mmol) were added toluene (10 mL) and styrene (0.34 mL, 2.9 mmol) by means of a syringe. The system was stirred at room temperature to yield a pale yellow, homogeneous solution. The solution was cooled to −55 °C and MeCOCOCl[11] (0.78 g, 7.3 mmol) was then added. After stirring of the system at −30 °C for 1.5 h, 30 mL of hexane was added to yield a slightly red pecipitate of **3a**, which was washed with Et_2O (20 mL × 4) at the same temperature and dried in vacuo (0.86 g, 97%). The product was analytically pure without further purification. *trans*-Pd(COCOPh)Cl$(PMePh_2)_2$ (**3b**) was similarly obtained using PhCOCOCl[11] instead of MeCOCOCl. Anal. (**3a**) Calcd for $C_{29}H_{29}ClO_2P_2Pd$: C, 56.8; H, 4.8; Cl, 5.8. Found: C, 57.3; H, 5.0; Cl, 5.7. (**3b**) Calcd for $C_{34}H_{31}ClO_2P_2Pd$: C, 60.5; H, 4.6; Cl, 5.3. Found: C, 60.6; H, 4.8; Cl, 5.4.

Acknowledgment. We are grateful for support of this work by a Grant-in-Aid for scientific research from the Ministry of Education, Japan, and by Kawakami Memorial Foundation for Engineering Research.

Registry No. 2a, 89177-93-5; **2b**, 84624-62-4; **3a**, 89177-94-6; **3b**, 89177-95-7; Pd$(PMePh_2)_2$B (B = Styrene), 70316-76-6; *trans*-Pd(COPh)Br$(PMePh_2)_2$, 89177-97-9; MeCOCOCl, 5704-66-5; PhCOCOCl, 25726-04-9; MeCOCOBr, 74100-44-0; PhCOCOBr, 89177-96-8; Et_2NH, 109-89-7.

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Syntheses of Some Methyldiplatinum(I) Complexes by Oxidative Addition or Reductive Elimination Reactions of Binuclear Complexes

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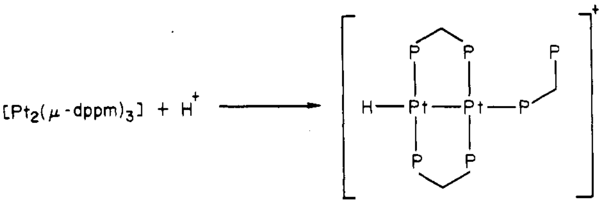
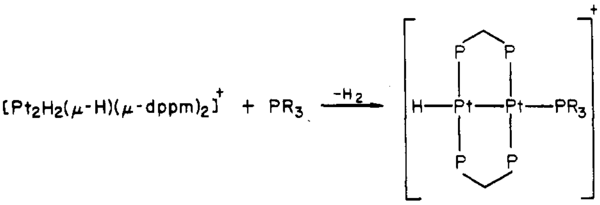
Oxidative addition of MeI to $[Pt_2(dppm)_3]$ in benzene followed by anion exchange with $K[PF_6]$ led to isolation of the first methyldiplatinum(I) complex $[Pt_2Me(\eta^1\text{-dppm})(\mu\text{-dppm})_2][PF_6]$, and further reaction with MeI in CH_2Cl_2 solution gave $[Pt_2Me_2(\mu\text{-I})(\mu\text{-dppm})_2][PF_6]$. Methyldiplatinum(I) complexes were also formed by reaction of tertiary phosphines (L = dppm, PPh_3, PMe_2Ph) with $[Pt_2H(\mu\text{-H})Me(\mu\text{-dppm})_2][SbF_6]$ to give $[Pt_2MeL(\mu\text{-dppm})_2][SbF_6]$ and H_2. The reductive elimination followed second-order kinetics, and an intermediate, $[H(Ph_3P)Pt(\mu\text{-H})(\mu\text{-dppm})_2PtMe][SbF_6]$, was detected by low-temperature NMR spectroscopy in the case with L = PPh_3.

Introduction

Syntheses of hydridoplatinum(I) complexes by oxidative addition to diplatinum(0) complexes[2-4] or reductive elimination from diplatinum(II) complexes,[5-10] stabilized by bridging bis(diphenylphosphino)methane (dppm or P⌒P) ligands, have been reported as shown, for example, in eq 1 and 2.



(1)



(2)

The mechanism of the binuclear reductive elimination reaction of eq 2 has been studied.[11]

In this paper the synthesis of methyldiplatinum(I) complexes by similar methods is described, together with

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(1) (a) University of Western Ontario. (b) University of Liverpool. This is contribution 304 from the photochemistry unit, University of Western Ontario.

