(μ-Methylene)diplatinum Complexes: Their Syntheses, Structures, and Properties

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Reaction of $[Pt_2HL(\mu\text{-dppm})_2][PF_6]$, **1**, dppm = $Ph_2PCH_2PPh_2$, with excess CH_2N_2 gives $[Pt_2Me(\mu\text{-}CH_2)L(\mu\text{-dppm})_2][PF_6]$, **2a**, L = CO, or **2b**, L = PMe_2Ph, but gives $[Pt_2Me(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$, **4**, when L = PPh_3, and this reacts slowly with CH_2Cl_2 to give $[Pt_2Cl(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$, **5**. The crystal and molecular structures of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, **6**, and $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-dppm})_2][PF_6]$, **5**, have been determined by X-ray analysis. **6** is tetragonal of space group $P4_32_12$, Z = 4, with a = 15.096 (5) Å and c = 26.349 (4) Å. The structure is based on 2238 intensities and refined to R = 0.060. **5** is monoclinic of space group $P2_1/c$, Z = 4, with a = 13.199 (2) Å, b = 17.866 (6) Å, c = 30.044 (4) Å, and β = 91.20 (3)°. R is 0.074 for 6552 reflections. The structural results indicate that both complexes are A-frames, with CH_2^{2-} and a pair of dppm ligands linking the two d^8 Pt(II) centers. The Pt···Pt distances, 3.151 (1) Å in **6** and 3.120 (2) Å in **5**, are too long to indicate direct metal–metal bonding. The Pt–C–Pt angles are 103.4 (7)° and 94.1 (10)° in **6** and **5**, respectively. Pyrolysis of **2a** gave CH_4 and CO, and reaction of **2a** with $NaBH_4$ or MeLi gave $[Pt_2(\mu\text{-H})Me_2(\mu\text{-dppm})_2][PF_6]$ or *cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$, respectively.

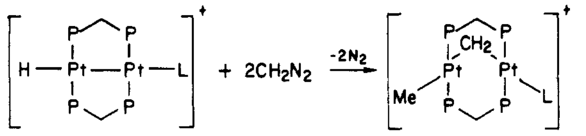
Introduction

There has been great interest in μ-methylene complexes of transition elements, since such compounds are useful for modeling proposed intermediates in a number of catalytic processes.[2-5] Most μ-methylene complexes contain a metal–metal bond and are therefore considered as dimetallacyclopropanes.[2,3] However, μ-methylene complexes without metal–metal bonds are also known.[5-12] This article reports the structure of the first such complex to be reported, namely, $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$,[6] dppm = $Ph_2PCH_2PPh_2$. Also described are the syntheses and properties of some methyl(μ-methylene)diplatinum complexes, which are models for intermediates in the Fischer–Tropsch synthesis,[13-15] and the structure of a (μ-methylene)(triphenylphosphineylide)diplatinum complex cation, $[Pt_2Cl(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2]^+$. A preliminary account of parts of this work has been published.[12]

Results and Discussion

Synthesis of New μ-Methylene Complexes. With the aim of preparing complexes containing $MePtCH_2Pt$ functional groups, the reactions of diazomethane with the complexes $[Pt_2HL(\mu\text{-dppm})_2][PF_6]$ were studied, where L = CO, PMe_2Ph, and PPh_3.[16,17]

When L = CO or PMe_2Ph, reactions using excess diazomethane occurred according to eq 1, $\overset{\frown}{P\ P}$ = dppm.



(1)

1a, L = CO
b, L = PMe_2Ph

2a, L = CO
b, L = PMe_2Ph

The products were air-stable, yellow crystalline solids, which were characterized by elemental analysis and by IR and NMR spectroscopies. For example, complex **2a** gave ν(CO) 2036 cm^{-1}, and the presence of terminal MePt and μ-CH_2Pt_2 groups was clearly demonstrated by the ^1H and $^1H(^{31}P)$ NMR spectra {δ −0.08 [t, ^3J(PH) = 6.0 Hz, ^2J(PtH) = 59 Hz, MePt], 2.71 [m, ^3J(PH) = 5 Hz ^2J(PtH) = 34 Hz, CH_2Pt_2]}. Two different couplings ^2J(PtH) for the μ-CH_2 group are expected, but only an average value could be determined. The $CH_AH_BP_2$ protons occurred as two separate resonances at δ 3.68 [^2J(PH) = 3.6 Hz, ^2J(HH) = 14 Hz, ^3J(PtH) = 49 Hz] and 4.16 [^5J(HH) = 14 Hz], as expected for "A-frame" molecules of this type,[6] and the dppm resonances in the $^{31}P\{^1H\}$ NMR spectrum occurred as a complex AA′BB′ system (parameters are given in the Experimental Section). The spectra due to **2b** were similar, but an extra signal was observed in the $^{31}P\{^1H\}$ NMR spectrum due to the PMe_2Ph ligand at δ −22.9 [^1J(PtP) = 1972 Hz], and the expected extra couplings due to the PMe_2Ph ligand were also observed. The low value for ^1J(PtPMe$_2$Ph) and the low value for the coupling ^2J(PtH) of the methylplatinum group show that the μ-CH_2 group exerts a strong trans influence.[5,16,17] This is expected for a group in which the CH_2Pt_2 unit contains two Pt–C σ-bonds, with no "carbene" character.

The formation of complexes **2** involves insertion of CH_2 units from diazomethane into both Pt–Pt and Pt–H bonds,

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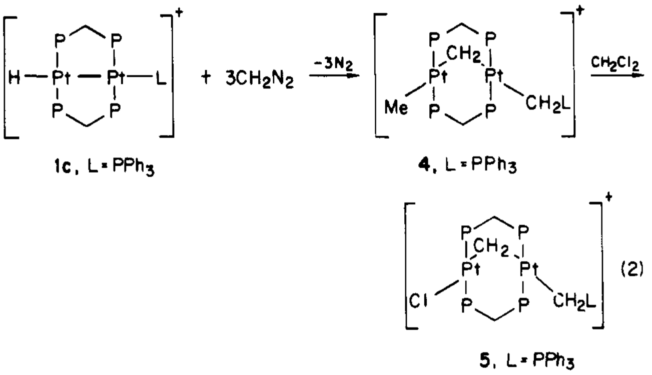
and an effort was made to determine the sequence of reactions. Reaction of **1a** in CH_2Cl_2 with a stoichiometric quantity of CH_2N_2 gave some starting material and a new complex containing a $(\mu\text{-}CH_2)Pt_2$ group but no MePt group. This complex could not be purified but was tentatively identified as $[Pt_2Cl(CO)(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^+$. It was presumably formed by reaction of initially formed $[Pt_2H(CO)(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^+$ with solvent CH_2Cl_2,[18] due to the hydridic nature of hydride trans to carbon. The experiment indicates that the first CH_2 insertion occurs at the Pt–Pt bond, and a one-step mechanism, as suggested by Espenson,[19] is considered probable. It was also shown that $[Pt_2Me(PMe_2Ph)(\mu\text{-dppm})_2]^+$, **3**, failed to react with CH_2N_2 (for reasons which are not known), and hence reaction of **1b** with CH_2N_2 *must* involve initial reaction at the Pt–Pt bond. Thus, if the initial reaction was at the Pt–H bond, complex **3** would be formed and would not react further with CH_2N_2.

The reaction of $[Pt_2H(PPh_3)(\mu\text{-dppm})_2]^+$ with CH_2N_2 was different and occurred according to eq 2, L = PPh_3 and $P\frown P$ = dppm.



