serum cap. The solution was stirred gently for 5 min after which the excess pressure caused by vaporization of dichloromethane was released through a fine syringe needle. A solution of dppm (0.0883 g, 0.230 mmol) in dichloromethane (1 mL) was then added with use of a syringe. The solution immediately became red-brown. After a few minutes, the gas was analyzed by mass spectrometry as described below, and dihydrogen (0.228 mmol, 99%) was found to be present. Isooctane was added slowly to the solution until crystallization commenced, and the mixture was then slowly evaporated to dryness under a stream of dinitrogen. This yielded yellow crystalline $[Pt_2H(\mu\text{-}dppm)_2(dppm)][PF_6]$ (0.398 g, 102%) identified by its IR spectrum which showed no trace of impurity.

For the determination of dihydrogen, the mass spectrometer slits were set wide at 0.040 in. so that flat-topped peaks were produced and a septum inlet, connected to the mass spectrometer via a leak, was used. Standard mixtures of dihydrogen and dinitrogen (saturated with dichloromethane) were made up as follows. Dichloromethane (4.0 mL) was added with use of a syringe to a dinitrogen-filled flask, matched in volume to that of the reaction flask. After the contents were stirred for 5 min, the excess pressure caused by vaporization of dichloromethane was released. A measured sample of dihydrogen was added with use of a gas syringe, and the flask was again stirred briefly. A 1.00-mL sample of this mixture was then removed and admitted to the inlet system with use of a gas syringe. A test with five such mixtures prepared from 5.00 mL of dihydrogen showed that the measured peak heights at m/e 2 had a standard deviation of 3%. A blank prepared with no dihydrogen confirmed that there was no significant background at m/e 2. A 1.00-mL sample (at 20 °C and 757 mmHg) of the gas in the reaction flask above was later taken and found to give a peak height of 12.25 cm. A standard mixture containing 5.35 mL of dihydrogen (at the above temperature and pressure) tested immediately afterward gave a peak height of 12.00 cm. The quantity of dihydrogen in the reaction flask was calculated to be 0.228 mmol.

In other experiments, the stoichiometry of the reaction was further studied by IR and NMR spectroscopy. For an IR study, eight separate samples of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (0.025 g, 0.019 mmol) in dichloromethane (0.5 mL) were treated with amounts of dppm varying from 0 to 2 molar proportions. Infrared spectra were run in a cell (NaCl windows) of 0.5 mm path length with a matched cell containing dichloromethane as reference. Values of ν(Pt–H) observed were 2110 and 2030 cm^{-1} for starting material and product, respectively. Log

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(I_0/I) values of these peaks indicated a roughly linear increase in product and decrease in starting material concentration until one molar proportion of dppm had been added. At this point, the starting material concentration had decreased to zero and no further change was observed on increasing the amount of dppm.

A similar set of reaction mixtures in 1,1,2,2-tetrachloroethane-d_2 was studied by ^{1}H NMR (60 MHz) spectroscopy (at 35 °C) observing the hydride resonances of both platinum complexes. The results were in agreement with those of the IR study although the relatively weak ^{1}H signals made this a less sensitive test of stoichiometry. Thus after one molar proportion of dppm had been added, the hydride resonances (δ −5.9 and −6.8)[2] of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ had disappeared completely and the intensity of the resonances (δ −8.8) of $[Pt_2H(dppm)(\mu\text{-dppm})_2]^+$ had reached a maximum. No further change was observed on increasing the amount of dppm up to two molar proportions. Between zero and one molar proportion of dppm, peaks due to both hydrides were observed, showing that rapid exchange between then did not occur.

(c) From $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. An approximately twofold excess of dppm (0.048 g, 0.12 mmol) in dichloromethane (2 mL) was added to a dichloromethane solution of $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ (0.082 g, 0.057 mmol in 8 mL). The solution was refluxed gently for 1 h during which time the methanethiol produced was removed by bubbling a slow stream of dinitrogen through the flask. Fresh solvent was added as necessary to maintain an approximately constant volume. Some of the solvent was then evaporated and methanol added to give $[Pt_2H(dppm)(\mu\text{-dppm})_2][PF_6]$ (0.066 g, 69%) as yellow crystals. Its IR spectrum indicated a contamination by a small amount of the μ-SMe complex.

