dark brown-red. The solvent was removed and the blackish mass obtained was extracted with benzene. The complex was crystallized from a benzene/*n*-hexane mixture to give pale yellow crystals identified as $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$.

Preparation of $[PdCl(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(L)]$ (L = PEt_3, PPh_3, PCy_3, PPh_2Me, $t\text{-}PBu_2Me$, $P(o\text{-}CH_3C_6H_4)_3$ $i\text{-}PPr_3$, and $AsPh_3$). In a typical reaction to a solution of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ (0.2 mmol) was added PPh_3 (0.4 mmol) and the reaction mixture was stirred overnight. Benzene was removed, and the white solid was crystallized from a benzene/*n*-hexane mixture.

All other complexes were prepared similarly. Physical, analytical and spectroscopic data are given in Table II.

Reaction of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ with Pyridine. To a solution of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ (0.15 mmol) in benzene was added pyridine (0.45 mmol) and the reaction mixture was refluxed for ~2 h. The solvent was removed in vacuo, and the white solid was crystallized from a benzene/*n*-pentane mixture.

Reaction of $NaBH_4$ with $PdH(Cl)(t\text{-}Bu_3P)_2$ (I), $PdCl(P\text{-}C)(P\text{-}t\text{-}Bu_3)$ (III), and $[Pd_2Cl_2(P\text{-}C)_2]$ (III) [(P-C) = $t\text{-}Bu_2PCMe_2CH_2$]. To a solution of $PdH(Cl)(t\text{-}Bu_3P)_2$ (I) (1.0 mmol) in dried ethanol was added excess of $NaBH_4$ (5.0 mmol) and the reaction mixture was stirred for ~2 h. The ethanol was removed under reduced pressure and the residue was extracted with *n*-hexane. On cooling of the *n*-hexane solution, white crystals were obtained in 65% yield. Physical, analytical, and spectroscopic data for this product showed it to be $(t\text{-}Bu_3P)_2Pd^0$.

Similarly, the reaction of $NaBH_4$ with $PdCl(P\text{-}C)(t\text{-}Bu_3P)$ (II) or $[Pd_2Cl_2(P\text{-}C)_2]$ (II) gave the complex $(t\text{-}Bu_3P)_2Pd^0$ in 62 and 30% yields, respectively.

Reaction of $PdH(Cl)(t\text{-}Bu_3P)_2$ with BuLi. To a suspension of $PdH(Cl)(t\text{-}Bu_3P)_2$ (1.0 mmol) in dry *n*-hexane (30 mL) was slowly added a solution of *n*-BuLi (1.1 mmol) in *n*-hexane with continuous stirring. The reaction mixture was stirred overnight and the contents were filtered. The filtrate was concentrated and cooled, and the white crystals thus obtained were identified as $(t\text{-}Bu_3P)_2Pd^0$.

Acknowledgment. The continued financial support of this work by the Natural Sciences and Engineering Research Council of Canada is greatly appreciated.

Registry No. *trans*-$PdH(Cl)(t\text{-}Bu_3P)_2$, 63166-71-2; *trans*-$PdH(CF_3COO)(t\text{-}Bu_3P)_2$, 62922-33-2; $PdCl(P\text{-}C)(t\text{-}Bu_3P)$, 63230-80-8; $Pd(CF_3COO)(P\text{-}C)(t\text{-}Bu_3P)$, 69721-10-4; $Pd_2Cl_2(P\text{-}C)_2$, 69393-58-4; $Pd_2(CF_3COO)_2(P\text{-}C)_2$, 69796-89-0; $PdCl(P\text{-}C)(Et_3P)$, 71000-98-1; $PdCl(P\text{-}C)(Ph_3P)$, 71000-99-2; $PdCl(P\text{-}C)(Ph_2MeP)$, 71001-00-8; $PdCl(P\text{-}C)(t\text{-}Bu_2MeP)$, 71031-53-3; $PdCl(P\text{-}C)(i\text{-}Pr_3P)$, 71001-01-9; $PdCl(P\text{-}C)(Cy_3P)$, 71001-02-0; $PdCl(P\text{-}C)((C_7H_7)P_3)$, 71001-03-1; $PdCl(P\text{-}C)(Ph_3As)$, 71001-04-2; $PdCl(P\text{-}C)(py)$, 71001-05-3; $PdCl_2(NCPh)_2$, 14873-63-3; $(t\text{-}Bu_3P)_2Pd$, 53199-31-8; HCl, 7647-01-0; CF_3COOH, 76-05-1.

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Synthesis and Characterization of Bis[μ-[bis(diphenylphosphino)methane]]-μ-methylene-dichlorodiplatinum and Related Complexes. Insertion of Methylene into a Pt–Pt Bond

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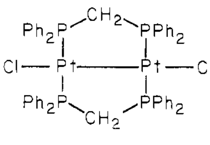
Reaction of the diplatinum(I) complex $[Pt_2Cl_2(\mu\text{-dppm})_2]$, dppm = bis(diphenylphosphino)methane, with CH_2N_2, SO_2, and S_8 gives the adducts $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-dppm})_2]$ where X = CH_2, SO_2, or S, respectively. Where X = CH_2, this represents the first example of simple addition of methylene to a metal–metal bond. Reaction of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ with MeSH gives $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. The structures of the complexes were deduced primarily with ^1H and ^{31}P NMR spectroscopy, and it is concluded that Pt–Pt bonding is absent or very weak in all cases.