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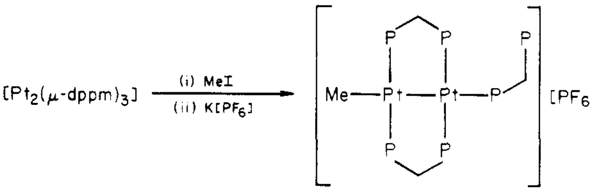
(11) Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277, *J. Am. Chem. Soc.* **1983**, *105*, 5797. The evidence for the structure of the adduct being as shown in eq 7 is discussed in detail in ref 11. Similar reasoning suggests the structure A, but the precise stereochemistry at the five-coordinate platinum center could be different.[11] We cannot eliminate the possibility of a low concentration of B, which might still exchange at −90 °C and hence give broad weak resonances which would not be detected.

a brief study of the mechanism of the reaction involving reductive elimination. Before publication of the preliminary communication of this work, no methylplatinum(I) complexes were known.[12]

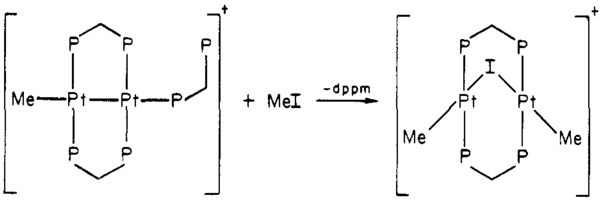
Results and Discussion

Synthesis of Methylplatinum(I) Complexes. Reaction of methyl iodide with $[Pt_2(\mu\text{-dppm})_3]$ in benzene solution led to precipitation of a yellow solid, presumed to be $[Pt_2Me(\eta^1\text{-dppm})(\mu\text{-dppm})_2]I$ (Ia), which gave $[Pt_2Me(\eta^1\text{-dppm})(\mu\text{-dppm})_2][PF_6]$ (Ib) on reaction with excess $K[PF_6]$ (eq 3).



(3)

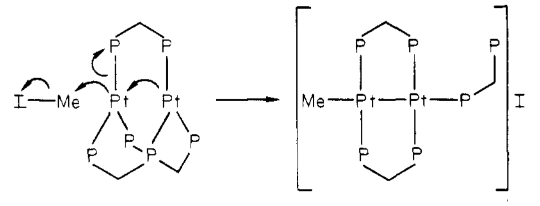
Neither Ia nor Ib in suspension in benzene reacted with further methyl iodide, but Ib in dichloromethane solution did react further with methyl iodide, largely according to eq 4.



(4)

Balch and co-workers have reported the similar reaction of $[Pd_2(\mu\text{-dppm})_3]$ with methyl iodide to give $[Pd_2Me_2(\mu\text{-}I)(\mu\text{-dppm})_2]I$, but they did not observe methylpalladium(I) intermediates.[13] The successful isolation of Ia and Ib in the present system is possible because the reaction of eq 4 is considerably slower than that of eq 1 and is facilitated by the insolubility of Ia in benzene.

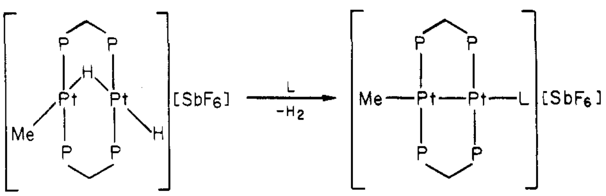
$[Pt_2(\mu\text{-dppm})_3]$ appears to be more reactive than mononuclear complexes, such as $[Pt(PPh_3)_3]$, toward oxidative addition, and it is probable that the second platinum center gives anchimeric assistance, perhaps according to eq 5.[14]



(5)

A second synthetic method involves the binuclear reductive elimination of hydrogen from the complex $[Pt_2H(\mu\text{-H})Me(\mu\text{-dppm})_2][SbF_6]$[15] (II) induced by reaction with tertiary phosphines (eq 6).

When L = PMe_2Ph, the reaction was rapid at room temperature, but, when L = dppm, reaction 6 appeared to take several hours to reach completion. In each case,



(6)

Ic, L = η^1-dppm
d, L = PMe_2Ph
e, L = PPh_3

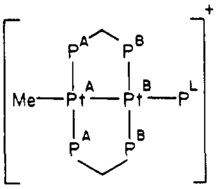
hydrogen but no methane was detected in the gas phase above the reaction mixture. When L = PPh_3, reaction was again slow and, in this case, hydrogen and methane were detected as gaseous products. Subsequent NMR studies showed the product to be a mixture of Ie and the known hydridoplatinum(I) complex cation $[Pt_2H(PPh_3)(\mu\text{-dppm})_2]^+$ (III) as the $[SbF_6]^-$ salt.[5] The mean of three determinations by integration of $^{31}P\{^1H\}$ NMR spectra of products from different syntheses gave the ratio of Ie:III = 85 ± 5:15 ± 5.

The methylplatinum(I) complexes (I) are yellow air-stable solids, which are soluble in solvents CH_2Cl_2 and $CHCl_3$. They can be stored as solids in the dark at room temperature for several months without decomposition but are somewhat photosensitive.

We have been unable to prepare a pure carbonyl derivative,[9] I with L = CO, by the reaction of eq 6. This reaction was very slow, and, though spectroscopic evidence indicated that the desired complex was formed, it could not be separated from unchanged starting material (short reaction times) or decomposition products (long reaction times).

Characterization of Methylplatinum(I) Complexes. The new complexes were characterized by elemental analysis and by their ^1H and $^{31}P\{^1H\}$ NMR spectra (Table I). In the ^1H NMR spectra of I, the MePt resonance appeared as a doublet of triplets. The doublet splitting arises from the long-range coupling to the ^{31}P nucleus of the ligand L, while the triplet splitting arises from the adjacent ^{31}P centers of the dppm ligands. A large coupling, $^3J(HPtPtL)$, through the Pt–Pt bond was previously noted in the analogous hydridoplatinum(I) complexes.[5]

The $^{31}P\{^1H\}$ NMR spectra are analyzed in terms of the labeling system below, and data are given in Table I.