Preparation of $[Pt_2H(L)(\mu\text{-dppm})_2][PF_6]$ (L = Me_2PhP, $MePh_2P$, and Ph_3P). A slight excess of dimethylphenylphosphine (0.11 g, 0.80 mmol) in dichloromethane (4 mL) was added to a solution of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (0.89 g, 0.68 mmol) in dichloromethane (10 mL). Effervescence occurred, and a deep red solution formed immediately. After the solution was stirred for 12 h, methanol (4 mL) was added. The solvent was then removed in a stream of dinitrogen, and the residue was washed with hexane (5 mL) to remove any traces of free phosphine and dried in vacuo. The crude orange product (1.03 g) was recrystallized from dichloromethane/methanol to yield yellow crystals of $[Pt_2H(Me_2PhP)(\mu\text{-dppm})_2][Pf_6]$ (0.74 g, 75%). Anal. Calcd for $[Pt_2H(Me_2PhP)(\mu\text{-dppm})_2][PF_6]$: C, 48.3; H, 3.9; P, 12.9; F, 7.9. Found: C, 48.1; H, 4.0; P, 13.0; F, 7.9.

The methyldiphenylphosphine analogue was prepared similarly in 76% yield after recrystallization from dichloroethane/methanol. Anal. Calcd for $[Pt_2H(MePh_2P)(\mu\text{-dppm})_2][PF_6]$: C, 50.3; H, 3.9. Found: C, 50.1; H, 3.9. The triphenylphosphine analogue was prepared from triphenylphosphine (0.19 g, 0.72 mmol) and $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (0.91 g, 0.70 mmol) in dichloromethane (12 mL). The crude product was washed with benzene (3 mL) and recrystallized from dichloromethane/methanol to afford the pure material (0.66 g, 60%). Anal. Calcd for $[Pt_2H(Ph_3P)(\mu\text{-dppm})_2][PF_6]$: C, 52.1; H, 3.9. Found: C, 52.0; H, 3.7.

Reactions of $[Pt_2H(dppm)(\mu\text{-dppm})_2][PF_6]$. (a) With $[PtCl_2(cod)]$. A mixture of the hydride (0.10 g, 0.059 mmol) and $[PtCl_2(cod)]$ (0.023 g, 0.061 mmol) was refluxed in methanol (10 mL) for 15 min and gave an orange solution. Some of the solvent was evaporated, and the solution then set aside to crystallize. The yellow solid thus obtained was shown to be $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (0.053 g, 0.043 mmol, 73%) by its IR spectrum.

(b) With Methanethiol. A saturated solution of methanethiol in dichloromethane was added dropwise with stirring to a solution of the hydride in the same solvent (0.11 g, 0.065 mmol in 3 mL) until the color became much paler. Approximately four drops were required. The solution was allowed to stand for 40 min, when it was evaporated down by about 50% and methanol was then added to give a yellow precipitate. This was recovered by filtration and shown to be $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ (0.065 g, 69%) by its IR spectrum.

Preparation of Complexes $[Pt(dppm)_2]X_2$ (X = Cl, Br, I, and PF_6). The three halide salts were prepared either by addition of two molar proportions of dppm to $[PtX_2(cod)]$ in dichloromethane or by the addition of one molar proportion of dppm to $[PtX_2(dppm)]$ in the same solvent. In each case the product was readily crystallized by addition of methanol. Yields obtained were between 60% and 80%. The sparingly soluble $[Pt(dppm)_2][PF_6]_2$ was obtained in yields of over 90% by addition of a methanol solution of ammonium hexafluorophosphate to a dichloromethane solution of $[Pt(dppm)_2]Cl_2$. Anal. Calcd for $[Pt(dppm)_2]Cl_2$: C, 58.04; H, 4.29; P, 11.97; Cl, 6.85. Found: C, 57.78; H, 4.20; P, 11.65; Cl, 6.70. Calcd for $[Pt(dppm)_2]Br_2$: C, 53.44; H, 3.95; P, 11.03; Br, 14.22. Found: C, 53.27; H, 3.85; P, 10.90; Br, 14.15. Calcd for $[Pt(dppm)_2]I_2$: C, 49.32; H, 3.64; P, 10.17; I, 20.84. Found: C, 49.47; H, 3.54; P, 10.06; I, 20.60. Calcd for $[Pt(dppm)_2][PF_6]_2$: C, 47.90; H, 3.54; F, 18.18. Found: C, 47.83; H, 3.45; F, 18.06. The colors of the complexes were white (X = Cl and PF_6), cream (X = Br), and pale yellow (X = I).

