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Methyl Group Transfer on Halogen Oxidation of Binuclear Methylplatinum Complexes: The Mechanism of Reaction and Structure of a Bridged Platinum(IV)–Platinum(II) Product

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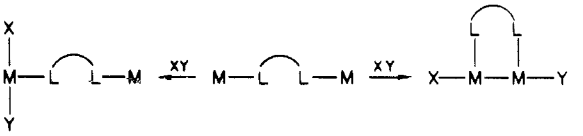
Reaction of $[Pt_2Me_4(\mu\text{-dmpm})_2]$, dmpm = $Me_2PCH_2PMe_2$, with halogens gave the bridged Pt(IV)–Pt(II) complexes $[Me_3Pt(\mu\text{-X})(\mu\text{-dmpm})_2PtMe]X$, **2a–c**, X = I, Br, and Cl, respectively, and, when X = I, further reaction with I_2 gave $[Me_3Pt(\mu\text{-I})(\mu\text{-dmpm})_2PtMe]I_3$ and $[Me_3Pt(\mu\text{-I})(\mu\text{-dmpm})_2PtI]I_3$. The complexes were characterized by NMR spectroscopy and, for **2a**, by an X-ray structure determination. The salt crystallizes in the orthorhombic space group *Pnma*, with four formula units in a cell of dimensions $a = 29.411$ (4), $b = 11.773$ (2), and $c = 8.783$ (1) Å. Full-matrix least-squares refinement on F using 1646 independent observations with $I \geq 3\sigma(I)$ converged at a conventional agreement factor $R = 0.035$. The cation has imposed *m* symmetry. The bridging iodine and dmpm ligands hold the octahedral Pt(IV) and the square-planar Pt(II) atoms 3.916 (1) Å apart. The formation of **2a** involves oxidative addition with methyl group migration between the two platinum centers; labeling studies show that the latter step is very largely an intramolecular process. A mechanism for the reaction is proposed.

Introduction

Oxidative addition reactions of bridged binuclear complexes may occur at only one of the metal centers or may involve both metals (eq 1).[1-11]

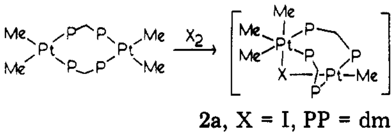


(1)

In a study of the oxidative addition of halogens to $[Pt_2Me_4(\mu\text{-dmpm})_2]$, **1**, dmpm = $Me_2PCH_2PMe_2$,[12] a variation of this behavior is observed in which oxidative addition is accompanied by a methyl-transfer reaction.[13] This paper gives details of the characterization of the products of these reactions and a proof that the methyl-transfer reaction is largely an intramolecular process.

Results and Discussion

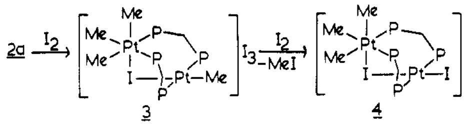
Synthesis and Characterization of Products. Reaction of one equivalent of halogens with complex **1** occurred according to eq 2 to give complexes **2a–c**. The complex $[Pt_2Me_4(\mu\text{-depm})_2]$, depm = $Et_2PCH_2PEt_2$, reacted similarly to give $[Pt_2Me_4(\mu\text{-I})(\mu\text{-depm})_2]I$, **2d**.



(2)

2a, X = I, PP = dmpm
b, X = Br, PP = dmpm
c, X = Cl, PP = dmpm
d, X = I, PP = depm

Complex **2a** reacted further with iodine to give first **3** and then **4** (eq 3). The analogous reactions of **2b** and **2c** with excess bromine or chlorine respectively gave insoluble complexes which were not fully characterized.



(3)

The products **2**, **3**, and **4** were characteried by their ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra (Tables I and II) and, for complex **2a**, by the $^{195}Pt\{^1H\}$ NMR spectrum (Figure 1). This spectrum gives the coupling constant $^2J(PtPt) = 81.4$ Hz, as well as confirming the PtP coupling constants from the ^{31}P NMR spectrum of **2a**. A 1:1 mixture of **3** and **4** has previously been characterized crystallographically,[13,14] and the structure of **2a** has now been determined. These appear to be the first mixed oxidation state bridged Pt(IV)–Pt(II) complexes known.