Introduction

Recently we have shown that platinum, when complexed with bis(diphenylphosphino)methane (dppm), readily forms a number of binuclear complexes in which the ligand adopts a bridging role.[2-5] An example is $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I), an air-stable complex containing two directly bonded platinum atoms in the formal oxidation state of I.[2,3]

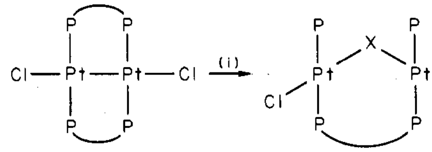


I

The platinum–platinum bond in this complex may, as we have previously shown, be reversibly protonated[4] or undergo reversible addition of carbon monoxide[3,5] to give complexes in which the added group, viz., H^+ or CO, bridges the two platinum atoms. The related ligand bis(diphenylarsino)methane (dpam) also gives a similar platinum–carbonyl complex, namely, $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$, although the dpam analogue of I is unknown.[5] The ability of dppm and similar ligands to promote the formation of binuclear complexes by bridging two atoms rather than chelating to one is demonstrated by the chemistries of other metals. Indeed, recent publications show that a concurrent and independent investigation of palladium gave remarkably similar results. Thus X-ray structural studies show that $[Pd_2Br_2(\mu\text{-dppm})_2]$[6,7]

contains a direct Pd–Pd bond and has a similar structure to that of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ and that $[Pd_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$,[7,8] interestingly, does not contain a direct Pd–Pd bond.[21] Balch and his co-workers[9,10] have also shown that carbon monoxide, isocyanides, and sulfur dioxide insert reversibly into the Pd–Pd bonds of the complexes $[Pd_2X_2(\mu\text{-dppm})_2]$ (X = Cl, Br), and X-ray structural determination on $[Pd_2(CNMe)_2(\mu\text{-CNMe})(\mu\text{-dppm})_2]$ and $[Pd_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2]$ shows the absence of direct Pd–Pd bonds in these products. Insertion of aryldiazonium ions in $[Pd_2Cl_2(\mu\text{-dppm})_2]$ has also been reported.[11] Working with the rhodium system, Kubiak and Eisenberg[12] have also shown the absence of a direct metal–metal bond in $[Rh_2(CO)_2(\mu\text{-S})(\mu\text{-dppm})_2]$. They aptly coined the term "A-frame" molecules to describe these bridged structures.

In this paper we report the following insertions of methylene, sulfur dioxide, and sulfur into the Pt–Pt bond of complex I and a further reaction between the hydride $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ and methanethiol.

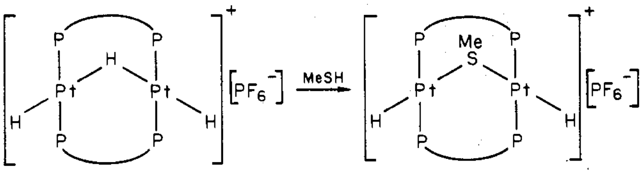


I

II, X = CH_2, (i) = CH_2N_2

III, X = SO_2, (i) = SO_2

IV, X = S, (i) = S_8



V

A preliminary account of this work has already been published.[13] The most interesting of these reactions is the insertion of methylene, via the use of diazomethane, to afford the complex $[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$. This is, as far as we are aware, the first reported reaction in which the grouping $M_2(\mu\text{-CH}_2)$ has been obtained by addition of CH_2 to a metal–metal bond in a complex, although a closely related reaction[14] involving displacement of a bridging carbonyl group affords a complex containing the $Rh_2(\mu\text{-CH}_2)$ unit.

Experimental Section

Preparation of Complexes. The complexes all retained solvent (dichloromethane) of crystallization despite vacuum drying (10^{-3} torr) at room temperature for several hours. Evidence for the presence of solvent came from NMR and mass spectral measurements and microanalyses. The latter were performed by Alfred Bernhardt Microanalytisches Laboratorium, Mülheim, West Germany.

Diazomethane was prepared from *N*-nitroso-*N*-methylurea by the published procedure.[15] Methanethiol (BDH Ltd) was used without further purification. Dichloromethane-d_2 (Aldrich Chemical Co. Inc.) and tetrachloroethane-d_2 (Stohler Isotope Chemicals) were dried with molecular sieves for 1–2 h immediately prior to their use as NMR solvents.

NMR spectra were recorded with a Bruker WH-90 spectrometer. In this paper, as in previous publications,[2-5,13,16] the convention of negative upfield shifts and positive downfield shifts (with respect to the reference) has been adopted.

$[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$. In one reaction, 15 mL of a 1% solution of diazomethane (~3.6 mmol) in diethyl ether was slowly added (30 min) to a solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$[2] (1.45 g, 1.10 mmol) in dichloromethane (40 mL) at 0 °C. During the addition a colorless gas was evolved and the solution darkened. The solution was allowed to stand for 12 h, and then the lemon yellow product was crystallized by evaporating the solution to half its original volume. The yield was 1.02 g (72%). The product was recrystallized by dissolving it in boiling dichloromethane (250 mL), filtering while hot to remove a trace of insoluble white impurity, and evaporating the solution down to 30 mL. The yield of recrystallized product was 0.83 g (58%). Anal. Calcd for $[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]\cdot 0.5CH_2Cl_2$: C, 48.08; H, 3.68; P, 9.63; Cl, 8.27. Found: C, 48.22; H, 3.67; P, 9.83; Cl, 8.03.