Results and Discussion

The diplatinum(I) hydride $[Pt_2H(dppm)(\mu\text{-dppm})_2][PF_6]$ (**4**) has been obtained in high yield by eq 1–3, the first two

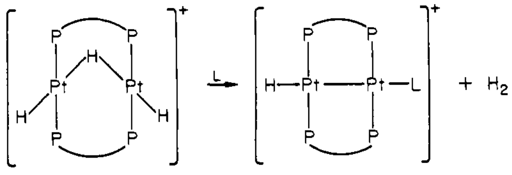
$$[Pt(dppm)_2]^{2+} \xrightarrow[{[PF_6]^-}]{NaBH_4} \underset{\mathbf{4}}{[Pt_2H(dppm)(\mu\text{-dppm})_2][PF_6]} \quad (1)$$

$$[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+ + dppm + [PF_6]^- \rightarrow \mathbf{4} + H_2 \quad (2)$$

$$[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2]^+ + dppm + [PF_6]^- \rightleftarrows \mathbf{4} + MeSH \quad (3)$$

of which are excellent preparative methods. The borohydride reduction (eq 1) of the dication $[Pt(dppm)_2]^{2+}$ is unusual since analogous complexes of other phosphines, including both mono- and diphosphines, yield platinum(0) complexes rather than hydrides.[17] However, we have been unable to find evidence for the formation of platinum(0) complexes in the above reaction. Indeed yields are so high, up to 91% on the basis of $[Pt(dppm)_2][PF_6]_2$, that other products can be present in only minor amounts. Knowledge of method 1 suggested method 2 as a logical development since the trihydride (**1**) itself is prepared by borohydride reduction of $[PtCl_2(dppm)]$. In fact, reaction 2 is rapid and essentially quantitative at room temperature. The observed stoichiometry of this reaction, i.e., the measured uptake of 1 mol of dppm and formation of 1 mol of dihydrogen, conveniently and conclusively establishes the formula of **4**. This is particularly important in regard to its hydride content. Both eq 2 and 3 provide novel examples of reductive elimination across two platinum centers, at least in a formal sense. The elimination of methanethiol is a reversible reaction since, in the presence of an excess of methanethiol in dichloromethane at room temperature, **4** affords $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ in good yield. This reaction too confirms the assigned formula of **4**.

The probable generality of $[Pt_2H(L)(\mu\text{-dppm})_2]^+$ as a structural type became evident on structural characterization of **4** (see below) which showed that one of the dppm ligands was behaving only as a monodentate ligand. It was therefore not surprising to find that the monophosphines Me_2PhP, $MePh_2P$, and Ph_3P also induced reductive elimination of dihydrogen from **1** giving further examples of diplatinum(I) hydrides (eq 4, bridging $Ph_2PCH_2PPh_2$ is represented by PP).



4, L = dppm
5, L = Me_2PhP
6, L = $MePh_2P$
7, L = Ph_3P

These reactions of **2** with phosphines are rapid at room temperature and give high yields of products. A similar but much slower reaction of **2** with carbon monoxide has also been observed by us.[13] However, ammonia, pyridine, and dimethyl sulfide do not react under the same mild conditions, and

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Table I. ^{1}H NMR Spectra of [$Pt_2HL(\mu\text{-dppm})_2$] [$PF_6$][a]