1c, L = PPh_3 **4**, L = PPh_3 **5**, L = PPh_3 (2)

The initial product was **4**, as characterized by the ^1H and ^{31}P NMR spectra, but this slowly reacted with the solvent CH_2Cl_2 to give **5** by cleavage of the methylplatinum group.[18] The spectroscopic characterization of **4** followed closely that for **2b**, except that resonances due to the triphenylphosphine ylide were observed. In the ^1H NMR spectrum, the CH_2L protons appeared at δ 1.77 [$^2J(PH)$ = 18 Hz, $^2J(PtH)$ = 68 Hz], and in the ^{31}P NMR spectrum the ylide signal was observed at δ 29.75 [$^2J(PtP)$ = 45 Hz, $^4J(PtP)$ = 27 Hz]. These parameters are similar to those observed for mononuclear triphenylphosphine ylide complexes of platinum.[20] Spectral data for **5** were similar, but no CH_3Pt resonances were observed and **5** was also characterized by X-ray crystallography (see below).

The insertion of CH_2 from diazomethane into a PtP bond is a new reaction, and we have no data on the mechanism. It could, for example, occur in a single step, or it could involve rearrangement of a $Pt(CH_2)(PPh_3)$ or $Pt(CH_2N_2)(PPh_3)$ intermediate by migratory insertion, or it could involve displacement of PPh_3, followed by nucleophilic attack by PPh_3 on a cationic $Pt{=}CH_2$ or $Pt(CH_2N_2)$ group. There are precedents for all of these mechanisms.[19-22] The formation of the ylide when L = PPh_3, but not when L = PMe_2Ph, suggests that the relief of steric strain is an important factor in influencing reactivity. In the ylide derivative the bulky PPh_3 group is further removed from the congested platinum center. In order to study the ylide formation separately, we have attempted to prepare complex **2** with L = PPh_3 by displacement of CO with PPh_3 from complex **2a**. However, no reaction occurred even under forcing conditions. Since PPh_3 normally displaces CO from platinum(II) complexes

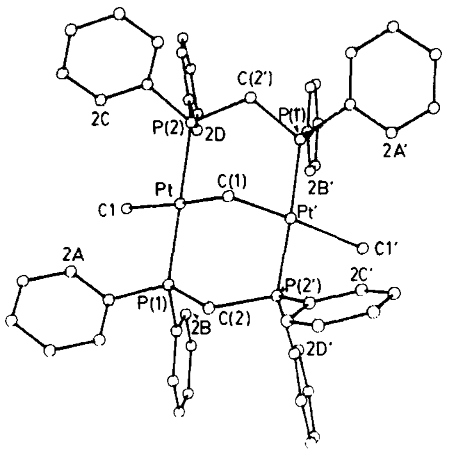


Figure 1. The molecular structure of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (**6**) viewed approximately along the crystallographic diad axis passing through C(1). Hydrogen atoms are omitted. The phenyl carbon atoms are numbered cyclically C(1n)···C(6n), starting with the carbon atom attached to phosphorus. Here and in Figure 3 only the sequence number of C(2n) is given for clarity.

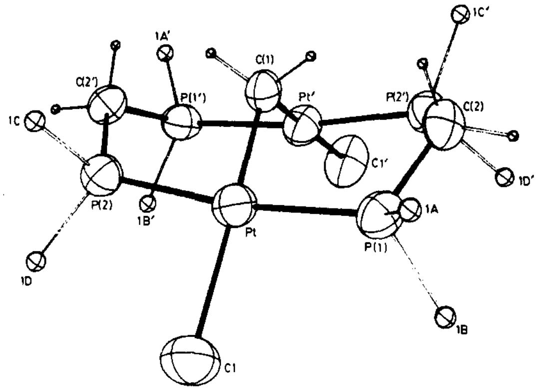


Figure 2. Another view of the $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (**6**) molecule. Phenyl carbon atoms not bonded to phosphorus are omitted, and only methylene hydrogen atoms are shown. The 50% probability ellipsoids are displayed, except for phenyl carbon and for hydrogen atoms which are represented by small spheres of arbitrary radius ($r_H < r_C$).

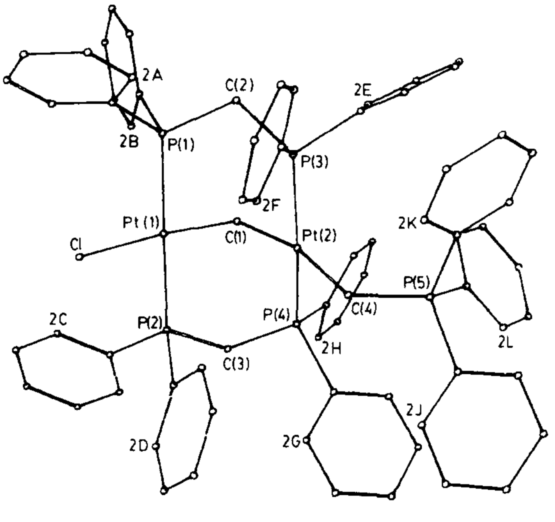


Figure 3. The structure of the $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^+$ cation.

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[18] Unfortunately, complexes **1**, **2**, and **4**, are not soluble in benzene, acetone, and other non-chlorinated organic solvents.

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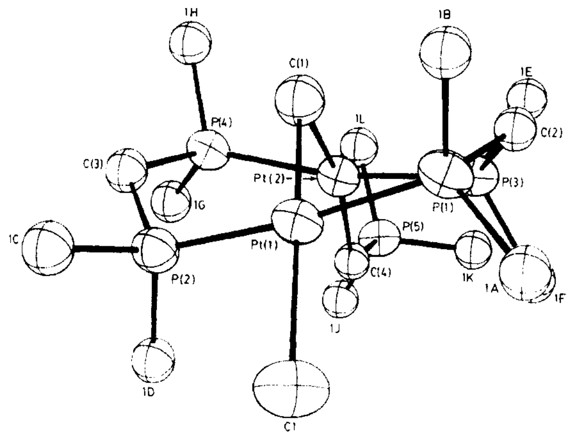

Figure 4. Another view of the $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]^+$ cation. Hydrogen atoms, and carbon atoms not bonded to Pt or P atoms, are omitted. The 50% probability ellipsoids are displayed.

Table I. Selected Interatomic Distances (Å) and Angles (deg) in $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$

Distances

Pt–P(1)	2.302 (5)	Pt–P(2)	2.286 (5)
Pt–Cl	2.439 (5)	Pt–C(1)	2.008 (13)
P(1)–C(2)	1.800 (17)	P(1)–C(1A)	1.796 (13)
P(1)–C(1B)	1.832 (18)	P(2)–C(2′)[a]	1.876 (16)
P(2)–C(1C)	1.793 (18)	P(2)–C(1D)	1.851 (13)

Angles

P(1)–Pt–P(2)	171.3 (2)	P(1)–Pt–Cl	94.5 (2)
P(1)–Pt–C(1)	87.7 (4)	P(2)–Pt–Cl	92.2 (2)
P(2)–Pt–C(1)	85.7 (4)	Cl–Pt–C(1)	177.8 (4)
Pt–P(1)–C(2)	114.7 (6)	Pt–P(1)–C(1A)	115.7 (6)
Pt–P(1)–C(1B)	118.1 (7)	C(2)–P(1)–C(1A)	101.2 (7)
C(2)–P(1)–C(1B)	102.3 (9)	C(1A)–P(1)–C(1B)	102.5 (7)
Pt–P(2)–C(2′)	113.3 (6)	Pt–P(2)–C(1C)	111.2 (7)
Pt–(P(2)–C(1D)	120.7 (7)	C(2′)–P(2)–C(1C)	104.7 (9)
C(2)–P(2)–C(1D)	101.8 (8)	C(1C)–P(2)–C(1D)	103.5 (9)
Pt–C(1)–Pt′	103.4 (7)	P(1)–C(2)–P(2′)	115.2 (9)

[a] Here and elsewhere the diad operation *y*, *x*, $\bar{z}$ relates primed atoms to the corresponding unprimed atoms in Table IV.

rapidly,[23] we suggest that steric effects are unfavorable in this case.