Other reactions on a somewhat smaller scale gave yields of between 55 and 65%. A comparison between reactions carried out at 0 °C and at 20 °C indicated that the former temperature is probably preferable.

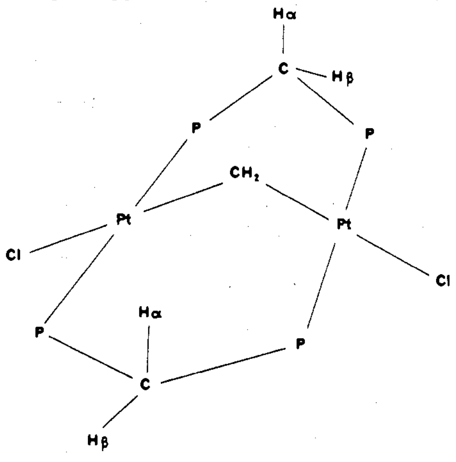
$[Pt_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2]$. In a typical preparation, sulfur dioxide was passed through a solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$[2] (0.23 g) in dichloromethane (4 mL) for 30 min. The orange solution was allowed to stand for 1 h. Isooctane was then slowly added, and the yellow crystalline product (0.22 g, 94%) was recovered by filtration. Anal. Calcd for $[Pt_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2]\cdot 0.5CH_2Cl_2$: C, 45.38; H, 3.40; Cl, 7.95; S, 2.39. Found: C, 45.14; H, 3.36; Cl, 8.05, S, 2.24.

$[Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]$. A solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$[2] (0.62 g, 0.47 mmol) in dichloromethane (25 mL) was stirred with finely powdered sulfur (0.03 g, 0.93 mmol), and the color of the solution slowly darkened to orange. After 3 h the excess of sulfur was removed by filtration. The orange microcrystalline product (0.48 g, 79%) was obtained by addition of isooctane to the filtrate. The product thus obtained was recrystallized by dissolving it in boiling dichloromethane and by filtering hot and evaporating the solution to one-fourth its original volume in a stream of nitrogen. The yield was 0.34 g (56% overall) of material with IR spectrum identical with that of the initial product. Anal. Calcd for $[Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]\cdot 0.2CH_2Cl_2$: C, 47.14; H, 3.50; Cl, 6.65; S, 2.51. Found: C, 46.53; H, 3.45; Cl, 6.69; S, 2.16.

$[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. Methanethiol was bubbled through an almost colorless solution of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$[4] (0.61 g) in dichloromethane (6 mL) for 30 min. The pale green solution was then allowed to stand in a stoppered flask for 2 days at 4 °C. The solution was then yellow, and a crop of yellow crystals (0.40 g) had separated, and these were recovered by filtration. A second crop (0.17 g), somewhat darker in color but with an identical IR spectrum, was obtained by evaporation of the filtrate to about half its volume followed by addition of methanol. The total yield was thus 0.57 g (85%). Anal. Calcd for $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]\cdot CH_2Cl_2$: C, 43.43; H, 3.58; Cl, 4.93; F, 7.93; S, 2.23. Found: C, 43.31; H, 3.57; Cl, 4.69; F, 7.92; S, 2.37.

Results

Synthesis and Characterization of $[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$ (II). On addition of diazomethane in ether to the pale yellow $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I) an orange-brown color, possibly indicative of an unstable complex of CH_2N_2 with I, develops immediately and then fades to yellow-orange in less than 1 min. The lemon yellow, methylene-bridged complex $[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$ (II), once isolated, is only sparingly soluble in dichloromethane but sufficiently so in the hot solvent for it to be separated from a small amount of white amorphous impurity, presumably polymethylene. Complex II appears indefinitely stable as a solid, and its solutions in $C_2D_2Cl_4$ are stable at least over a period of weeks. The presence of a $Pt_2(\mu\text{-CH}_2)$ group in II is shown by a ^1H resonance (Table



II

Table I. ^1H NMR Data for the μ-dppm Groups[a]

complex	$\delta(CH_2)$, ppm	^3J-(PtH), Hz	^2J-(HH), Hz
$[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (II)	2.90[b]	57	13
	3.80[b]	10	
$[Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$ (III)	2.84[c]	31.0	14
	4.42[c]	11.2	
$[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ (IV)	2.77[d]	62	12
	4.89[d]	12	
$[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ (V)	4.12[e]		
	3.82[f]		
	4.51[f]		
$[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I)[g]	4.46	54.0	

[a] At 60 MHz (35 °C) in $C_2D_2Cl_4$ unless otherwise indicated. [b] At 80 °C. [c] At 70 °C. [d] Also observed at 220 MHz. [e] At 50 °C: δ (PtH), −10.80; ^1J(PtH), 1152 Hz. [f] At −40 °C: δ(PtH), −10.75; ^1J(PtH), 1146 Hz. [g] Data from ref 2.

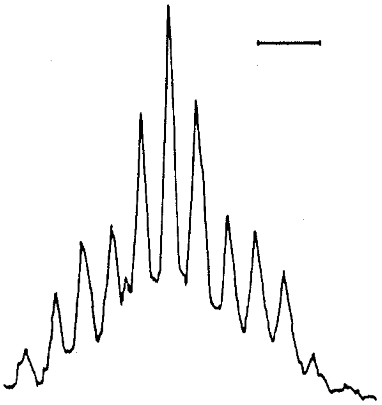


Figure 1. ^1H NMR spectrum (90 MHz) of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ in the region of the CH_2Pt_2 resonance. The resonance is centered at δ 1.08, and the bar represents 20 Hz.