	PtH resonance						CH$_2$ resonance		MeP resonance		
L	δ(PtH)	^{3}J(HL),[b] Hz	^{2}J(PH),[c] Hz	^{3}J(PH),[c] Hz	^{1}J(PtH), Hz	^{2}J(PtH), Hz	δ(CH$_2$)	J(PtH), Hz	δ(MeP)	^{2}J(PH), Hz	^{3}J(PtH), Hz
PMe$_2$Ph	−7.82 m	45	13	7	999	66	5.10 s	38, 68	0.64 d	7.9	20
PMePh$_2$	−8.38 m	47	16	8	1005	*d*	5.10 s	40, 68	1.22 d	11	15
PPh$_3$	−8.97 m	45	9.5	9.5	1005	*d*	4.98 s	40, 72			
dppm[e]	−8.8 br				980		*g*				
dppm[f]	−8.40 d	45	*d*	*d*	980	*d*	*g*				

[a] Solvent CD$_2$Cl$_2$. [b] Coupling J(H–Pt–Pt–P). [c] Couplings to dppm ^{31}P atoms. [d] Not resolved. [e] At 30 °C. [f] At −30 °C. [g] Complex ill-resolved temperature-dependent peaks.

Table II. ^{31}P{^{1}H} NMR Spectra of [$Pt_2HL(\mu\text{-dppm})_2$][$PF_6$][a]

	μ-dppm resonances					L resonances					
									N', Hz		
L	δ(P^{A})	^{1}J(PtP^{A}), Hz	δ(P^{B})	^{1}J(PtP^{B}), Hz	N,[b] Hz	δ(P)	^{1}J(PtP), Hz	^{2}J(PtP), Hz	calcd	found	J(PP),[d] Hz
PMe$_2$Ph	4.89	3470	6.27	2884	82[e]	0.79	2188	576	2764	2760	12
PMePh$_2$	7.01	3484	7.68	2850	70	11.92	2162	592	2754	2750	11
PPh$_3$	6.94	3532	7.95	2894	73	27.10	2181	596	2777	2780	*f*
dppm[g]	7.41	3540	8.77	2880	75	20.49[g]	2340	660	*f*	*f*	*f*
dppm[h]	8.15	3510	8.64	2880	75	20.49[h]	2190	620	*f*	*f*	*f*
dppm[i]	6.91	3500	7.41	2850	75	21.48[i]	2190	620	*f*	*f*	*f*

[a] Solvent CH$_2$Cl$_2$ unless otherwise specified; reference (MeO)$_3$PO in acetone. [b] $N = {}^{2}J(P^{A}P^{B}) + {}^{3}J(P^{A}P^{B'})$. [c] $N' = {}^{1}J(PtP) + {}^{2}J(PtP)$. [d] Coupling in apparent quintet due to coupling with dppm ^{31}P atoms. [e] $^{2}J(P^{A}P^{B}) = 59$ Hz; $^{3}J(P^{A}P^{B'}) = 23$ Hz. [f] Not resolved. [g] δ(free ^{31}P) −30.37, doublet, J(PP) = ca. 60 Hz, at 30 °C. [h] δ(free ^{31}P) −32.10, doublet, J(PP) = 85 Hz, at 0 °C. [i] δ(free ^{31}P) −33.95, doublet, J(PP) = 107 Hz, at −80 °C.

pyridine does not react even under reflux in dichloromethane. Triphenylarsine does react with **1**, but the reaction appears more complex than those of the organophosphines, and we were unable to isolate a pure product.

Preliminary investigations show that reductive elimination of H_2 from **1** in the solid state or in acetonitrile solution is easily induced photochemically on irradiation at 366 nm.