Structures of the μ-Methylene Complexes. The structures of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$, **6**, and $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-}dppm)_2][PF_6]$, **5**, where dppm = $Ph_2PCH_2PPh_2$, have been determined by X-ray diffraction. They are shown in Figures 1–4, , and selected interatomic distances and angles are presented in Table I and II. Molecules of **6** lie astride a crystallographic diad axis.

In **6** the metal atoms are spanned by two bridging dppm ligands in a mutually trans arrangement. They are also linked by a CH_2^{2-} methylene ligand lying at the apex of the Cl–Pt–C–Pt–Cl linkage, which is perpendicular to the Pt_2P_4 mean plane (dihedral angle 90°). Each d^8 Pt(II) metal center is surrounded by a square-planar *trans*-P_2ClC donor set. A similar molecular framework is found in the cation of **5**, which can be considered formally as derived from **6** by replacement of a chloro ligand with the sterically more demanding ylide $Ph_3P{=}CH_2$. Thus both complexes adopt A-frame structures.[24]

The most noteworthy structural feature of **6** and **5** is the geometry of the $Pt–CH_2–Pt$ bridge. The Pt⋯Pt separations, 3.151 (1) Å in **6** and 3.120 (2) Å in **5**, fall well outside the range considered typical of Pt–Pt single bonds [ca. 2.531 (1)–2.890 (2) Å].[25] Thus the presence of significant Pt-Pt bonding is neither indicated by the observed Pt⋯Pt separations nor required by the 16-electron count of the metal ions. Extended Hückel molecular orbital calculations of Hoffman and Hoffman[26] have led to a similar conclusion regarding the absence of a direct metal–metal bonding interaction in a hypothetical methylene-bridged molecular A-frame, $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}H_2PCH_2PH_2)_2]^{2-}$, which is isoelectronic with **6** and **5**. In contrast to dimetallacyclopropane systems, which have been extensively studied recently and where formation of M_2C three-membered rings leads to constrained M–C–M angles of 76–81°,[2,3,13] in **6** and **5** the Pt–C–Pt angles are greater than 90°. In both **6** and **5** the methylene groups are positioned symmetrically relative to the metal centers, but the average values of the Pt–C distances [2.01 (2) and 2.13 (2) Å, respectively] are slightly different in the two complexes, as are the Pt–C–Pt angles [103.4 (7) and 94.1 (10)°].

Table II. Selected Interatomic Distances (Å) and Angles (deg) in $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$

Distances

Pt(1)–Pt(2)	3.120 (2)	Pt(1)–P(1)	2.258 (7)
Pt(1)–P(2)	2.276 (7)	Pt(1)–Cl(1)	2.429 (8)
Pt(1)–C(1)	2.130 (25)	Pt(2)–P(3)	2.283 (7)
Pt(2)–P(4)	2.265 (7)	Pt(2)–C(1)	2.131 (26)
Pt(2)–C(4)	2.145 (21)	P(1)–C(2)	1.862 (21)
P(1)–C(1A)	1.818 (21)	P(1)–C(1B)	1.871 (15)
P(2)–C(3)	1.851 (23)	P(2)–C(1C)	1.827 (29)
P(2)–C(1D)	1.856 (20)	P(3)–C(2)	1.878 (22)
P(3)–C(1E)	1.855 (18)	P(3)–C(1F)	1.824 (15)
P(4)–C(3)	1.848 (23)	P(4)–C(1G)	1.833 (23)
P(4)–C(1H)	1.834 (19)	P(5)–C(4)	1.845 (22)
P(5)–C(1F)	1.813 (17)	P(5)–C(1J)	1.837 (23)
P(5)–C(1K)	1.803 (20)		

Angles

P(1)–Pt(1)–P(2)	174.3 (3)	P(1)–Pt(1)–Cl	95.0 (3)
P(1)–Pt(1)–C(1)	88.0 (7)	P(2)–Pt(1)–Cl	89.6 (3)
P(2)–Pt(1)–C(1)	87.7 (7)	Cl–Pt(1)–C(1)	175.0 (8)
P(3)–Pt(2)–P(4)	167.7 (3)	P(3)–Pt(2)–C(1)	91.3 (7)
P(3)–Pt(2)–C(4)	96.4 (6)	P(4)–Pt(2)–C(1)	78.3 (7)
P(4)–Pt(2)–C(4)	95.1 (6)	C(1)–Pt(2)–C(4)	166.6 (9)
Pt(1)–P(1)–C(2)	114.3 (7)	Pt(1)–P(1)–C(1A)	117.0 (7)
Pt(1)–P(1)–C(1B)	111.9 (8)	C(2)–P(1)–C(1A)	107.0 (10)
C(2)–P(1)–C(1B)	102.0 (11)	C(1A)–P(1)–C(1B)	103.0 (10)
Pt(1)–P(2)–C(3)	115.6 (8)	Pt(1)–P(2)–C(1C)	117.1 (11)
Pt(1)–P(2)–C(1D)	112.5 (8)	C(3)–P(2)–C(1C)	101.8 (12)
C(3)–P(2)–C(1D)	102.0 (11)	C(1C)–P(2)–C(1D)	106.1 (13)
Pt(2)–P(3)–C(2)	118.4 (7)	Pt(2)–P(3)–C(1E)	109.6 (8)
Pt(2)–P(3)–C(1F)	119.0 (66)	C(2)–P(3)–C(1E)	99.8 (11)
C(2)–P(3)–C(1F)	99.8 (8)	C(1E)–P(3)–C(1F)	108.2 (10)
Pt(2)–P(4)–C(3)	114.8 (8)	Pt(2)–P(4)–C(1G)	119.1 (9)
Pt(2)–P(4)–C(1H)	113.6 (6)	C(3)–P(4)–C(1G)	102.9 (13)
C(3)–P(4)–C(1H)	101.2 (10)	C(1G)–P(4)–C(1H)	103.0 (12)
C(4)–P(5)–C(1J)	111.8 (13)	C(4)–P(5)–C(1K)	109.7 (11)
C(4)–P(5)–C(1L)	115.6 (10)	C(1H)–P(5)–C(1K)	105.5 (12)
C(1J)–P(5)–C(1L)	106.6 (12)	C(1K)–P(5)–C(1L)	107.1 (10)
Pt(1)–C(1)–Pt(2)	94.1 (10)	P(1)–C(2)–P(3)	114.4 (11)
P(2)–C(3)–P(4)	116.0 (13)	Pt(2)–C(4)–P(5)	127.9 (11)

Other features of the metal coordination are as expected for divalent platinum. In both compounds the Pt–Cl distances are quite long, 2.439 (5) Å in **6** and 2.429 (8) Å in **5**, indicating that bridging CH_2^{2-} has the high trans influence typical of other σ-carbon donor ligands at platinum.[27] The Pt–P bond lengths in **6** [2.286 (5)–2.302 (5) Å] are on average slightly longer than the corresponding distances in **5** [2.258 (7)–2.283 (7) Å]. In **6**, although the Cl and μ-CH_2 groups are virtually exactly trans to each

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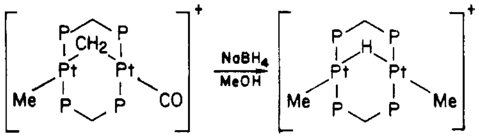
other [C–Pt–Cl = 177.8 (4)°], the P–Pt–P angle is narrowed to 171.3 (2)°. In **5** the Pt(1) atom also shows only a slight distortion from ideal square-planar coordination, alternate ligand donor atoms lying 0.069–0.085 Å above and below the $PtClP_2C$ coordination plane. The sterically more crowded environment of Pt(2) is revealed by more significant tetrahedral distortions of its square plane: the P(4)–Pt(2)–C(1) angle is only 78.3 (7)° and the ligand donor atoms are displaced by 0.138–0.186 Å from the $Pt(2)C_2P_2$ coordination plane.