I) at δ 1.08 at 80 °C (in $C_2D_2Cl_4$), consisting of 13 observable peaks (Figure 1) with regular spacings of approximately 9 Hz. These are interpreted as arising from coupling to ^{195}Pt atoms which are part of a Pt_2 unit and from further coupling to four equivalent ^{31}P atoms. The former coupling gives rise to a 1:8:17:8:1 pattern (to the nearest integer), assuming coupling of equal magnitude to either of the Pt atoms, and the latter to the usual 1:4:6:4:1 quintet. Thus five sets of quintets are to be expected, but it is assumed that two lines of each quintet are now imposed on those of each adjacent quintet. The coupling constants $^2J(PtH) = 54$ Hz and $^3J(PH) = 9$ Hz are derived on this basis. Thus a pattern of 17 lines is expected, the inner 13 of which should have relative intensities of 0.06:0.11:0.31:0.45:0.47:0.74:1.00:0.74:0.47:0.45:0.31:0.11:0.06. The observed peaks are in good agreement with these values and agreement in respect to approximately equal intensities for the second and third peaks on each side of the center is worth noting. The outer lines, too weak to be observed, should have relative intensities 0.04 and 0.01 on each side. The observed intensities cannot be matched with those derived for a similar system of coupling to one platinum atom (a 1:4:1 pattern) and four equivalent ^{31}P atoms. The better of two possible arragements of 13 lines that can be thus derived is 1:4:6:4:5:16:24:16:5:4:6:4:1, clearly not in accord with the observed spectrum. Thus the observed resonance provides strong evidence for the presence of a symmetrical $Pt_2(\mu\text{-}CH_2)$ bridge.

The ^1H resonances of the CH_2 groups of the μ-dppm ligands (Figure 2, Table I) are also interesting in that they show the presence of two different resonances as proved by observing them at 60 and 100 MHz. This is in contrast to the CH_2 groups of, say, complex I where the four CH_2 protons are effectively equivalent, only one 1:8:17:8:1 resonance being observed (coupling to ^{31}P is not resolved).[2] Clearly the presence of the bridging CH_2 group in II creates a nonequivalence in the protons of the $P\text{–}CH_2\text{–}P$ groups, which are distinguished by α and β in structure II. The basic doublet-of-doublets structure of the resonances (see Figure 2) is thus explained by $H_\alpha\text{–}H_\beta$ coupling [$^2J(HH) = 13.0$ Hz], creating an AB quartet. One of these hydrogen atoms has a much larger coupling constant with the platinums [$^3J(PtH) = 58$ Hz) than the other [$^3J(PtH) = 10$ Hz): the center three peaks of the 1:8:17:8:1 pattern were observed. Superimposed upon this structure lies the 1:2:1 triplet splitting due to the phosphorus atoms [$^2J(PH) = 3$ Hz], which has only been resolved for the higher field resonance.

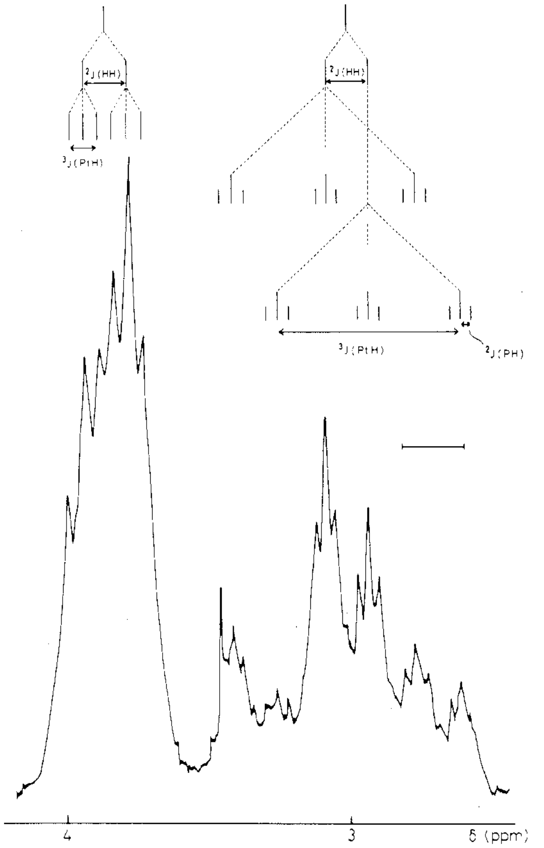


Figure 2. ^1H NMR spectrum (90 MHz) of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ in the region of the CH_2P_2 resonance. The bar represents 20 Hz.

A feature of the ^1H NMR spectrum is that the $Pt_2(\mu\text{-}CH_2)$ and $P\text{–}CH_2\text{–}P$ resonances are better resolved at 80 °C than at 35 °C. The former resonance at 35 °C although ill-resolved is less symmetrical about the center than at 80 °C. This is thought to be due to insufficiently rapid interconversion of different conformations of the fused nonplanar five-membered Pt_2P_2C rings of the $Pt_2(\mu\text{-dppm})_2$ system.