Complexes **4–7** are air-stable yellow crystalline solids, soluble and stable in solvents such as dichloromethane and propanone. The color of thier solutions is deep red-brown. The presence of a terminal Pt–H group is shown by an IR band in the region of 2000 cm^{-1}. When **4** is crystallized from dichloromethane or dichloroethane, ν(Pt–H) is at 2037 cm^{-1}, but when recrystallized from propanone or dichloromethane/propanol (containing a very large proportion of the latter), it is at 2000 cm^{-1}, and other features of the IR spectrum are similarly affected. We assume this is due to different crystal structures or minor differences in molecular conformation. In solution in dichloromethane, ν(Pt–H) is at 2030 cm^{-1}. Similar behavior is shown by **5**, with crystals obtained from dichloromethane having ν(Pt–H) at 2029 cm^{-1} and from propanone having ν(Pt–H) at 1993 cm^{-1}. For **6** and **7**, this absorption (for dichloromethane crystallized material) is at 1990 and 2006 cm^{-1}, respectively. Complex **4** is rapidly decomposed by carbon tetrachloride and more slowly by chloroform. Under mild conditions, no reaction of **4** has been observed with simple olefins and with carbon monoxide. The reaction with [PtCl$_2$(cod)] to afford the previously characterized diplatinum(I) complex [$Pt_2Cl_2(\mu\text{-dppm})_2$] may be understood as an exchange process in which hydride and phosphine ligands in **4** are replaced by chloride.

Complex **4** decomposes rapidly in the presence of acid (HCl or HClO$_4$) giving unidentified products but is remarkably stable in the presence of base. Thus sodium hydroxide in methanol, even at the boiling point for several minutes, has no effect on it nor has treatment with a base such as triethylamine. Similar attempts to deprotonate complex **7** were also unsuccessful. Treatment of **7** with the bases triethylamine, sodium methoxide in methanol, sodium borohydride, and lithium aluminum hydride led only to the recovery of the unchanged complex. No change was also observed when **7** was treated with these bases in the presence of added triphenylphosphine. These experiments are significant since **4** is formally the protonated form of the platinum(0) complex [$Pt_2(dppm)_3$] reported by Vaska.[18] Other similar, but mononuclear, complexes [L_3PtH]$^+$ (L = organophosphine) are readily deprotonated.[19] It would be interesting to know whether **4** is in fact formed by protonation of [$Pt_2(dppm)_3$], but we have been unable to investigate this since details of its preparation have yet to be published.

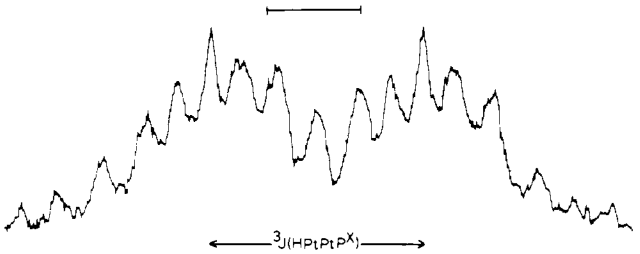

Figure 1. ^{1}H NMR spectrum (100 MHz) of complex **5** in CD$_2$Cl$_2$, showing only the central part of the platinum hydride resonance. The bar represents 20 Hz.

The mechanism of the binuclear reductive elimination reaction eq 4 is not known. Although the overall reaction involves binuclear reductive elimination,[20,21] it is certainly possible that the reductive elimination of H_2 occurs at a single metal center. This aspect is being studied further.

Characterization by NMR Spectroscopy. The structures of complexes **5–7** are assigned by analogy with the structure of **4**, which has been determined crystallographically,[12] and the ^{1}H and ^{31}P NMR spectra are fully in accord with the proposal. Complexes **4–7** are similar to the unsymmetrically substituted

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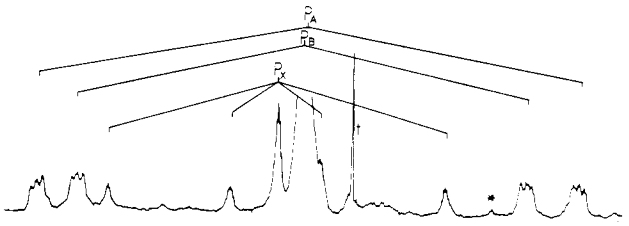


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (40.5 MHz) of complex **6** in CH_2Cl_2. The peak marked † is due to reference $(MeO)_3PO$ and that marked * is due to the N' coupling (see text and Table II).