Structure Description. The crystals of **2a** are built up from complex cations, iodide anions, and molecules of dichloromethane solvent. All three species lie on a crystallographic mirror plane. A stereoview of the complex cation is presented in Figure 2, showing the atom numbering scheme, with non-hydrogen atoms drawn as 50% probability thermal ellipsoids. There are no unusual contacts between cations, anions, and solvent molecules, for the closest nonbonding distances of approach between cations (H3C2···H3C3 = 2.41 Å), between solvent molecules and cations (Cl1···H3C6 = 3.11 Å and H1C9···H1C2 = 2.71 Å), and between cation and anion (I2···H1C2 = 3.15Å) are

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Table I. ^{1}H NMR Data for the Products

	PtCH_3			PCH_3			P$_2$CH_2		
complex	δ	^3J(PH), Hz	^2J(PtH), Hz	δ	^2J + ^4J(PH), Hz	^3J(PtH), Hz	δ	^2J(H^{a}H^b), Hz	^3J(PtH), Hz
2a	0.86 (t)[b]	7.0	83	1.50 (d)	7.5	13.0	2.98 (m)	14	2.5
	0.94 (m)[c]	4.0	54.5	1.68 (t)	7.0	30.5	3.94 (m)		22
	0.96 (t)[d]	9.0	71	1.87 (t)	6.5	29.5			
				1.93 (d)	7.0	11.0			
2b	0.81 (t)[b]	6.5	86	1.49 (d)	8.0	13.5	2.93 (m)	15	3
	0.84 (m)[c]	2.0[e]	53.5	1.59 (t)	7.0	33.5	3.32 (m)		22
	0.87 (t)[d]	9.5	74	1.74 (t)	6.5	29.0			
				2.00 (d)	8.5	10.0			
2c	0.78 (t)[b]	4.5	83	1.49–2.25 (m)			2.74 (m)	14	...[f]
	0.81 (m)[c]	2.0[e]	50				3.10 (m)		...
	0.87 (t)[d]	8.0	77						
4	1.02 (m)[c]	2.0[e]	53.5	1.56 (d)[g]	8.0	14.0	3.43 (m)	14.5	...[f]
	1.20 (t)[d]	9.0	73	2.18 (t)	8.0	16.0	4.09 (m)		...
				2.28 (t)	8.0	26.0			

[a] Solvent CDCl$_3$, except for 4 when solvent was acetone-d_6. Definitions of Me^1, Me^2, and Me^3 are given in Figure 1. [b] Me^3. [c] Me^2. [d] Me^1. [e] ^3J(P^{a}H) + ^3J(P$^{a\prime}$H). [f] Not resolved. [g] One PCH_3 proton resonance is overlapped by solvent signal.

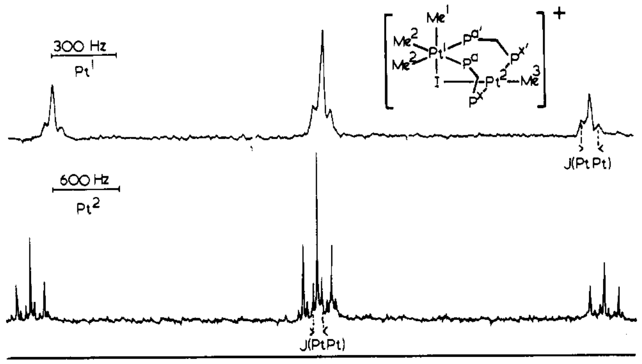


Figure 1. ^{195}Pt NMR spectrum (64.5 MHz) of complex **2a**. The Pt(IV) resonance Pt^1 is centered at δ −2490 ppm; the Pt(II) resonance Pt^2 is centered at δ −3117 ppm from external aqueous K$_2$[PtCl$_4$].

Table II. ^{31}P NMR Data for the Products

complex	δ	^1J(PtP), Hz	^3J(PtP), Hz	^2J(P^{a}P^x) + ^4J(P^{a}P$^{x\prime}$), Hz	solv
2a	−13.9 (t)[a]	2621		16	CDCl$_3$
	−41.7 (t)[b]	1216	129		
2b	−9.2 (t)[a]	2663		18	CDCl$_3$
	−50.0 (t)[b]	1234.9	121.1		
2c	−6.2 (t)[a]	2685.8		20	CDCl$_3$
	−30.4 (t)[b]	1241.5	116		
2d	3.75 (t)[a]	2640		13	
	−27.65 (t)	1132	111		
4	−23.7 (t)[a]	2152		15	(CD$_3$)$_2$CO
	−37.6 (t)[b]	1241	112		

[a] P^x. [b] P^a. See Figure 1 for definition of P^a and P^x.

all greater than the sums of the appropriate van der Waals' radii. Selected bond distances and angles are presented in Table III.