The $^{31}P\{^1H\}$ NMR spectrum of II represents a spin system similar to that of the parent complex I and to other complexes with a symmetrical $Pt_2X_2(\mu\text{-dppm})_2$ skeleton, showing that all the phosphorus atoms are chemically equivalent. The coupling constants (Table II) were obtained as described for the μ-SO_2 complex (III) below. The chief differences between I and II arise in the signs and magnitudes of the coupling constants: $^2J(PtP)$ is positive for II but negative for I, and the value of the long-range trans coupling constant $^3J(PPtPtP)$ is much smaller for II than for I. We have argued elsewhere that these differences are due to the absence of the Pt–Pt bond and hence a considerably greater Pt–Pt separation in complex II than in the parent I.[16] In agreement with this, the AB subspectra observed in the ^{31}P NMR spectrum of I due to species containing two ^{195}Pt atoms,[17] and which appear well separated

Table II. ^{31}P NMR Spectra of the Complexes

compd	$\delta(P)$[a]	^1J-(PtP), Hz	^2J-(PtP), Hz	^3J-(PP), Hz	^3J-(PP), Hz	N',[b] Hz
II	+10.05	3388	+73	23	6	3462 (3461)
III	+19.5	3588	+273	43	0	3864 (3861)
IV	+1.45	2884	c	c	c	c
V	+9.95	2999	c	c	c	c
	+9.15	2910				
I[d]	−0.02	2936	−136	62.5	26.4	2800 (2800)

[a] From trimethyl phosphate reference, in CD_2Cl_2 or $C_2D_2Cl_4$. [b] $N' = {}^1J(PtP) + {}^2J(PtP)$, calculated values are given in parentheses. [c] Not resolved. [d] Data from ref 2.

from other resonances since the value of ^1J(PtPt) is very large (8197 Hz), are not observed for II, indicating a much lower value of ^1J(PtPt) and hence presumably much weaker (if any) Pt–Pt bonding interaction.

Synthesis and Characterization of [$Pt_2Cl_2(\mu$-X)(μ-dppm)$_2$] (X = SO_2, S). Reaction between complex I and sulfur dioxide occurs readily, as shown by an immediate deepening of the yellow color, when excess of the gas is bubbled through a dichloromethane solution. It is essentially complete after the solution has been standing at room temperature for ~1 h. The yellow μ-SO_2 complex [$Pt_2Cl_2(\mu$-$SO_2)(\mu$-dppm)$_2$] (III) may then be crystallized in excellent yield (94%). Shorter reaction times give product contaminated with unreacted complex I. Complex III, in contrast to [$Pd_2Cl_2(\mu$-$SO_2)(\mu$-dppm)$_2$],[9] does not lose SO_2 on passing nitrogen through its solution in dichloromethane, on boiling its solution in this solvent, or on heating the solid in vacuo at 80 °C for 1 h. However, it does lose SO_2 when its solution in $C_2H_4Cl_2$ is heated under reflux for 2 h: subsequent evaporation of the solvent gives I in good yield.

The related sulfur complex [$Pt_2Cl_2(\mu$-S)(μ-dppm)$_2$] (IV) is formed in good yield (79%) merely by stirring a dichloromethane solution of I with a suspension of sulfur and removing the excess of sulfur by filtration.

Their NMR spectra prove that both of these complexes have the binuclear symmetrically bridged structures. Thus both III and IV show two ^1H resonances (Table I) for the H_α and H_β atoms of the P–CH_2–P groups, and Pt–H and H_α–H_β coupling but not P–H coupling is observed. As was the case for complex II, the resolution is better at slightly elevated temperatures. In the case of the μ-S complex (IV), the resonance at δ 2.77 has ^3J(Pt–H) sufficiently greater than ^2J(H–H) for the inner pair of ^{195}Pt satellites to be separated from the central peak, and their relative intensities (approximately half that of the central peak) confirm that the group is bridging two platinum atoms. In none of these resonances is it possible to observe the weak outer satellites of the 1:8:17:8:1 system. In the other P–CH_2–P resonance of IV and in both P–CH_2–P resonances of III, Pt–H and H–H splittings overlap, but the peaks are readily analyzed and J values assigned (Table I).

The $^{31}P\{^1H\}$ NMR spectrum of III is illustrated in Figure 3. The analysis of the ^{31}P NMR of species containing the $Pt_2X_2(\mu$-dppm)$_2$ skeleton (and the spin-labeling system) has been discussed in detail elsewhere.[2,4,5,16] However, as shown by the comparison of the low-field satellite structures of I and III in Figure 4, the introduction of the bridging SO_2 has dramatically changed the appearance of the spectrum [a similar pattern is observed for the μ-CH_2 complex (II) (vide supra) and for [$Pt_2Cl_2(\mu$-CO)(μ-dppm)$_2$][5,16]]. The triplet appearance of the satellite of III is due to the parameters N and L having the same magnitude.

$$N = J(AA'') + J(AA''')$$

$$L = J(AA'') - J(AA''')$$

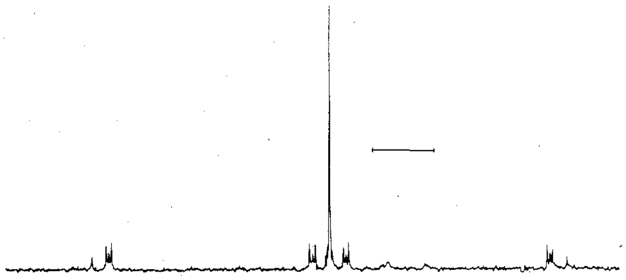


Figure 3. ^{31}P NMR spectrum (36.4 MHz) of [$Pt_2Cl_2(\mu$-$SO_2)(\mu$-dppm)$_2$]. Field strength increases from left to right and the bar represents 500 Hz.