The spectra were complex but were very similar to those of the analogous hydrido derivatives $[Pt_2HL(\mu\text{-dppm})_2]^+$ which have been discussed in detail.[5,9] As for the hydrido derivatives,[5] the coupling constant $^1J(Pt^BP^L)$ for complexes I is small, indicating an efficient transmission of the trans influence of the hydride or methyl ligand through the Pt–Pt bond. Fackler has seen a similar effect in the structures of gold(II) complexes with gold–gold bonds.[16] In the platinum(I) complexes, the methyl ligand exerts a slightly greater trans influence than the hydride ligand.[5]

For complex Ia, with L = η^1-dppm, at −80 °C, separate signals due to the coordinated and free phosphorus atoms of the η^1-dppm ligand were observed (Table I), with a

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[14] It is possible that the η^2-dppm to η^1-dppm transformation occurs before or after the oxidative addition step. For comparison, $[Pt(PPh_3)_3]$ gives oxidative addition with MeI but $[Pt(PPh_3)_2]$, which is formed by reversible loss of PPh_3, reacts much faster. In both cases the product is $[PtIMe(PPh_3)_2]$. Pearson, R. G.; Rajaram, J. *Inorg. Chem.* **1974**, *13*, 246.

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Table I. ^1H and $^{31}P\{^1H\}$ NMR Data for Complexes I[a]

L	MePt[b]				CH_2P_2[b]	dppm[b]				L[b]			
	δ(Me)	$^2J(Pt^AH)$	$^3J(P^AH)$	$^4J(P^LH)$[c]	$\delta(CH_2)$	$\delta(P^A)$	$^1J(Pt^AP^A)$	$\delta(P^B)$	$^1J(Pt^BP^B)$	$\delta(P^L)$	$^1J(PtP^L)$	$^2J(PtP^L)$	$J(PP)$[d]
PMe_2Ph[e]	−0.14	58.9	6.4	2.3	4.91	7.33	3510	2.25	2960	−0.47	2054	476	14.8
PPh_3	−0.05	59.6	6.6	2.4	4.91	8.37	3510	3.21	2976	26.77	2040	490	13.8
η^1-dppm	−0.09	58.5	6.4	*f*	5.0[g]	9.06	3550	2.27	2970	23.4[h] −31.9[h,i]	2020	435	14.0 94[j]
CO	−0.02	59	6.8	. . .	5.1	3.71	3300	5.67	2860	. . .			

[a] The solvent is CH_2Cl_2 or CD_2Cl_2. [b] δ in ppm and J in Hz. [c] Coupling to ^{31}P of L. [d] Apparent quintet, $J(PP) = {}^2J(PP) + {}^3J(PP)$. [e] δ(MeP) 0.65 ($^2J(PH) = 8$, $^3J(PtH) = 18$ Hz). [f] Not resolved; $^3J(PtMe) = 6$ Hz. [g] Very complex and temperature-dependent signals. [h] From spectrum recorded at −80 °C. [i] Noncoordinated phosphorus of η^1-dppm. [j] $^2J(PCH_2P)$.

Table II. Kinetic Data for Reaction of Equation 5 in CH_2ClCH_2Cl at 25 °C[a]

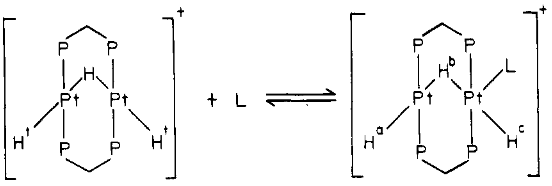
L	10^3[L], mol L^{-1}	10^4k_{obsd},[b,c] s^{-1}	L	10^3[L], mol L^{-1}	10^4k_{obsd},[b,d] s^{-1}
dppm	0.72	1.4	PPh_3	1.10	0.49
	1.44	3.4		2.20	0.88
	2.16	4.6		4.40	1.8
	2.88	6.6		6.60	2.8

[a] $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2][SbF_6]$ at concentration 0.77 × 10^{-4} mol L^{-1} in each case. [b] Observed first-order rate constant. [c] Mean $k_2 = k_{obsd}/[L] = 0.22 \pm 0.02$ L mol^{-1} s^{-1}. [d] Mean $k_2 = 0.042 \pm 0.003$ L mol^{-1} s^{-1}.

coupling, $^2J(PCH_2P)$, of 94 Hz. However, at room temperature, separate signals were still observed but this $^2J(PCH_2P)$ coupling was lost. This is attributed to the onset of a fluxional process involving exchange of coordinated and free ^{31}P centers of the η^1-dppm ligand and was also seen for the corresponding hydridoplatinum(I) complex.[5]

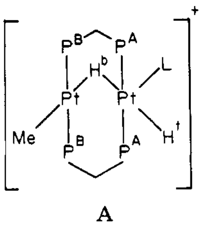
Kinetic Studies of the Reductive Elimination. A brief kinetic study of the reductive elimination of eq 6 was carried out in order to compare the reactivities of the complex cations $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$, studied earlier,[11] and $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2]^+$. Reactions when L = PPh_3 or dppm could be monitored by UV–visible spectroscopy, under conditions with a large excess of ligand, L. Absorbance increased throughout the region 450–300 nm as reaction proceeded, the change being greatest at ~330 nm. Graphs of ln ($A_\infty - A_t$) vs. t gave straight line plots from which the first-order rate constants, k_{obsd}, were calculated. Data are given in Table II. Then graphs of k_{obsd} vs. [L] gave reasonable straight line plots, and the rate law for the reaction is therefore $-d/dt\,[II] = k_2[II][L]$. The second-order rate constants were k_2 (L mol^{-1} s^{-1}) = 0.22 for L = dppm and 0.04 for L = PPh_3. For comparison, the corresponding rate constants for reactions of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ were k_2 (L mol^{-1} s^{-1}) = 10.9 for L = dppm and 1.6 for L = PPh_3.[11] The methyl derivative II reacts 40–50 times more slowly than $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$.