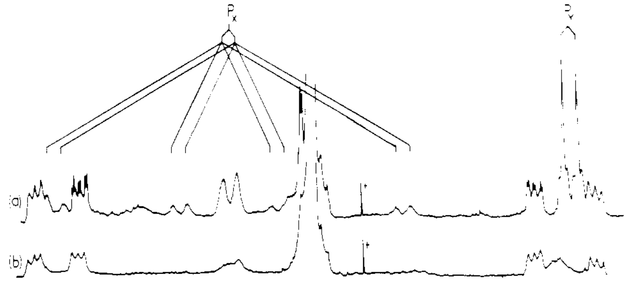
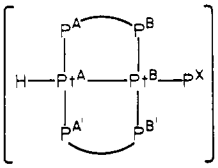


Figure 3. $^{31}P\{^1H\}$ NMR spectra (40.5 MHz) of complex **4** in CH_2Cl_2: (a) spectrum at −20 °C; (b) spectrum at 30 °C. The peak marked † is due to reference $(MeO)_3PO$. Only assignments for P_X and P_Y are shown; assignments for P_A and P_B are as for complex **6**.

diplatinum complex of $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]$ in containing four isotopomers[22] with different spin systems resulting from the presence of ^{195}Pt (natural abundance 33.8%). However, the NMR spectra may be conveniently considered in terms of the following labeling system (data are given in Tables I and II):



In the ^1H NMR spectra the platinum–hydride resonance in **5**–**7** is very complex (Figure 1) due to coupling with P^A, P^B, P^X, Pt^A, and Pt^B (in molecules containing ^{195}Pt (natural abundance 33.8%). Of particular interest is the large value of $^3J(H\text{–}Pt\text{–}Pt\text{–}P^X)$, indicating effective transmission of coupling through the Pt–Pt bond. A similar effect was observed in the dipositive ions $[Pt_2L_2(\mu\text{-dppm})_2]^{2+}$ (L = PMe_2Ph or $PMePh_2$), where a large coupling $^3J(L\text{–}Pt\text{–}Pt\text{–}L)$ was present.[23] The long-range coupling $^2J(H\text{–}Pt^A\text{–}Pt^B)$ was resolved only in complex **5**; in the other compounds the expected resonances were obscured by the complex central resonance due to isotopomers containing no ^{195}Pt atoms.

The methylene protons of the dppm ligands in complexes **5**–**7** appeared as a central singlet with two sets of one-fourth intensity satellites due to coupling with the nonequivalent Pt^A and Pt^B in molecules containing a single ^{195}Pt atom, and weak satellites due to isotopomers with two ^{195}Pt atoms were also seen. Coupling to ^{31}P atoms was not resolved.

The $^{31}P\{^1H\}$ NMR spectra of **5**–**7** were very complex (Table II). For example, complex **5** gave a central quintet resonance due to the PMe_2Ph phosphorus atom coupling to the four ^{31}P atoms of the dppm ligands in a closely coupled spin system. Two sets of one-fourth intensity satellites due to couplings $^1J(Pt^BP^X)$ and $^2J(Pt^AP^X)$ in molecules containing a single ^{195}Pt atom were observed, and weaker satellites separated by $^1J(Pt^BP^X) + {}^2J(Pt^AP^X)$ (N' in Table II) were also observed. These arise from molecules containing two ^{195}Pt atoms, and the magnitude of N' shows that $^1J(Pt^BP^X)$ and $^2J(Pt^AP^X)$ have the same sign, both being positive couplings.[2] The chemical shifts of the dppm phosphorus atoms P^A and P^B were similar and gave a broad singlet in the ^{31}P NMR spectrum. However, the nonequivalence of P^A and P^B was demonstrated by the appearance of two sets of satellites due to the different couplings $^1J(Pt^AP^A)$ and $^1J(Pt^BP^B)$ (Table II), and the accurate chemical shifts $\delta(P^A)$ and $\delta(P^B)$ were calculated from the midpoint of each pair of ^{195}Pt satellites. The assignments of P^A and P^B to specific phosphorus atoms is based only on the similarity of the lower $^1J(PtP)$ coupling constant to that in $[Pt_2(PMe_2Ph)_2(\mu\text{-dppm})_2]^{2+}$, where dppm is cis to PMe_2Ph, and this coupling is therefore tentatively assigned as $^1J(Pt^BP^B)$ in **5**–**7**.[23] For **5**–**7** the satellites show fine structure similar to that observed in other diplatinum complexes such as $[Pt_2Cl_2(\mu\text{-dppm})_2]$[15] but with an additional doublet splitting due to the presence of P^X. A doublet splitting $N = J(P^AP^{B'})$ is prominent,[2,15] and values are given in Table II. A typical spectrum is shown in Figure 2.