The $Pt_2P_4C_3$ bicyclo[3.3.1]nonane system in **6** contains the identical twist–boat rings (Figure 2), with CH_2–Pt–P–CH_2 torsion angles of −5.9 (7) and 25.2 (7)° about the Pt–P(1) and Pt–P(2) bonds, respectively. A similar but less symmetrical conformation is found in **5** (Figure 4), with near-zero CH_2–Pt–P–CH_2 torsion angles of 4.4 (11) and 8.2 (11)° about the Pt(1)–P(2) and Pt(2)–P(3) bonds, respectively. This conformation leads to steric crowding around the bridging methylene groups: in **6** the transannular C(1)···C(2) contact is 3.00 (2) Å and the corresponding values in **5** are 3.03 (3) and 3.27 (3) Å. If the methylene hydrogen atoms are positioned assuming regular valency angles and a C–H bond length of 1.07 Å, then the corresponding H···H contacts across the ring are about 2.0 Å, which is substantially less than the van der Waals diameter for H of 2.4 Å suggested by Pauling.[28] The adoption of these strained ring conformations in **6** and **5** is, in our view, a consequence of the steric bulk of the phosphorus phenyl substituents. The twist–boat–twist–boat arrangement ensures that the axial phenyl groups [rings B and D in **6** and rings A, D, F, and G in **5**] are kept away from the methylene bridges.

In **5** the ylide P(5)–C bonds are indistinguishable in length from comparable linkages involving dppm phosphorus atoms. The difference between the P(5)–C(4) bond length of 1.85 (2) Å and the corresponding value[29] of 1.78 (1) Å in *cis*-$[PtI(CH_2PPh_3)(PPh_3)_2]^+$ is of debatable significance, but both bonds are undoubtedly longer than the $P{=}CH_2$ distance of 1.661 (8) Å in $Ph_3P{=}CH_2$ itself.[30] There is a slight distortion of the valency angles at P(5) in **5**: the C(4)–P(5)–Ph angles are all somewhat greater than the tetrahedral angle [110 (1)–116 (1)°], whereas the Ph–P(5)–Ph angles are all somewhat smaller [106 (1)–107 (1)°]. A similar trend is found in $Ph_3P{=}CH_2$, where the mean C—P=C and C—P—C angles are 114° and 105°, respectively.[30] The most striking feature of the ylide ligand geometry is, however, the Pt(2)–C(4)–P(5) angle of 128 (1)°, which is some 24° greater than the Pt–C(1)–Pt angle. Despite this the Pt(2)–C(4) distance is equal to the bridging Pt–C bond lengths to well within experimental error. It also agrees well with the Pt–C(ylide) distance of 2.12 (1) Å in *cis*-$[PtI(CH_2PPh_3)(PPh_3)_2]^+$.[29]

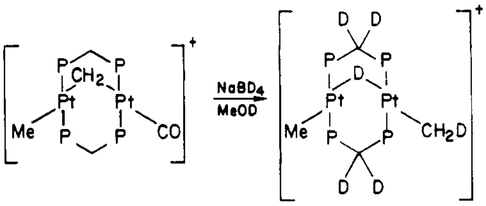
Reactions of the μ-Methylene Complexes. Complexes **2** are of interest as models for intermediates in the Fischer–Tropsch synthesis,[2,3] and we have examined the pyrolysis and reduction of **2a** in order to determine if C–C coupling between the μ-CH_2 group and the CH_3Pt or PtCO group occurs during such reactions. No such coupling was observed, perhaps because of the unfavorable trans orientation of the organic groups in **2a**.

Pyrolysis of **2a** occurred at temperatures in the region 180–210 °C, but only CO and CH_4 were detected as products. Complex **2a** did not react with H_2, but reduction did occur with $Na[BH_4]$ in methanol (eq 3, P^P = dppm), with evolution of CO and CH_4.



(3)

When this reaction was carried out with $NaBD_4$/MeOD, the product, as analyzed by $^2H\{^1H\}$ NMR, was largely that of eq 4.[31]

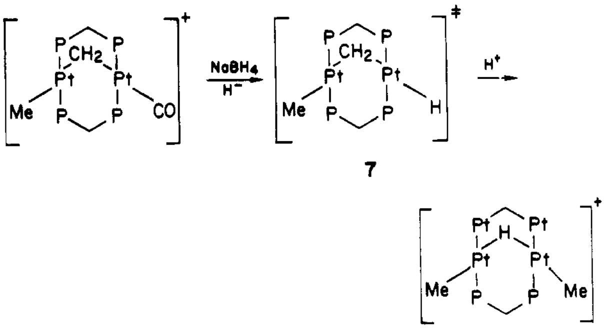


(4)

The $^2H\{^1H\}$ NMR spectrum contained resonances in the hydride, methyl, and CH_2P_2 positions with approximate relative intensities of 1:2:4.[31]

Treatment of **2a** with excess MeLi gave *cis,cis*-$[Pt_2Me_4(\mu\text{-dppm})_2]$, and this product was also formed from MeLi and $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, **6**. Treatment of **6** with excess $Na[BH_4]$ gave $[Pt_2H_3(\mu\text{-dppm})_2]^+$ and methane, and $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2]^+$ was detected by $^{31}P\{^1H\}$ NMR as an intermediate in this reaction. Treatment of **6** with lesser amounts of MeLi gave $[Pt_2Me_3(\mu\text{-dppm})_2]^+$.

In the above reactions, it is expected that hydride or methyl groups from $NaBH_4$ or MeLi will initially displace the terminal CO ligand from **2a**[31] or the chloride ligands from **6**, but no neutral hydrido μ-methylene or methyl μ-methylene complexes were isolated. Instead, these proposed intermediates are protonated at the μ-CH_2 group, which is expected to be very electron rich when trans to two methyl or hydride ligands, to give cationic methylplatinum complexes. The proposed sequence of reactions is illustrated for the reaction of **2a** with $NaBH_4$ in eq 5.[31]



(5)

In the reactions with $NaBH_4$/MeOH, the proton needed in the second step is probably derived from the methanol solvent, but the source of H^+ is less clear in the reactions with methyllithium. We tentatively suggest that the source may be the CH_2P_2 groups of the dppm ligands, which are readily deprotonated by strong bases and are shown (eq 4) to undergo exchange with deuterium in basic media.[32]

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(28) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 260.

(29) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

(30) Daly, J. J. "Perspectives in Structural Chemistry"; Dunitz, J. D.; Ibers, J. A., Eds.; Wiley: New York, 1970: Vol. III, p 165.

(31) The incorporation of deuterium in the MePt groups is about twice that expected from eq 4. Together with the observation of methane in the gaseous products, this suggests that part of the reaction occurs by reduction of the terminal PtCO to a $PtCD_3$ group to give $[Pt_2Me(CH_2D)(CD_3)(dppm)_2]^+$, followed by further reaction with $NaBD_4$ to displace one of the methyl groups by hydride. If this were a random process, the ratio of deuterium in PtH:PtMe:CH_2P_2 groups in the product would be 1:2.7:4.