Detection and Energetics of a Reaction Intermediate. Reaction of PPh_3 with $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ has been shown to give a 1:1 adduct according to eq 7, L = PPh_3. The NMR spectra indicated that exchange according to eq 7 was slow at −90 °C but rapid on the NMR time scale above −80 °C.[11]

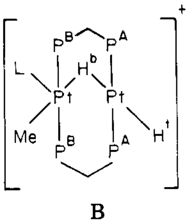


(7)

With respect to $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ [$\delta(H^t)$ −6.9 ($^1J(PtH^t) = 1138$ Hz)], it was found that H^a appeared downfield [$\delta(H^a)$ −4.9 ($^1J(PtH^a) = 1140$ Hz)] while H^c appeared upfield [$\delta(H^c)$ −12.4 ($^1J(PtH) = 765$ Hz)] and the $^1J(PtH)$ coupling constant was considerably lower.[11] Now, in the reaction with the less symmetrical $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2]^+$, the phosphine ligand could add at either Pt center to give A or B.



A



B

Table III. ^{1}H NMR Data at Varying Temperatures and Equilibrium Constants for Formation of A

T, °C	$\delta(CH_2P_2)$	δ(MePt)	K,[a] L mol^{-1}	$\delta(H^b)$	K,[b] L mol^{-1}	$\delta(H^t)$	K,[c] L mol^{-1}
−90	5.65, 3.13	−0.05[d]	...	−9.99[e]	...	−11.93[f]	...
−70	5.65, 3.13	−0.03	990	−9.70	830	−11.45	710
−50	4.39	−0.01	227	−9.44	210	−11.02	170
−30	4.47	+0.06	21	−8.77	33	−10.11	34
−20	4.50	+0.06	21	−8.40	16	−9.54	16
−10	4.56	+0.14	3.2	−8.07	9.1	−9.04	9.1
30	4.59	+0.19	0.7	−7.00	1.1	−7.40	1.0
−90[g]	5.54, 3.98	0.21		−6.57		−6.75	

[a] These values are inaccurate due to the small shift range for δ(Me) and were not used to calculate ΔH° and ΔS°. [b] Calculated from $\delta(H^b)$. [c] Calculated from $\delta(H^t)$. [d] ^2J(PtMe) = 68 Hz. [e] ^1J(PtH) = 530 Hz. [f] ^1J(PtH) = 780 Hz. [g] Data for $[Pt_2MeH(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ in absence of PPh_3. Other data with $[Pt]^0 = [PPh_3]^0 = 0.154$ M.

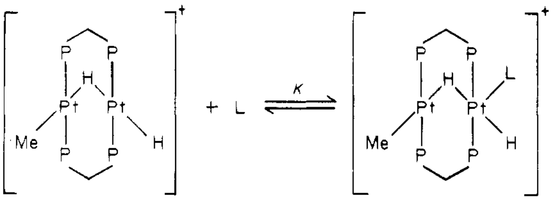
Table IV. $^{31}P\{^1H\}$ NMR Data at Varying Temperatures and Equilibrium Constants for Formation of A

T, °C	(P^A),[a] ppm	K,[b] L mol^{-1}	(P^B),[a] ppm	K,[c] L mol^{-1}
−90[d]	9.88[e]	...	−4.35[f]	
−80	9.47		−4.35	
−60[g]	11.46	112	−1.38	265
−40	12.25	43	1.58	55
−20	13.43	14	4.32	18
0	14.82	5	5.53	14
...	17.1[h]		15.6[h]	

[a] Recorded with $[Pt_2]^0 = [PPh_3]^0 = 0.146$ M. [b] Calculated from $\delta(P^A)$. [c] Calculated from $\delta(P^B)$. [d] $\delta(PPh_3)$ 4.7, compare to −9.1 ppm for free PPh_3. The temperature dependence of this shift is not reported since, in many cases, it overlapped with the more intense P^B resonance and accurate shifts could not be obtained. [e] ^1J(PtP) = 2880 Hz. [f] ^1J(PtP) = 3230 Hz. This coupling decreased with increasing temperature. [g] Fast exchange at this temperature. [h] Values in the absence of PPh_3; $^1J(PtP^A)$ = 2793 and $^1J(PtP^B)$ = 2895 Hz.