Of some interest are the magnitudes of the coupling constants $^1J(Pt^AH)$ and $^1J(Pt^BP^X)$ in these complexes. The values of $^1J(Pt^AH)$ can be taken to indicate that Pt^B has a trans influence rather less than that of a tertiary phosphine ligand (cf. $^1J(PtH)$ = 840 Hz in $[PtH(PMePh_2)_3]^+$),[24] while the magnitude of $^1J(Pt^BP^X)$ indicates that Pt^A has a trans influence rather higher than that of a tertiary phosphine (cf. $^1J(PtP)$ = 2889 Hz in *trans*-$[PtClMe(PMe_2Ph)_2]$).[25] This phenomenon can be understood in terms of the strong σ-donor hydride making Pt^A a stronger donor than Pt^B, with a weaker σ-donor phosphine substituent, and hence Pt^A has a higher trans influence than Pt^B. There is good evidence that the trans influence of a ligand in platinum complexes is largely determined by its σ-donor ability.[24]

The NMR spectra of complex **4** are temperature dependent owing to fluxionality. In the ^1H NMR spectrum the PtH resonance appeared as a broad singlet at room temperature but at −80 °C appeared as a broad doublet with the coupling $^3J(H\text{–}Pt^A\text{–}Pt^B\text{–}P^X)$ similar to the values found for **5**–**7**. The couplings to P^A and P^B were not resolved even at low temperature, and the coupling $^1J(Pt^AH)$ was similar to values for **5**–**7**.

The $^{31}P\{^1H\}$ NMR spectrum of **4** at elevated temperature (40 °C) showed resonances due to the μ-dppm phosphorus atoms P^A and P^B similar to those for complexes **5**–**7**, and these resonances could be analyzed as before (Table II). However, only broad humps were present due to the monodentate dppm. At lower temperatures, additional doublet resonances appeared due to P^X and the additional free phosphorus atom, P^Y, the doublets being due to the extra coupling constant $^2J(P^XP^Y)$. The resonance due to P^X showed the expected couplings to Pt^A and Pt^B as found for **5**–**7**, but no platinum coupling to P^Y was observed (Figure 3). The resonances due to P^X and P^Y became sharper, and the coupling constant $^2J(P^XP^Y)$ increased as the temperature decreased (Table II).

The low-temperature ^{31}P NMR spectrum shows that **4** has the same structure in solution as in the solid state with two μ-dppm and one η^1-dppm ligand. At higher temperatures, no exchange between the μ-dppm and η^1-dppm lignds is found on the NMR time scale, but fluxionality involving the η^1-dppm ligand is observed. This could be due to restricted rotation about the $Pt\text{–}P^X$ bond at low temperature or due to P^Y for P^X

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exchange. The loss of the coupling ${}^3J(\mathrm{HPt^APt^BP^X})$ at high temperature favors the latter interpretation. A ^{31}P NMR spectrum in the high-temperature limit should distinguish between the possible mechanisms unambiguously, but we have been unable to obtain such a spectrum.

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Stereochemistry and Mechanisms of Cleavage of Compounds of the Type (η^5-C_5H_5)Fe(CO)$_2$(alkyl) with Copper(II) Reagents and Halogens. Possible Roles of Solvent Cage Processes in Organometallic Cleavage Reactions