(32) Further protonation to regenerate dppm would occur during hydrolytic workup of the products.

Table III. Crystallographic Data

	6	5
formula	$C_{51}H_{46}Cl_2P_4Pt_2$	$C_{70}H_{63}ClF_6P_6Pt_2$
fw, amu	1243.9	1629.7
cryst system	tetragonal	monoclinic
space group	$P4_32_12$	$P2_1/c$
a, Å	15.096 (5)	13.199 (2)
b, Å		17.866 (6)
c, Å	26.349 (4)	30.044 (4)
β, deg		91.20 (3)
V, Å^3	6005	7083
Z	4	4
$F(000)$, electrons	2408	3200
d(calcd), g cm^{-3}	1.376	1.528
μ(Mo Kα), cm^{-1}	49.2	42.1
absn factors on F^2	0.76–1.64	
intensity measurements		
scan type	$\theta/2\theta$	$\theta/2\theta$
scan width ($\Delta\omega$), deg	0.50	0.75
max counting time, s	140	120
2θ range	4–44	4–44
q^a	0.03	0.04
unique reflctns	4204	9753
final refinement		
unique reflctns used [$I \geq 3\sigma(I)$]	2238	6552
refined parameters	116	233
largest shift/error	0.42	0.43
R^b	0.0597	0.0739
$R_w{}^b$	0.0595	0.0967
weights, w	$\sigma^{-2}(F)$	unit
$\lvert\Delta_\rho\rvert^c$ e Å^{-3}	0.78	3.73

[a] Manojlović-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 2427. [b] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$; $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$. [c] Largest function value in final difference synthesis.

The protonation of the μ-methylene group in $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ has been studied earlier,[33] but these proposed intermediates, such as 7, must be very much more reactive.

Table IV. Fractional Atomic Coordinates and Isotropic Vibrational Parameters for $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$

	x/a	y/b	z/c	U,^{a} Å^2
Pt	−0.12807 (4)	−0.22125 (4)	−0.04637 (2)	0.0504 (4)
P(1)	−0.2164 (3)	−0.1346 (3)	−0.0975 (1)	0.050 (3)
P(2)	−0.0275 (3)	−0.2884 (3)	0.0058 (2)	0.050 (3)
Cl	−0.1394 (4)	−0.3521 (3)	−0.1003 (2)	0.075 (4)
C(1)	−0.1163 (10)	−0.1163	0.0000	0.043 (12)
C(2)	−0.2421 (10)	−0.0271 (11)	−0.0719 (5)	0.048 (11)
C(1A)	−0.1699 (11)	−0.1053 (10)	−0.1580 (4)	0.056 (5)
C(2A)	−0.1127 (9)	−0.1662 (11)	−0.1792 (8)	0.081 (6)
C(3A)	−0.0748 (14)	−0.1496 (8)	−0.2259 (9)	0.114 (8)
C(4A)	−0.0940 (11)	−0.0721 (10)	−0.2513 (4)	0.105 (7)
C(5A)	−0.1512 (9)	−0.0111 (11)	−0.2301 (8)	0.084 (7)
C(6A)	−0.1892 (14)	−0.0277 (8)	−0.1834 (9)	0.075 (6)
C(1B)	−0.3259 (11)	−0.1770 (15)	−0.1149 (5)	0.063 (5)
C(2B)	−0.3494 (6)	−0.2610 (15)	−0.0991 (8)	0.066 (5)
C(3B)	−0.4314 (11)	−0.2950 (7)	−0.1116 (6)	0.107 (8)
C(4B)	−0.4898 (11)	−0.2451 (15)	−0.1400 (5)	0.089 (7)
C(5B)	−0.4663 (6)	−0.1612 (15)	−0.1558 (8)	0.107 (8)
C(6B)	−0.3844 (11)	−0.1271 (7)	−0.1433 (6)	0.093 (6)
C(1C)	0.0835 (10)	−0.2722 (11)	−0.0167 (8)	0.069 (5)
C(2C)	0.0964 (16)	−0.2926 (19)	−0.0672 (6)	0.120 (9)
C(3C)	0.1790 (19)	−0.2820 (14)	−0.00888 (6)	0.179 (14)
C(4C)	0.2487 (10)	−0.2510 (11)	−0.0598 (8)	0.150 (11)
C(5C)	0.2357 (16)	−0.2305 (19)	−0.0094 (6)	0.108 (8)
C(6C)	0.1531 (19)	−0.2411 (14)	0.0122 (6)	0.081 (6)
C(1D)	−0.0329 (13)	−0.4090 (8)	0.1080 (7)	0.061 (5)
C(2D)	−0.1120 (8)	−0.4533 (16)	0.0115 (8)	0.070 (5)
C(3D)	−0.1178 (11)	−0.5424 (14)	0.0229 (4)	0.098 (7)
C(4D)	−0.0444 (13)	−0.5871 (8)	0.0408 (7)	0.112 (8)
C(5D)	0.0347 (8)	−0.5427 (16)	0.0473 (8)	0.130 (10)
C(6D)	0.0404 (11)	−0.4537 (14)	0.0359 (4)	0.100 (8)
C(S1)	0.0017 (19)	0.0321 (18)	0.0994 (9)	0.122 (9)
C(S2)	−0.0225 (19)	0.1465 (18)	0.0240 (9)	0.127 (10)
C(S3)	0.0185 (22)	0.2154 (21)	0.1190 (11)	0.156 (11)
C(S4)	−0.1211 (27)	0.1244 (27)	0.1601 (13)	0.202 (15)

[a] $U = {}^1/_3(U_{11} + U_{22} + U_{33})$ for Pt to C(2). For other atoms U defines the isotropic temperature factor $\exp((-8\pi^2U \sin^2\theta)/\lambda)$.

Experimental Section

^{1}H and ^{31}P NMR spectra were recorded with a Varian XL100 spectrometer and ^{2}H NMR spectra a Varian XL200 spectrometer. ^{1}H and ^{31}P chemical shifts are quoted with respect to Me_4Si and trimethyl phosphate, respectively. Assignments of J(PH) and J(PtH) in the ^{1}H NMR spectra were confirmed by recording the $^1H\{^{31}P\}$ NMR spectra. All syntheses were carried out by using standard inert-atmosphere techniques.

$[Pt_2Me(\mu\text{-}CH_2)(PMe_2Ph)(\mu\text{-dppm})_2][PF_6]$. To a solution of $[Pt_2H(PMe_2Ph)(\mu\text{-dppm})_2][PF_6]$ (0.3 g) in CH_2Cl_2 (30 mL) was added CH_2N_2 in ether (10 mL, 1%, 10-fold excess). The mixture was stirred for 16 h at room temperature, the solvents were removed under vacuum, and the product was recrystallized from CH_2Cl_2/ether: yield 0.32 g (93%); mp 149–155 °C. NMR in CD_2Cl_2: ^{1}H δ −0.85 [t, ^3J(PH) = 6.1, ^2J(PtH) = 58.8 Hz, *Me*Pt]; 1.45 (m, CH_2Pt_2), 3.60 [m, ^2J(HH) = 14.4 Hz, ^2J(PH) = 3 Hz, ^3J(PtH) = 51.1 Hz, $CH^AH^BP_2$], 4.15 [m, ^2J(HH) = 14.4 Hz, $CH^AH^BP_2$], 0.69 [*d*, ^2J(PH) = 8.2 Hz, ^3J(PtH) = 17.8 Hz, CH_3P]; ^{31}P δ −22.94 [m, ^2J(PP) = 24 Hz, ^1J(PtP) = 1972 Hz, *P*Me_2Ph], 13.09 [m, ^1J(PtP) = 3320 Hz, dppm], 18.91 [m, ^1J(PtP) = 3080 Hz, dppm]. Anal. Calcd for $C_{60}H_{60}F_6P_6Pt_2$: C, 49.0; H, 4.1. Found: C, 48.8; H, 4.1.