In the ^1H NMR spectrum of a solution of $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2]^+$ with PPh_3 at −90 °C a resonance is observed at $\delta(H^t)$ −11.93 (^1H(PtH) = 780 Hz) compared to a value of δ (H^t) −6.75 (^1J(PtH) = 1130 Hz) for the parent complex. This strongly indicates structure A in which the phosphine adds selectively to the hydride end of the molecule. This is supported further by the observation that the coupling constant ^2J(PtH) associated with the methylplatinum group is 68 Hz in both A and the parent complex (Table III) whereas a reduced ^2J(PtH) value would be expected for B. The remainder of the spectroscopic characterization of A follows very closely that of $[Pt_2H_2(\mu\text{-}H)(PPh_3)(\mu\text{-dppm})_2]^+$, and NMR data are given in Tables III and IV.

At −70 °C and higher temperatures fast exchange was observed, according to eq 8, L = PPh_3, as evidenced by loss of the $^1J(PtPPh_3)$ coupling in the ^{31}P NMR spectra.



(8)

From the variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra it was possible to calculate the equilibrium constant K, at each temperature by a number of independent parameters (Tables III and IV). The values obtained, though approximate, are reasonably self-consistent and indicate a rapid decrease in K with increasing temperature. Some reaction occurred above 15 °C, and values in this region are tentative. A graph of ln K vs. $1/T$ is given in Figure 1 and gives ΔH° = −34 ± 4 kJ mol^{-1}, ΔS° = −110 ± 10 J K^{-1} mol^{-1}, and ΔG° (273 K) = −4.3 ± 0.5 J K^{-1} mol^{-1}.

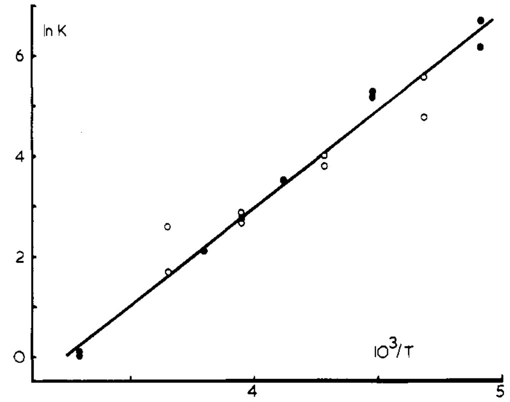


Figure 1. Graph of ln K vs. $10^3/T$ (K), where K is the equilibrium constant for formation of A, in units of L mol^{-1}: closed circles, data from ^1H NMR; open circles, data from $^{31}P\{^1H\}$ NMR.

These parameters may be compared to those for reaction of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ with PPh_3 for which ΔH° = −41 ± 2 kJ mol^{-1}, ΔS° = −108 ± 4 kJ mol^{-1}, and ΔG° (273 K) = −11.5 ± 0.5 kJ mol^{-1}.[11] The difference is in the ΔH° term and probably results from a long-range electronic effect, with methyl being a slightly stronger donor than hydride and reducing the Lewis acidity of the distal (as well as the proximal) platinum center.[17]

A correlation between the equilibrium constant, K, and the observed second-order rate constant, k_2, for the overall binuclear reductive elimination for reactions of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ with different ligands has been noted.[11] The ratios of k_2/K at 298 K for reactions of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ and $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2]^+$ with PPh_3 are given by $k_2/K \approx 1.6/35 = 0.046$ s^{-1} and $k_2/K \approx 0.042/1.3 = 0.032$ s^{-1}, respectively, and indicate that this correlation also holds for the methyl derivative. We note also that $[Pt_2(\mu\text{-}H)Me_2(\mu\text{-dppm})_2]^+$ does not form a complex with PPh_3 and also fails to undergo reductive elimination on treatment with PPh_3. These observations suggest that the reductive elimination occurs from the adduct of structure A rather than B.[18] If this is the case, the mechanistic implications are interesting. By comparison to previous work,[11] the most likely mechanism involving eventual reductive elimination at a single platinum center would involve intermediate E in Scheme I and this should lead selectively to methane loss. However, binuclear reductive elimination from C or D (Scheme I) would give hydrogen or methane respectively. To obtain

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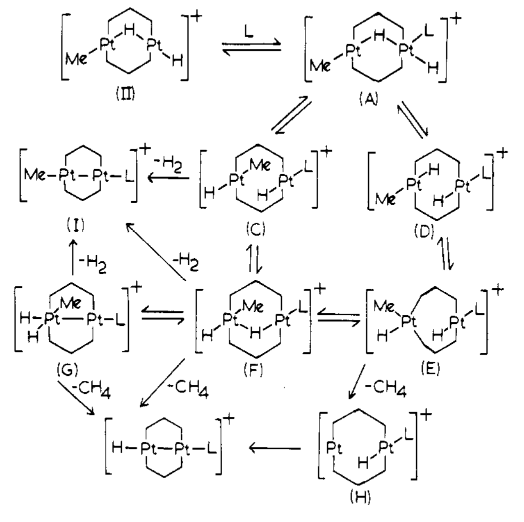
(17) Further support for attack at the PtH center is derived from the observation that $[Pt_2(\mu\text{-}H)Me_2(\mu\text{-dppm})_2][PF_6]$ fails to form a complex with PPh_3 in detectable quantity. Note that methyl gives a higher long-range trans influence in complexes I than does hydride, indicating that it is a slightly stronger donor in these complexes. Of course, attack at the MePt center may also be disfavored by steric factors.

(18) The correlation in no way constitutes a proof. It is posoible that attack at the MePt center to give B *may* be followed by a particularly favorable reductive elimination step.