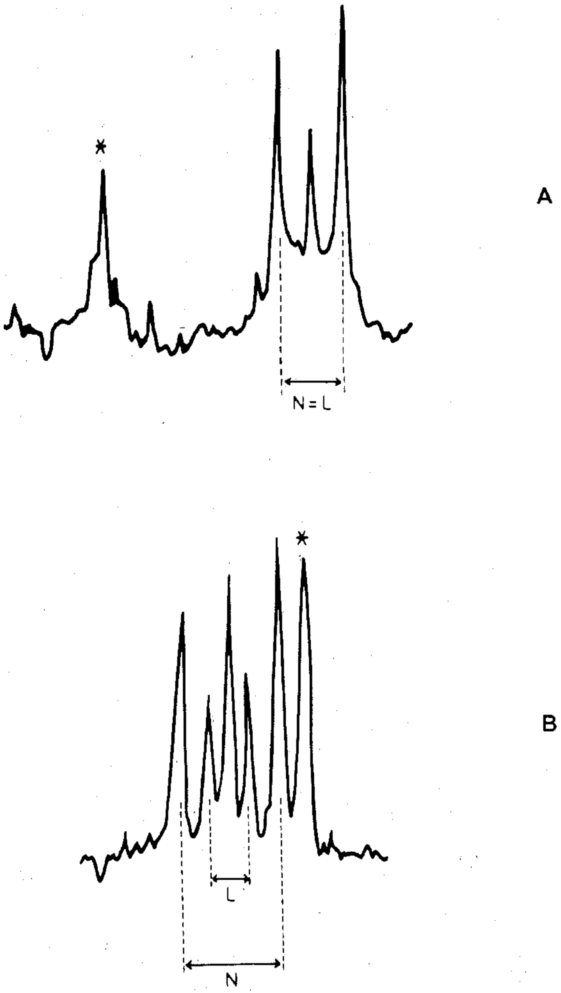


Figure 4. Low-field ^{195}Pt satellites in the ^{31}P NMR (36.4 MHz) spectra of (A) [$Pt_2Cl_2(\mu$-$SO_2)(\mu$-dppm)$_2$] and (B) [$Pt_2Cl_2(\mu$-dppm)$_2$]. The asterisked peaks are due to the AA'A''A'''XX' spin system, and the horizontal scale is in arbitrary units.

Hence, the trans coupling constant $J(AA''')$ must be zero in complexes showing this distinctive pattern. It thus follows[16] that there is no Pt–Pt bonding interaction in III. This is in accord with the known crystallographic data on [$Pd_2Cl_2(\mu$-CO)(μ-dpam)$_2$],[7,8] [$Pt_2Cl_2(\mu$-CO)(μ-dpam)$_2$],[18] [$Pd_2Cl_2(\mu$-$SO_2)(\mu$-dppm)$_2$],[9] and [$Rh_2(CO)_2(\mu$-S)(μ-dppm)$_2$],[12] which reveal metal–metal distances which would normally be considered too long to accommodate a bonding interaction. The NMR data would confirm that the expected solid-state structure is maintained in solution. The $^{31}P\{^1H\}$ NMR spectrum of IV is poorly resolved, showing only a simple triplet pattern, similar to that observed for V at 80 °C. This is discussed in the following section.

The infrared spectra of both III and IV contain the expected ν(Pt–Cl) bands (Table III), and that of III contains bands at

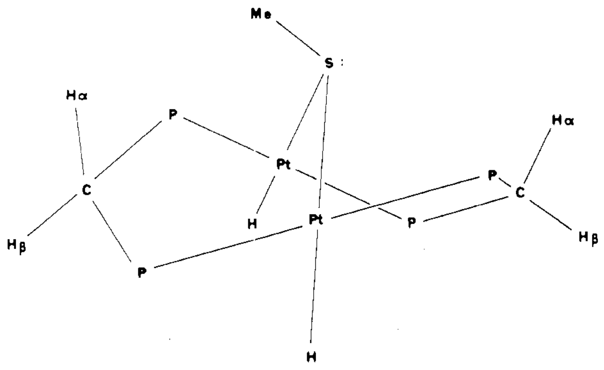
Table III. Infrared Spectral Data

complex	ν(Pt–Cl), cm^{-1}	ν(Pt–H), cm^{-1}
$[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (II)	255	
$[Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$ (III)	274	
$[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ (IV)	286	
$[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I)^a	249	
$[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ (V)		2152
$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]^b$		2137
$[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]^b$	317	2190

^{a} Data from ref 2. ^{b} Data from ref 4.

1148, 1024, and 555 cm^{-1}, confirming the presence of SO_2.[19] These compare with the reported bands at 1165, 1157, 1041, and 1028 cm^{-1} for the analogous palladium compound,[9] the doubling up being due (presumably) to the presence of two slightly different molecules of the latter complex in the unit cell.

Synthesis and Characterization of $[Pt_2H_2[\mu\text{-SMe})(\mu\text{-dppm})_2][PF_3]$ (V). When an excess of methanethiol is bubbled through a dichloromethane solution of the hydride $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$, the solution changes from almost colorless to pale green. When the solution is allowed to stand for 1–2 days, the color becomes yellow-orange as the reaction proceeds to completion. The yellow $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ (V) may then be crystallized. The net result of the reaction is the replacement of a bridging H^- group by a bridging SMe^- group. Hydrogen gas is presumed to be the other product of the reaction. The presence of hydride in complex V is shown by ν(Pt–H) at 2152 cm^{-1} in the infrared spectrum. For comparison the complexes $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ have ν(Pt–H) bands at 2137 and 2190 cm^{-1}, respectively.