$[Pt_2Me(\mu\text{-}CH_2)(CO)(\mu\text{-dppm})_2][PF_6]$. This was prepared similarly from $[Pt_2H(CO)(\mu\text{-dppm})_2][PF_6]$, except that the reaction was carried out under CO atmosphere to inhibit decomposition of starting material: yield 90%; mp 220–225 °C dec; IR (Nujol) 2036 cm^{-1} [ν(CO)]. NMR in CD_2Cl_2: ^{1}H δ −0.08 [t, ^3J(PH) = 6.0 Hz, ^2J(PtH) = 58.6 Hz, *Me*Pt], 2.71 [m, ^3J(PH) = 5 Hz, ^2J(PtH) = 34 Hz, CH_2Pt_2], 3.68 [m, $^2J(H^AH^B)$ = 14.4 Hz, ^2J(PH) = 3.6 Hz, ^3J(PtH) = 49.2 Hz, $CH^AH^BP_2$], 4.16 [m, $^2J(H^AH^B)$ = 14.4 Hz, $CH^AH^BP_2$]; ^{31}P δ 7.65 [m, ^1J(PtP) = 3162 Hz, dppm], 17.53 [m, ^1J(PtP) = 3055 Hz, dppm]. Anal. Calcd for $C_{53}H_{49}F_6P_5OPt_2$: C, 46.8; H, 3.6. Found: C, 46.8; H, 3.6.

$[Pt_2Me(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2Cl(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$. Reaction of $[Pt_2H(PPh_3)(\mu\text{-dppm})_2][PF_6]$ (0.55 g) in CH_2Cl_2 (15 mL) with CH_2N_2 in ether (18 mL, 0.65%) for 18 h as above gave a mixture of the above products (0.49 g). Slow recrystallization from CH_2Cl_2/hexane gave pure $[Pt_2Cl(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2][PF_6]$: mp 187–192 °C dec. NMR in CD_2Cl_2: δ 1.57 (m, CH_2Pt_2), 1.77 [m, CH_2PPh_3), 2.97 and 3.93 (m, CH_2P_2); ^{31}P δ 16.17 [m, ^1J(PtP) = 3450 Hz, ^2J(PP) = 56 Hz, ^3J(PP) = 26 Hz, dppm], 18.52 [m, ^1J(PtP) = 3310 Hz, dppm], 28.29 [m, ^2J(PtP) = 48 Hz, ^4J(PtP) = 19 Hz CH_2*P*Ph_3]. Anal. Calcd for $C_{70}H_{63}P_6F_6ClPt_2$: C, 51.6; H, 3.9 Found: C, 51.5; H, 3.9.

A similar reaction using a reaction time of 4 h gave $[Pt_2Me(\mu\text{-}CH_2)(CH_2PPh_3)(\mu\text{-dppm})_2)[PF_6]$, with an impurity of the above chloro derivative. NMR in CD_2Cl_2: −0.40 [t, ^3J(PH) = 5 Hz, ^2J(PtH) = 56 Hz, *Me*Pt], 1.50 [m, ^3J(PH) = 9 Hz, ^2J(PtH) = 50 Hz, CH_2Pt_2], 1.77 [m, ^2J(PH) = 18 Hz, ^2J(PtH) = 68 Hz, CH_2PPh_3], 2.99 and 3.93 [m, $^2J(H^AH^B)$ = 14.4 Hz, $CH^AH^BP_2$]; ^{31}P 11.48 [m, ^1J(PtP) = 3330 Hz, dppm], 13.28 [m, ^1J(PtP) = 3325 Hz, dppm], 29.75 [m, ^2J(PtP) = 45 Hz, ^4J(PtP) = 27 Hz, CH_2*P*Ph_3]. Recrystallization from CH_2Cl_2/hexane gave the chloro derivative, and this methyl derivatives has therefore not been obtained in analytically pure form.[18]

The complexes $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$, $[Pt_2H(\eta^1\text{-dppm})(\mu\text{-dppm})_2)][PF_6]$, and $[Pt_2Me(PMe_2Ph)(\mu\text{-dppm})_2][PF_6]$ failed to react with CH_2N_2.

Pyrolysis of $[Pt_2Me(\mu\text{-}CH_2)(CO)(\mu\text{-dppm})_2][PF_6]$. A sample of this complex (0.025 g) in an evacuated flask was heated to the decomposition point (180–210 °C). The gaseous products were sampled through a septum and analyzed by GC using Porapak Q and molecular sieve 5A columns. CH_4 and CO were detected as the only gaseous products.

Reduction of $[Pt_2Me(\mu\text{-}CH_2)(CO)(\mu\text{-dppm})_2][PF_6]$. A suspension of the above complex (0.10 g) in MeOH (5 mL) was

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[33] Azam, K. A.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1396.

Table V. Fractional Atomic Coordinates and Isotropic Vibrational Parameters for $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-dppm})_2][PF_6]$