Scheme I



the observed selectivity for hydrogen formation with reductive elimination at a single metal center, it would be necessary to propose intermediates such as F or G, which might be expected to be high energy species.[19] We favor the binuclear reductive elimination of H_2 from C as the principle route, although the evidence is by no means conclusive.

Experimental Section

^1H and ^{31}P NMR spectra were recorded on Varian XL100 and XL200 and Bruker WM250 spectrometers.

The complex $Pt_2(dppm)_3$ was prepared from $Pt(PPh_3)_4$ and dppm in hot ethanol as described elsewhere.[2] Solid $Pt_2(dppm)_3$ was handled in the air, but when stored for more than 24 h, it was placed in sealed tubes under vacuum. Solutions and reaction mixtures containing $Pt_2(dppm)_3$ were manipulated under nitrogen by using standard Schlenk procedures, but reaction products were worked up in the air. Syntheses from $[Pt_2H(\mu\text{-}H)Me(\mu\text{-}dppm)_2][SbF_6]$ were carried out under nitrogen. Hydrogen analyses were carried out, as described in detail previously,[8] by GC using a 6 ft × $^1/_8$ in. molecular sieve 5A column. The calibration was performed by injecting known volumes of hydrogen into the reaction flask, fitted with a serum cap and containing solvent only, and then sampling as in the reaction mixtures (see below). Elemental analyses were performed by Bernhardt (Germany) or Guelph Chemical Laboratory (Canada).

Synthesis of $[Pt_2Me(\eta^1\text{-}dppm)(\mu\text{-}dppm)_2][PF_6]$. Iodomethane in benzene (0.82 mL of solution containing 0.085 g, 0.60 mmol, of CH_3I) was added to a solution of $[Pt_2(dppm)_3]$ (0.921 g, 0.597 mmol) in benzene (8 mL) in a Schlenk tube. The mixture was stirred at room temperature for 3.5 h when the deep red solution became yellow and a yellow precipitate was formed. The precipitate, presumably impure $[Pt_2Me(dppm)_3][I]$ (0.996 g, 99%), was recovered by filtration, washed with benzene (5 mL) and cyclohexane (5 mL), and dried in vacuo. It was converted to the hexafluorophosphate salt by dissolving it in dichloromethane (10 mL) and adding a solution of KPF_6 (0.544 g, 2.96 mmol) in water (10 mL). The mixture was stirred for 45 min. The organic phase was separated, washed with water, and dried (molecular sieve). Slow addition of cyclohexane gave orange-yellow crystals of the product (0.857 g, 84% overall yield) which were recovered by filtration and dried in vacuo. Anal. Calcd for $[Pt_2Me(dppm)_3][PF_6]\cdot 0.35CH_2Cl_2$: C, 52.9; H, 4.0; Cl, 1.4; F, 6.6; P, 12.5. Found: C, 52.3; H, 4.1; Cl, 1.4; F, 6.8; P, 12.4.

Other similar reactions gave yields in the range 60–84%. Use of more than one molar proportion of iodomethane (up to approximately 4 molar proportions) appeared to result in marginally lower yields of slightly less pure product.

An alternative and convenient procedure avoiding the need to isolate pure $[Pt_2(dppm)_3]$ was to prepare this starting material in situ in benzene from $[Pt(PPh_3)_4]$ and dppm. In a typical experiment, $[Pt(PPh_3)_4]$ (3.36 g, 2.70 mmol), dppm (2.08 g, 5.40 mmol), and benzene (25 mL) were placed in a Schlenk tube. The deep red solution thus obtained was reacted with iodomethane (0.194 g, 1.37 mmol) in benzene (2.7 mL), and the reaction products were worked up as described above to yield pure $[Pt_2Me(dppm)_3][PF_6]$ (1.55 g, 67%).

Synthesis of $[Pt_2Me(\eta^1\text{-}dppm)(\mu\text{-}dppm)_2][SbF_6]$. A yellow solution of $[Pt_2H_2Me(dppm)_2][SbF_6]$ (0.1 g, 0.071 mmol) and dppm (0.03 g, 0.07 mmol) in CH_2Cl_2 (20 mL) was stirred under N_2 for 18 h at room temperature. The solution was concentrated by evaporation, and the yellow product was crystallized out by addition of diethyl ether (yield 0.122 g, 96% based on Pt): mp 190–195 °C dec; IR (Nujol) $\nu(SbF_6^-)$ 654, 250 cm^{-1}. Anal. Calcd for $[Pt_2Me(dppm)_3][SbF_6]$: C, 50.9; H, 3.9. Found: C, 50.9; H, 3.8.

Synthesis of $[Pt_2Me(PMe_2Ph)(\mu\text{-}dppm)_2][SbF_6]$. A solution of $[Pt_2H_2CH_3(dppm)_2][SbF_6]$ (0.1 g, 0.071 mmol) in CH_2Cl_2 (5 mL) in a 10-mL flask fitted with a serum cap. Instant deepening of color was observed. After 1.5 h, a sample of gas above the solution was removed with a gas syringe and analyzed by GC (molecular sieve column). H_2 was detected (94% yield) but no methane. The solution was concentrated by evaporation, and addition of diethyl ether gave yellow orange crystals of the product (yield 0.088 g, 80%, repeat experiment gave 91% yield, based on Pt): mp 175–180 °C; IR (Nujol mull) ν (SbF_6^-). Anal. Calcd for $[Pt_2Me(PMe_2Ph)(dppm)_2][SbF_6]$: C, 45.8; H, 3.8. Found: C, 45.8; H, 3.8.