V

The NMR spectra of complex V show several interesting features. Over the temperature range 35–75 °C, the ^1H resonance of the μ-SCH_3 group (Figure 5) shows a well-resolved and characteristic 1:8:17:8:1 diplatinum pattern [δ 2.38; ^3J(Pt–H) = 24.6 Hz]. Both of the weak outer satellites may be clearly distinguished. Thus the symmetrical bridging nature of this group appears established. Some broadening of this resonance occurs as the temperature is lowered, and at −40 °C the more intense pair of ^{195}Pt satellites are observed as fairly well-defined shoulders to the main peak. The ^1H resonances of the Pt–H groups are of the 1:4:1 pattern, i.e., show short range Pt–H coupling only. This is in contrast to $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$, the terminal Pt–H groups of which have two sets of ^{195}Pt satellites, giving a 1:1:4:1:1 pattern, as a result of both short and long range Pt–H coupling.[4] The absence of long range coupling in V presumably indicates the absence of a direct Pt–Pt bond. The Pt–H resonances are independent of temperature over the range −40 to +75 °C.

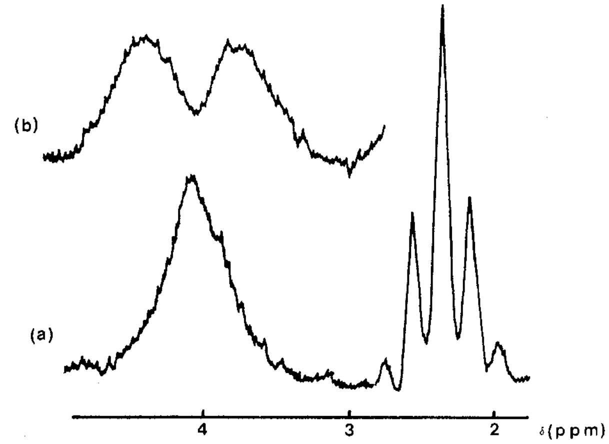


Figure 5. ^1H NMR spectrum (60 MHz) of $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$ in the region of the CH_3S and CH_2P_2 resonances: (a) 50 °C, (b) −5 °C.

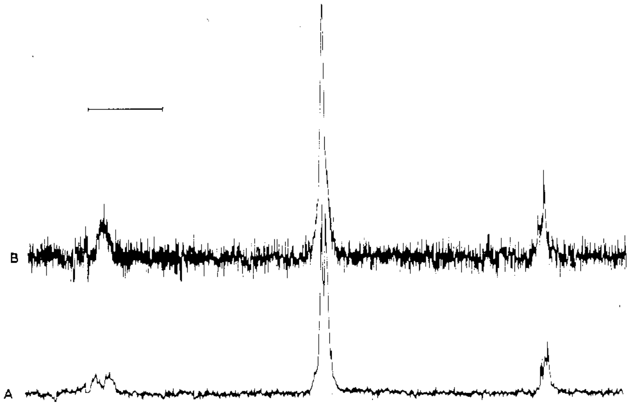


Figure 6. ^{31}P NMR spectrum (36.4 MHz) of $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$: (A) 40 °C, (B) 80 °C. Field strength increases from left to right, and the bar represents 500 Hz.

In the ^{31}P spectrum (Table II) the presence of two resonances observed at 40 °C indicates that the CH_3 group lies to one side of the $Pt_2(\mu\text{-}S)$ plane, lowering the symmetry and causing the two μ-dppm groups to become nonequivalent. The nonequivalent phosphorus atoms have slightly different chemical shifts and give a central A_2B_2 multiplet. The coupling constants $^1J(^{195}Pt^{31}P)$ are also slightly different, and this causes asymmetry in the ^{195}Pt satellite peaks. More rapid inversion at sulfur accounts for the fact that at 80 °C, only one broad ^{31}P resonance is observed (Figure 6). The form of the high-temperature spectrum is similar to that of the room-temperature spectrum of IV, and clearly a similar equivalencing process must be occurring in both molecules. A detailed study of the fluxional processes in these, and related, S- and SR-bridged complexes is currently being undertaken, in order to elucidate the mechanism of this phenomenon. Evidence for a fluxional process is also found in the ^1H NMR spectrum of V. The ^1H resonance of the CH_2 groups of the μ-dppm ligands (in contrast to those of complexes II–IV) appears as only one broad peak over the temperature range 35–75 °C. Thus the H_α and H_β atoms appear to be equivalent. When the temperature is lowered, the resonance broadens further, and at −5 and −40 °C two broad resonances are observed—presumably the expected resonances for H_α and H_β, although no fine structure is observed (Figure 5). A discussion of the mechanism of this process will be reserved until further experimental data on related systems are available.

Discussion

The ability of the ligand dppm to bridge between metal atoms, and hence to hold two metal atoms in close proximity, is now well established. New chemistry can result since other groups may also bridge between the metal atoms,[3-5] and the remarkably easy formation of complexes containing Pt–CH$_2$–Pt, Pt–SO$_2$–Pt, and Pt–S–Pt units along with the Pt$_2$(μ-dppm)$_2$ framework illustrates this effect nicely. Fortunately, the ^{1}H and ^{31}P NMR spectra of the complexes are very rich and allow positive structural assignments to be made. These spectra also indicate that the Pt–Pt bond in I is effectively broken when the group CH$_2$, SO$_2$, or S is added to I.