	x/a	y/b	z/c	U,[a] Å^2		x/a	y/b	z/c	U,[a] Å^2
Pt(1)	0.09418 (7)	0.18509 (5)	0.17611 (3)	0.0458 (6)	C(3F)	0.1111 (20)	−0.0541 (16)	0.2836 (5)	0.082 (9)
Pt(2)	0.29505 (7)	0.09419 (5)	0.16907 (3)	0.0438 (5)	C(4F)	0.1314 (10)	−0.0621 (7)	0.3286 (5)	0.087 (9)
P(1)	0.1284 (4)	0.2279 (4)	0.2455 (2)	0.046 (4)	C(5F)	0.2057 (18)	−0.0191 (16)	0.3490 (5)	0.090 (10)
P(2)	0.0691 (4)	0.1517 (4)	0.1036 (2)	0.048 (4)	C(6F)	0.2598 (20)	0.0318 (16)	0.3244 (5)	0.061 (7)
P(3)	0.3030 (4)	0.1082 (3)	0.2446 (2)	0.045 (4)	C(1G)	0.3123 (26)	0.0228 (11)	0.0595 (9)	0.053 (6)
P(4)	0.2973 (4)	0.1065 (4)	0.0940 (2)	0.046 (4)	C(2G)	0.2296 (15)	−0.0163 (13)	0.0430 (10)	0.072 (8)
P(5)	0.4290 (5)	−0.0805 (4)	0.1711 (2)	0.049 (4)	C(3G)	0.2436 (20)	−0.0791 (17)	0.0171 (5)	0.091 (10)
Cl	−0.0789 (6)	0.1486 (5)	0.1915 (3)	0.087 (6)	C(4G)	0.3404 (26)	−0.1026 (11)	0.0076 (9)	0.085 (9)
C(1)	0.2480 (19)	0.2075 (14)	0.1605 (8)	0.059 (7)	C(5G)	0.4231 (15)	−0.0635 (13)	0.0242 (10)	0.088 (9)
C(2)	0.2530 (15)	0.1971 (12)	0.2693 (7)	0.040 (5)	C(6G)	0.4090 (20)	−0.0008 (17)	0.0501 (5)	0.066 (7)
C(3)	0.1837 (16)	0.1517 (13)	0.0691 (7)	0.047 (6)	C(1H)	0.3979 (13)	0.1684 (10)	0.0746 (4)	0.053 (6)
C(4)	0.3109 (15)	−0.0253 (12)	0.1687 (7)	0.040 (5)	C(2H)	0.3978 (20)	0.1951 (18)	0.0315 (6)	0.070 (8)
C(1A)	0.0343 (15)	0.2098 (7)	0.2875 (7)	0.047 (6)	C(3H)	0.4728 (15)	0.2435 (15)	0.0182 (6)	0.078 (8)
C(2A)	0.0484 (14)	0.1576 (15)	0.3209 (11)	0.076 (8)	C(4H)	0.5481 (13)	0.2652 (10)	0.0481 (4)	0.085 (9)
C(3A)	−0.0270 (9)	0.1452 (14)	0.3512 (8)	0.090 (10)	C(5H)	0.5483 (20)	0.2386 (18)	0.0912 (6)	0.084 (9)
C(4A)	−0.1165 (15)	0.1850 (7)	0.3480 (7)	0.084 (9)	C(6H)	0.4732 (15)	0.1902 (15)	0.1044 (6)	0.070 (8)
C(5A)	−0.1306 (14)	0.2372 (15)	0.3146 (11)	0.079 (9)	C(1J)	0.4149 (25)	−0.1704 (12)	0.1419 (8)	0.053 (6)
C(6A)	−0.0551 (9)	0.2496 (14)	0.2843 (8)	0.064 (7)	C(2J)	0.3371 (15)	−0.1824 (14)	0.1113 (11)	0.066 (7)
C(1B)	0.1412 (19)	0.3322 (7)	0.2468 (8)	0.045 (6)	C(3J)	0.3310 (19)	−0.2493 (19)	0.0885 (7)	0.086 (9)
C(2B)	0.1383 (23)	0.3714 (14)	0.2073 (6)	0.058 (7)	C(4J)	0.4028 (25)	−0.3042 (12)	0.0962 (8)	0.085 (9)
C(3B)	0.1455 (11)	0.4484 (13)	0.2076 (6)	0.079 (9)	C(5J)	0.4806 (15)	−0.2922 (14)	0.1268 (11)	0.085 (9)
C(4B)	0.1555 (19)	0.4863 (7)	0.2475 (8)	0.083 (9)	C(6J)	0.4866 (19)	−0.2253 (19)	0.1496 (7)	0.081 (9)
C(5B)	0.1584 (23)	0.4471 (14)	0.2871 (6)	0.077 (8)	C(1K)	0.4598 (15)	−0.1041 (15)	0.2281 (6)	0.051 (6)
C(6B)	0.1513 (11)	0.3700 (13)	0.2867 (6)	0.067 (7)	C(2K)	0.3833 (11)	−0.1226 (16)	0.2567 (8)	0.056 (6)
C(1C)	−0.0181 (11)	0.2091 (18)	0.0702 (11)	0.055 (6)	C(3K)	0.4064 (12)	−0.1425 (7)	0.3001 (6)	0.073 (8)
C(2C)	−0.1008 (20)	0.2393 (15)	0.0910 (5)	0.094 (10)	C(4K)	0.5060 (15)	−0.1440 (15)	0.3149 (6)	0.074 (8)
C(3C)	−0.1683 (21)	0.2838 (10)	0.0673 (11)	0.105 (11)	C(5K)	0.5826 (11)	−0.1255 (16)	0.2863 (8)	0.071 (8)
C(4C)	−0.1531 (11)	0.2981 (18)	0.0228 (11)	0.090 (10)	C(6K)	0.5595 (12)	−0.1056 (7)	0.2429 (6)	0.062 (7)
C(5C)	−0.0703 (20)	0.2679 (15)	0.0020 (5)	0.092 (10)	C(1L)	0.5395 (10)	−0.0351 (11)	0.1485 (6)	0.055 (6)
C(6C)	−0.0028 (21)	0.2234 (10)	0.0257 (11)	0.080 (9)	C(2L)	0.5935 (23)	−0.0674 (13)	0.1146 (7)	0.068 (8)
C(1D)	0.0240 (20)	0.0537 (9)	0.0974 (7)	0.047 (6)	C(3L)	0.6791 (22)	−0.0325 (9)	0.0990 (9)	0.083 (9)
C(2D)	−0.0304 (9)	0.0293 (14)	0.0605 (8)	0.066 (7)	C(4L)	0.7106 (10)	0.0346 (11)	0.1173 (6)	0.083 (9)
C(3D)	−0.0559 (21)	−0.0454 (17)	0.0564 (5)	0.080 (9)	C(5L)	0.6566 (23)	0.0669 (13)	0.1511 (7)	0.077 (8)
C(4D)	−0.0270 (20)	−0.0955 (9)	0.0892 (7)	0.077 (8)	C(6L)	0.5711 (22)	0.0320 (9)	0.1667 (9)	0.060 (7)
C(5D)	0.0273 (9)	−0.0710 (14)	0.1261 (8)	0.086 (9)	P(6)	0.2294 (8)	0.2160 (8)	0.4298 (3)	0.122 (12)
C(6D)	0.0528 (21)	0.0036 (17)	0.1302 (5)	0.062 (7)	F(1)[b]	0.3409	0.2590	0.4330	0.238 (7)[c]
C(1E)	0.4374 (11)	0.1143 (16)	0.2635 (8)	0.045 (6)	F(2)	0.2442	0.1925	0.4779	0.238
C(2E)	0.4933 (10)	0.1720 (15)	0.2459 (9)	0.057 (6)	F(3)	0.2065	0.2986	0.4569	0.238
C(3E)	0.5961 (12)	0.1763 (7)	0.2546 (5)	0.078 (8)	F(4)	0.1157	0.2232	0.4242	0.238
C(4E)	0.6431 (11)	0.1230 (16)	0.2811 (8)	0.085 (9)	F(5)	0.2595	0.1724	0.3937	0.238
C(5E)	0.5872 (10)	0.0653 (15)	0.2988 (9)	0.079 (9)	F(6)	0.2079	0.2610	0.3845	0.238
C(6E)	0.4844 (12)	0.0609 (7)	0.2900 (5)	0.061 (7)	Cl(S1)	0.7965	0.0361	0.4318	0.176 (11)
C(1F)	0.2394 (10)	0.0398 (7)	0.2794 (5)	0.049 (6)	Cl(S2)	0.2535	0.1296	0.5880	0.175 (11)
C(2F)	0.1651 (18)	−0.0032 (16)	0.2590 (5)	0.057 (6)					

[a] $U = {}^1/_3(U_{11} + U_{22} + U_{33})$ for Pt(1) to Cl, otherwise it defines the isotropic temperature factor (see Table IV footnote). [b] The positions of F(1) to Cl(S2) were obtained from difference syntheses and not subsequently refined. [c] Common to F(1) to F(6).

treated with $NaBH_4$ (0.02 g) in MeOH (2 mL), and the mixture was stirred at room temperature for 2 h. Both CH_4 and CO were detected by GC in the gaseous products. The solvent was evaporated under vacuum, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated to a small volume, and ether was added to precipitate the product, identified as $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (0.06 g, 59%) by the ^1H and ^{31}P NMR spectra, which were identical with those of an authentic sample.

The similar reduction with $NaBD_4$ in MeOD gave $[Pt_2Me(CH_2D)(\mu\text{-}D)(\mu\text{-dppm-}d_4)_2][PF_6]$, identified by the ^1H and ^2H NMR spectra. ^2H NMR: −7.3 [$^1J(PtD)$ = 79 Hz calcd 78.7 Hz, $Pt_2(\mu\text{-}D)$], 0.18 [$^2J(PtD)$ = 10 Hz calcd 10.4 Hz, PtCH2*D*], 4.59 (CD_2P_2).