Synthesis of $[Pt_2Me(PPh_3)(\mu\text{-}dppm)_2][SbF_6]$. A solution of $[Pt_2H_2Me(\mu\text{-}dppm)_2][SbF_6]$ (0.12 g) and PPh_3 (0.0225 g) in CH_2Cl_2 (10 mL) was stirred under N_2 at room temperature for 2 days. The solution was concentrated by evaporation, and a yellow product was crystallized out by adding diethyl ether. Both I [ν(PtH) at 2020 cm^{-1}] and ^1H NMR [δ(PtH) −8.92 (^3J(PH) = 46 Hz)] showed the presence of $[HPt_2(PPh_3)(\mu\text{-}dppm)_2][SbF_6]$ (15% impurity). IR showed an (SbF_6) absorption at 658 and 285 cm^{-1} (yield 0.11 g). Anal. Calcd for $[Pt_2Me(PPh_3)(\mu\text{-}dppm)_2][SbF_6]$: C, 49.6; H, 3.7. Calcd for $0.85[Pt_2Me(PPh_3)(\mu\text{-}dppm)_2]$ $0.15[Pt_2H(PPh_3)(\mu\text{-}dppm)_2][SbF_6]$: C, 49.5; H, 3.7. Found: C, 49.2; H, 3.5.

Attempted Reaction of $[Pt_2H_2(CH_3)(dppm)_2][SbF_6]$ with CO. A flask containing a solution of $[Pt_2H_2(Me)dppm_2][SbF_6]$ (0.1 g, 0.07 mmol) in CH_2Cl_2 (5 mL) was fitted with a serum cap. CO was passed over the solution for 15 min. The solution was stirred at room temperature for 60 h. Evolution of H_2 was detected by GC. Solvent volume was reduced by evaporation, and a yellow brown product was obtained upon addition of diethyl ether. IR spectrum showed an absorption at 2030 cm^{-1} [ν(CO)]. ^1H and $^{31}P\{^1H\}$ NMR spectra (Table I) indicated the presence of approximately equal amounts of starting material and $[Pt_2Me(CO)(\mu\text{-}dppm)_2][SbF_6]$. When the experiment was repeated by using a longer reaction time (7 days) or using a higher pressure of CO (120 psi), no starting material remained but much decomposition occurred.

Reaction of $[Pt_2Me(dppm)_3][PF_6]$ with Iodomethane in Dichloromethane: Preparation of $[Pt_2Me_2(\mu\text{-}I)(\mu\text{-}dppm)_2][PF_6]$. Iodomethane (0.546 g, 3.84 mmol) was added to a solution of $[Pt_2Me(dppm)_3][PF_6]$ (0.401 g, 0.236 mmol) in dichloromethane (8 mL). After 20 h at 20 °C, the orange-yellow solution became yellow. Solvent was then evaporated in a stream of nitrogen to the point of crystallization when the product was crystallized by the addition of cyclohexane and was recovered by filtration. Recrystallization from dichloromethane and cyclohexane afforded $[Pt_2Me_2(\mu\text{-}I)(\mu\text{-}dppm)_2][PF_6]$ (0.200 g, 57%) as pale yellow crystals: ^1H NMR (CD_2Cl_2) δ 0.64 [t, ^3J(PH) = 7, ^2J(PtH) = 83 Hz, MePt], 5.04 [m, ^2J(PH) = 3, ^3J(PtH) = 54, Hz, $CH^aH^bP_2$], 4.60 [m, ^2J(PH) = 6, ^3J(PtH) ≈ 0, $^2J(H^aH^b)$ = 14 Hz, $CH^aH^bP_2$]; ^{31}P NMR 10.4 [s, ^1J(PtP) = 2946, ^2J(PtP) = 36, $J(P^aP^b)$ = 32, $J(P^aP^{b'})$ = 3.7 Hz)]. Note that the presence of nonequivalent

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[19] In $Pt_2(\mu\text{-}H)$ complexes it is proposed that electrons from an electron-rich Pt–H bond are donated to an electron-deficient Pt center. Species F would require donation from the most protonic Pt–H group in C (Scheme I) to the electron-rich MePtH center in C and is thus predicted to be unfavorable. For a related discussion: Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Szostak, R.; Strouse, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1983**, *22*, 2332. Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Ibid.* **1983**, *22*, 2324.

$CH^aH^bP_2$ protons proves that inversion of the A frame is slow on the NMR time scale. Anal. Calcd C, 42.8; H, 3.5; F, 7.8; P, 10.6. Found: C, 42.7; H, 3.4; F, 7.9;, P, 10.6.

Another similar reaction was monitored by ^{31}P NMR spectroscopy. This showed that while significant reaction occurred after 1 h, substantially complete reaction required 24 h. The formation of a number of unidentified minor phorphous-containing impurities was revealed as well as the formation of some $[Pt(dppm)_2]^{2+}$ cation (δ −59 m). This was confirmed by treatment of the solution with excess of aqueous KPF_6 when $[Pt(dppm)_2][PF_6]_2$ (11% based on platinum), identified by its infrared spectrum, was precipitated. After this treatment the reaction solution no longer exhibited the resonance at −59 ppm but was otherwise unchanged.