Complex V, containing the Pt$_2$(μ-SMe)(μ-dppm)$_2$ bridging structure, is interesting in that it shows two fluxional processes. One of these can be identified as an inversion at the bridging sulfur atom, a process which has been observed in other diplatinum complexes.[20] However, a second fluxional process which renders the CH$_2$ protons of each dppm ligand effectively equivalent on the NMR time scale is more unusual. A similar effect has been observed in the complex ion [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$]$^+$, but in this case exchange of bridging and terminal hydride ligands was observed.[4]

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Note Added in Proof. Since submission of this paper, the structure of [Pt$_2$Cl$_2$(μ-CO)(μ-dpam)$_2$] has been determined and found to be similar to its palladium analogue in not containing a direct metal–metal bond. See ref 18.

Registry No. I, 61250-65-5; II, 68851-49-0; III, 68851-13-8; IV, 68851-48-9; V, 69215-82-3; [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$][PF$_6$], 63911-00-2.

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Removal of Ligands from Bis(triphenylphosphine)copper(I) Boranes: Preparation of CuB$_3$H$_8$ and Cu$_2$B$_{10}$H$_{10}$ and Evidence for the Existence of P(C$_6$H$_5$)$_3$CuB$_3$H$_8$ and P(C$_6$H$_5$)$_3$CuBH$_4$ in Solution

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Treatment of bis(triphenylphosphine)copper(I) boranes with B$_2$H$_6$ results in ligand removal through the formation of P(C$_6$H$_5$)$_3$·BH$_3$. The complexes CuB$_3$H$_8$ and Cu$_2$B$_{10}$H$_{10}$ have been prepared from reactions of [P(C$_6$H$_5$)$_3$]$_2$CuB$_3$H$_8$ and {[P(C$_6$H$_5$)$_3$]$_2$Cu}$_2$B$_{10}$H$_{10}$ with B$_2$H$_6$ in CH$_2$Cl$_2$ at 0 °C. The previously unreported CuB$_3$H$_8$ is only slightly soluble in chlorinated hydrocarbons. Evidence for the intermediate species P(C$_6$H$_5$)$_3$CuB$_3$H$_8$ is presented. The reaction of [P(C$_6$H$_5$)$_3$]$_2$CuBH$_4$ with excess B$_2$H$_6$ in CH$_2$Cl$_2$ at −78 °C results in the removal of only 1 mol of P(C$_6$H$_5$)$_3$/mol of complex. The resulting product, P(C$_6$H$_5$)$_3$CuBH$_4$, decomposes rapidly above −10 °C.

Introduction

A number of L$_2$Cu$^{\mathrm{I}}$ boranes have been reported in which L = an organophosphine.[1-18] Examples which are pertinent to this study are [P(C$_6$H$_5$)$_3$]$_2$CuBH$_4$,[1-7] [P(C$_6$H$_5$)$_3$]$_2$CuB$_3$H$_8$,[6-15] and {[P(C$_6$H$_5$)$_3$]$_2$Cu}$_2$B$_{10}$H$_{10}$.[16-18] In these compounds the borane unit appears to be a bidentate ligand with two Cu–H–B three-center bonds per copper atom. Phosphorus-31 NMR spectra indicate that the phosphine ligands of [P(C$_6$H$_5$)$_3$]$_2$CuB$_3$H$_8$ are labile in solution.[8-10,19] The labile character of these phosphine ligands suggested to us the possibility of "capturing" them, thereby producing copper(I) boranes which contain less than two phosphines per molecule. To this end we have succeeded in "tying-up" labile phosphine molecules by adding B$_2$H$_6$ to form P(C$_6$H$_5$)$_3$·BH$_3$. We describe below reactions of B$_2$H$_6$ with bis(triphenylphosphine)copper(I) boranes to give the isolable species CuB$_3$H$_8$ and Cu$_2$B$_{10}$H$_{10}$ and solutions of P(C$_6$H$_5$)$_3$CuB$_3$H$_8$ and P(C$_6$H$_5$)$_3$CuBH$_4$.

Results and Discussion

Cu$_2$B$_{10}$H$_{10}$ and CuB$_3$H$_8$. The complexes {[P(C$_6$H$_5$)$_3$]$_2$Cu}$_2$B$_{10}$H$_{10}$ and [P(C$_6$H$_5$)$_3$]$_2$CuB$_3$H$_8$ react with B$_2$H$_6$ in CH$_2$Cl$_2$ at room temperature according to the following equations.

$$\{[\mathrm{P(C_6H_5)_3}]_2\mathrm{Cu}\}_2\mathrm{B_{10}H_{10}} + 2\mathrm{B_2H_6} \rightarrow \mathrm{Cu_2B_{10}H_{10}} + 4\mathrm{P(C_6H_5)_3{\cdot}BH_3} \quad (1)$$

$$[\mathrm{P(C_6H_5)_3}]_2\mathrm{CuB_3H_8} + \mathrm{B_2H_6} \rightarrow \mathrm{CuB_3H_8} + 2\mathrm{P(C_6H_5)_3{\cdot}BH_3} \quad (2)$$

The structure of Cu$_2$B$_{10}$H$_{10}$ prepared by reaction of copper(II) salts with B$_{10}$H$_{10}$$^{2-}$ salts[16,20,21] reveals B$_{10}$H$_{10}$ polyhedra of D_{4d} symmetry, each joined to four other polyhedra by