Reduction of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ and methylation reactions were carried out in similar ways. In all cases, the products were identified by the ^1H and $^{31}P\{^1H\}$ NMR spectra by comparison with spectra of authentic samples.

X-ray Structure Analyses of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, 6, and $[Pt_2Cl(CH_2PPh_3)(\mu\text{-}CH_2)(\mu\text{-dppm})_2][PF_6]$, 5. The experimental and computational procedures used in both analyses are standard in this laboratory (Glasgow) and have previously been described in detail.[34] X-ray measurements were made at ambient temperature (22 ± 1 °C) with molybdenum radiation, λ = 0.71069 Å, on an Enraf-Nonius CAD4F diffractometer. Both structures were solved by Patterson and Fourier methods and the final parameters for both are derived from full-matrix least-squares refinements. Pertinent details of the two analyses are presented in Table III.

For 6 a yellow crystal of dimensions ca. 0.20 × 0.10 × 0.10 mm, grown by diffusion of methanol into a CH_2Cl_2 solution, was mounted in a Lindemann glass capillary. Crystals of 6 decompose in the X-ray beam, and the rate of decomposition increases with exposure time. Two sets of intensity measurements were made. The results reported here are derived from the second experiment, during which the intensity standards declined linearly to 80% of their original values in the course of measuring the first 3500 intensities and thereafter decreased more rapidly. The experiment was terminated when the intensity standards reached 50% of their original values. The data thus obtained comprise all independent reflections out to 2θ = 44° and some beyond this limit. They were corrected for crystal decomposition and also for absorption. The latter correction was made empirically[35] owing to the problems in defining the geometry of the capillary-mounted crystal specimen.

At a late stage in the analysis of 6 it became apparent that the crystals contained disordered solvent molecules. These were

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[34] Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W. *Organometallics* **1982**, *1*, 1421.

[35] Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

partially modelled by including the atoms C(S1)–C(S4) (see Table IV) in the calculations with isotropic temperature factors. The solvent molecules could not be identified crystallographically, although from the method of preparation, it is likely that they are either CH_2Cl_2 or MeOH. The closest approach between C(S1)–C(S4) atoms and a non-hydrogen atom of **6** is 3.18 (5) Å to C(3C). The formula for **6** in Table III and quantities calculated directly therefrom contain no allowance for the unidentified solvent.

In the final full-matrix least-squares calculations for **6** the phenyl rings were refined as rigid hexagons of 1.38-Å side. Anisotropic temperature factors were used only for Pt, Cl, P, and methylene C atoms. The structure factors included contributions for the scattering of geometrically positioned hydrogen atoms. The isotropic thermal parameters of the hydrogen atoms were kept equal to those of the carbon atoms to which they were attached. The choice of space group as $P4_32_12$, rather than the enantiomeric $P4_12_12$, was confirmed by refining the Rogers chirality parameter η; its final value was 1.02 (5), satisfactorily close to +1.[36]

For **5** the X-ray measurements were made with a yellow, irregularly shaped crystal fragment of dimensions ca. 0.40 × 0.30 × 0.20 mm, mounted in air. The intensities of 12 940 reflections were measured. Averaging 4802 observations to obtain 2284 independent intensities gave $R_{\text{int}} = 0.073$, fairly close to the final value of the conventional R factor (see Table III). The data were not corrected for absorption effects: application of the Gaussian quadrature method was precluded by our inability to define adequately the shape of the crystal fragment used, and an attempt to apply an empirical correction[35] was unsuccessful, presumably because of the serious disorder problems (see below).

In the final full-matrix least-squares calculations for **5** the 11 phenyl rings were treated as rigid hexagons of 1.386-side. Anisotropic temperature factors were applied only to Pt, Cl, and P atoms. No allowance was made for the scattering of the hydrogen atoms. The analysis was hampered and its accuracy diminished by two problems. First, the fluorine atoms of the $[PF_6]^-$ anion are disordered and a satisfactory geometry for the anion could not be obtained. After many attempts the final fluorine atom positions (Table V) were derived from a difference synthesis and not further refined; an isotropic thermal parameter common to all six fluorine atoms was, however, included in the final refinement calculations. The P–F bond lengths are 1.40–1.72 Å, and the F–P–F angles are 71–124° and 148–165°. Secondly, crystals of **5** also contain disordered solvent, believed to be CH_2Cl_2 from the method of preparation and confirmed by NMR spectroscopy. The final model included two Cl atoms with occupancies of 0.5 to allow for the scattering of the disordered solvent. As with **6**, the empirical formula and associated quantities in Table III for **5** make no allowance for the disordered solvent. The final difference synthesis contains function values up to 3.7 e $Å^{-3}$, mainly close to the Pt atoms and in the region of the $[PF_6]^-$. The analysis of **5** must therefore be regarded as of limited accuracy, although we consider that the structure of the complex cation has been established without ambiguity.

Anisotropic thermal parameters and assumed hydrogen atom positions for **6** and anisotropic thermal parameters for **5** are presented in Tables VI–VIII, and final $|F_o|$ and $|F_c|$ values in Table IX and X.[37] The calculations were performed on a GOULD SEL 32/27 minicomputer using the locally developed GX program system.[38] Scattering factors and anomalous dispersion corrections were taken from ref 39.

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Registry No. **1a**, 74587-82-9; **1b**, 78064-41-2; **1c**, 77275-77-5; **2a**, 83571-85-1; **2b**, 83571-87-3; **4**, 83576-64-1; **5**, 83576-66-3; **6**, 68851-49-0; $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$, 77275-79-7; $[Pt_2Me(CH_2D)(\mu\text{-}D)(\pm\text{-dppm-}d_4)_2][PF_6]$, 97042-57-4; CH_2N_2, 334-88-3.

Supplementary Material Available: Table VI, anisotropic atomic thermal parameters, and Table VII, hydrogen positions for 6; Table VII, anisotropic atomic thermal parameters for 5; Tables IX and X, final $|F_o|$ and $|F_c|$ values for **6** and **5**, respectively (49 pages). Ordering information is given on any current masthead page.

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Synthesis of Binuclear Platinum(IV) Complexes with $Pt(CH_2)_nPt$ Units

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The complex $[PtMe_2(N{\frown}N)]$, $N{\frown}N$ = 1,10-phenanthroline, reacts with a series of organic halides to give new platinum(IV) complexes characterized as $[PtXMe_2R(N{\frown}N)]$ (R = Me, Et, *n*-Pr, *n*-Bu, $CH_2C_6H_4CH_2Br$, $(CH_2)_nX$; n = 0, 1,3, 5; X = Br, I). Complexes $[PtIMe_2\{(CH_2)_nI\}(N{\frown}N)]$ (n = 3–5) react further with $[PtMe_2(N{\frown}N)]$ to produce binuclear complexes $[Pt_2I_2Me_4\{\mu\text{-}(CH_2)_n\}(N{\frown}N)_2]$. The complexes are characterized by elemental analysis and NMR and in the case of the binuclear complexes by pyrolysis.

Introduction

Fischer and Tropsch[1] originally suggested the polymerization of methylene groups on a metal surface to account for the formation of products in the Fischer–Tropsch reactions. Recent evidence[2] has been found to be consistent with this proposal, and this has resulted in considerable current interest in binuclear complexes containing bridging methylene or polymethylene groups. A possible route to such complexes is by the use of α,ω-dihaloalkanes, annd this paper deals with the formation of platinum(IV) com-

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