Treatment of $[Pt_2Me(dppm)_3][PF_6]$ with Iodomethane in Benzene. Iodomethane (0.23 g, 1.50 mmol) was added to a suspension of $[Pt_2Me(dppm)_3][PF_6]$ (0.060 g, 0.035 mmol) in benzene (3 mL) and stirred at 20 °C for 5 h. The yellow solid was recovered by filtration, was washed with benzene, and was found (infrared) to be unchanged starting material (0.054 g, 90%).

Kinetic Studies.[11] Solutions of $[Pt_2H(\mu\text{-}H)(Me(\mu\text{-}dppm)_2][SbF_6]$ (1 mL, 7.71×10^{-4} M) and dppm (2 mL, 7.20×10^{-3} M) were mixed and diluted to a volume of 10 mL. Part of this solution was added to a 1-cm quartz cuvette held in the cell compartment (thermostated with circulating water to 25 °C) of a Cary spectrophotometer. Spectra (450–300 nm) were recorded at suitable intervals until no further change occurred. A graph of ln $[A_\infty - A]$ vs. time, where A is the absorbance at 330 nm, gave a good straight line plot from which the first-order rate constant, k_{obsd} was calculated. The same method was used for reactions with PPh_3.

Variable-Temperature NMR Studies.[11] Triphenylphosphine (0.77 mmol) was added to a solution of $[Pt_2H(\mu\text{-}H)Me(\mu\text{-}dppm)_2][SbF_6]$ (0.077 mmol) in CD_2Cl_2 (0.50 mL) in an NMR tube cooled to −78 °C. After dissolution of the PPh_3 at −78 °C, the tube was added to the probe (precooled to −90 °C) of a Varian XL100 NMR spectrometer. The ^1H NMR spectrum was recorded, and further spectra were recorded at higher temperatures (Table III) until reaction to give H_2 and methyldiplatinum(I) complex was significant. The variable-temperature $^{31}P\{^1H\}$ NMR spectra were obtained in a similar way but with a Varian XL200 NMR spectrometer.

A similar experiment was carried out by using PPh_3 (1.5×10^{-4} mol) and $[Pt_2(\mu\text{-}H)Me_2(\mu\text{-}dppm)_2][PF_6]$ (0.66×10^{-4} mol) in CD_2Cl_2 (1.3 mL). ^1H and $^{31}P\{^1H\}$ NMR spectra from −90 to 0 °C showed only signals due to the reagents, with no evidence for complex formation.

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Registry No. Ia, 84190-20-5; Ib, 84190-22-7; Ic, 84190-23-8; Id, 84190-06-7; Ie, 84190-25-0; II, 89378-06-3; $[Pt_2Me(CO)(\mu\text{-}dppm)_2][SbF_6]$, 89378-02-9; $[Pt_2Me_2(\mu\text{-}I)(\mu\text{-}dppm)_2][PF_6]$, 89378-04-1; $[Pt(dppm)_2][PF_6]_2$, 72950-65-3; $[Pt_2(dppm)_3]$, 69152-81-4; $[Pt(PPh_3)_4]$, 14221-02-4; MeI, 74-88-4.

Photoisomerization of *cis*,*cis*-1,5-Cyclooctadiene in the Presence of Copper(I) Complexes: Wavelength Dependence

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Irradiation of $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ or Cu(acac)(cc-1,5-COD) in the presence of an excess of cc-1,5-COD in methanol catalytically gave ct-1,5-COD as the exclusive product at wavelengths >290 nm and TCO plus minor amounts of tt-1,5-COD at wavelengths >240 nm. Cu(acac)(cc-1,5-COD) was generated in situ by photoreduction, electrolysis, or metathesis under appropriate conditions. Sparingly soluble $[CuCl(ct\text{-}1,5\text{-}COD)]_2$ was isolated and identified as the immediate intermediate in the photorearrangement to TCO. The stoichiometric interconvertibility between $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ and $[CuCl(ct\text{-}1,5\text{-}COD)]_2$ by >290-nm irradiation was established from the presence of an isosbestic point in UV spectra. A definite mechanism was proposed to account for the rearrangements.

Aromatic ketones with high triplet state energy (e.g., xanthone, benzophenone, acetophenone, etc.) sensitize the photoreduction of bis(acetylacetonato)copper(II), $Cu(acac)_2$, in hydrogen atom donating solvents, such as methanol or tetrahydrofuran, to give copper (I) complexes.[1-4] Kinetic and mechanistic investigations show that the primary photoreaction is the electron transfer from $Cu(acac)_2$ to triplet-state ketones and that the hydrogen-transfer step determines the overall efficiency of the photoreduction.[3] The proposed reaction pattern is summarized below, where L represents appropriate ligands:

$$Cu(acac)_2 + Ph_2CO \xrightleftharpoons{h\nu} Cu(acac)^+ + acac\cdot + Ph_2CO^{-\cdot}$$

$$Cu(acac)^+ + Ph_2CO^{-\cdot} + xL \rightarrow Cu(acac)L_x + Ph_2CO$$

$$2acac\cdot + CH_3OH \rightarrow 2acacH + CH_2O$$

It is also well-known that in the presence of copper(I) complexes, olefins undergo photoreactions involving rearrangements, cycloadditions, and fragmentations.[5,6] Among them, the cuprous chloride catalyzed photorearrangement[7-11] of *cis*,*cis*-1,5-cyclooctadiene (cc-1,5-COD) to

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