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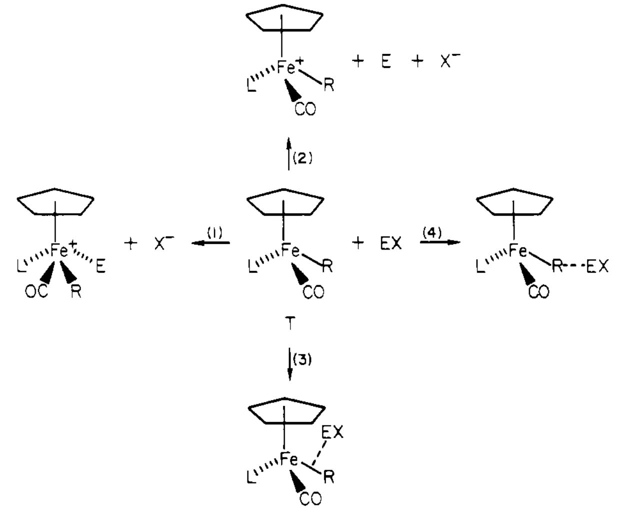
Cleavage reactions by a variety of copper(II) reagents of the compounds FpR (Fp = (η^5-C_5H_5)Fe(CO)$_2$; R = Me, Et, *n*-Bu, $PhCH_2CH_2$, *threo*-PhCHDCHD, $PhCH_2{}^{13}CH_2$, $Me_3CCH_2CH_2$, $PhCH_2$, (*R*)-(−)-PhCHD, Me_3CCH_2, *s*-Bu) and (η^5-C_5H_5)FeCOPPh$_3$R (R = $PhCH_2$, (*R*)-(−)-PhCHD) are studied and compared with similar electrochemical and halogen cleavage reactions. In general, reaction of FpR with a copper(II) halide, CuX_2, yields $[FpR^+][CuX_2^-]$ via a one-electron-transfer process. When R = Me or $PhCH_2$, the ion pair breaks down within the solvent cage via nucleophilic attack by halide ion on the α-carbon atom of R, the products being RX (inversion of configuration) and the iron radical Fp·. The latter then abstracts halogen from copper(II) halide or halogenated solvent. When R = *n*-Bu on $Me_3CCH_2CH_2$, the components of $[FpR^+][CuX_2^-]$ diffuse from the solvent cage and the cation undergoes homolysis of the iron–carbon bonds to give Fp^+ and R·; the latter abstracts halogen from copper(II) halide or halogenated compound. The major difference between the two series appears to be the proclivity of R to undergo S_N2-type processes, i.e., $PhCH_2$, Me > *n*-Bu, $Me_3CCH_2CH_2$, although the benzyl system will also undergo homolysis to yield benzyl radicals when good nucleophiles are absent. Reactions of $FpCH_2CH_2Ph$ proceed by a third route, dissociation of phenonium ions. It is also shown that halogen cleavage reactions of the compounds FpR in nonprotic solvents probably proceed via a two-electron-transfer process. The presumed intermediates, $[FpRX^+][X^-]$, appear to undergo more facile nucleophilic attack by halide ion on the α-carbon atom of R than do the species FpR^+, yielding RX (inversion of configuration) and FpX.

Introduction

Reactions involving cleavage of transition-metal–carbon σ bonds are central to much of the more interesting chemistry of organo transition-metal compounds, although mechanistic features are, in many cases, still rather controversial.[1] Cleavage reactions by electrophilic reagents EX (E = H, HgX, CuX, TlX_2, X; X = Cl, Br, I) have been much studied,[2] in particular of compounds of the general formula (η^5-C_5H_5)Fe(CO)LR (I) (L = CO, tertiary phosphine; R = alkyl), which are both easy to prepare and relatively stable to heat and to air oxidation.

The compounds I are generally cleaved by electrophiles EX to yield RE and (η^5-C_5H_5)Fe(CO)LX, and mechanistic investigations to date have involved kinetic and stereochemical (at iron and the α-carbon) studies of cleavage by protic acids,[3-7] mercury(II) halides,[3-5,8-12] copper(II) halides,[13] and the halogens.[3-5,10,14-16] Mechanisms proposed on the basis of these studies have included oxidative addition (eq 1), one-electron transfer (eq 2), and classical S_E2 (eq 3, 4) processes, as shown in Scheme I. Hereafter cleavage reactions involving oxidative attack at the metal, as in eq 1 and 2, will be referred to as S_E(oxidative) processes.[17]

Scheme I



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