The [Me$_3$Pt(μ-I)(μ-dmpm)$_2$PtMe] cations contain square-planar Pt(II) and octahedral Pt(IV) centers, linked by two bridging dmpm ligands, and an iodide ligand. The overall geometry is the same as that found earlier,[13,14] albeit more accurately determined in the absence of disorder. The expected square-planar coordination geometry is observed at Pt1, the Pt(II) center, with trans P ligands, though there are significant deviations from planarity (Table S5). The Pt(II)–P bond length of 2.295 (4) Å is indistinguishable from that determined earlier and references cited therein,[14] while the Pt1–I1 bond distance of 2.680 (1) Å is significantly longer, as might be expected for a Pt–I bond trans to a methyl rather than methyl/iodo ligand combination. The coordination geometry at Pt2, the Pt(IV) center, is octahedral, with cis P and cis methyl ligands and significantly longer bond lengths (Pt2–I1 = 2.810 (2) and Pt2–P2 = 2.378 (4) Å) than are found at the Pt(II) center.[13,14] The three bridging ligands hold the two Pt atoms 3.916 (1) Å apart, a distance significantly longer than that of 3.863 (1) Å found in the mixture of 3 and 4,[14] and there is a comparable though less significant increase in the P⋯P bite distance of 3.11 (1) Å to 3.126 (5) Å. Although the Pt1⋯Pt2 distance increases in the present study, the Pt1–I1–Pt2 angle decreases, due presumably to the longer Pt1–I1 bond. Torsion angles (Table S6) in the dmpm ligand are indistinguishable from those in the earlier study, and remaining interatomic distances and angles are unexceptionable.

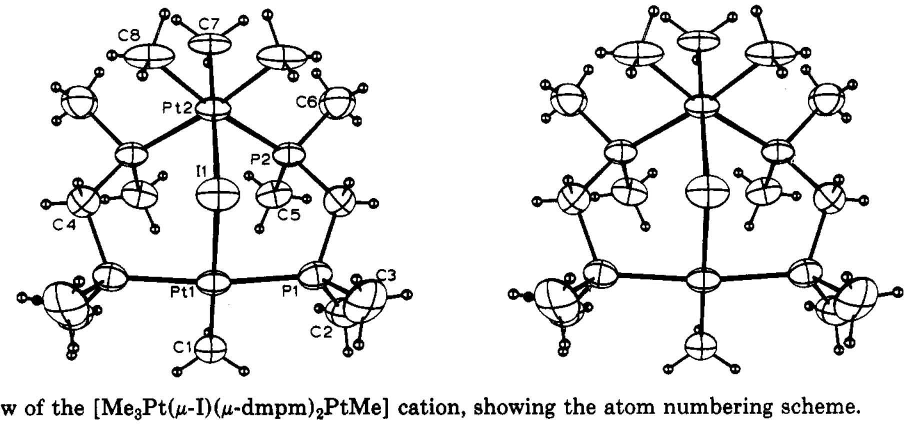


Figure 2. Stereoview of the [Me$_3$Pt(μ-I)(μ-dmpm)$_2$PtMe] cation, showing the atom numbering scheme.

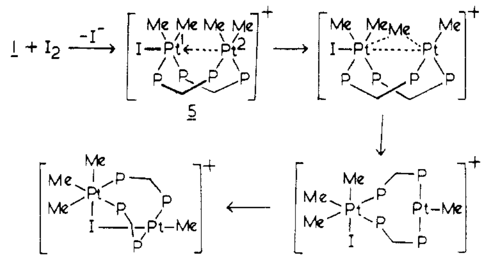
Table III. Bond Distances (Å) and Bond Angles (deg)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Pt1	I1	2.680 (1)	Pt2	C7	2.083 (21)	P1	C3	1.835 (15)
Pt1	P1	2.295 (4)	Pt2	C8	2.104 (15)	P1	C4	1.809 (13)
Pt1	C1	2.081 (20)	Cl1	C9	1.66 (3)	P2	C4	1.850 (13)
Pt2	I1	2.810 (2)	Cl2	C9	1.67 (4)	P2	C5	1.814 (12)
Pt2	P2	2.378 (4)	P1	C2	1.798 (14)	P2	C6	1.806 (15)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
I1	Pt1	P1	88.89 (9)	P2	Pt2	C8	87.1 (5)	C3	P1	C4	102.3 (8)
I1	Pt1	C1	175.5 (6)	C7	Pt2	C8	88.8 (6)	Pt2	P2	C4	113.6 (4)
P1	Pt1	P1	171.5 (2)	C8	Pt2	C8	85.0 (9)	Pt2	P2	C5	123.0 (5)
P1	Pt1	C1	91.4 (1)	Pt1	I1	Pt2	90.97 (4)	Pt2	P2	C6	112.4 (5)
I1	Pt2	P2	94.48 (8)	Pt1	P1	C2	117.7 (5)	C4	P2	C5	103.5 (6)
I1	Pt2	C7	173.4 (5)	Pt1	P1	C3	115.7 (6)	C4	P2	C6	101.3 (7)
I1	Pt2	C8	86.4 (4)	Pt1	P1	C4	112.9 (5)	C5	P2	C6	100.2 (7)
P2	Pt2	P2	100.8 (2)	C2	P1	C3	102.3 (8)	P1	C4	P2	117.3 (7)
P2	Pt2	C7	89.7 (4)	C2	P1	C4	104.1 (7)	C11	C9	C12	118 (2)

[a] Numbers in parentheses in this and other tables are estimated standard deviations in the least significant digits.

Scheme I



The Mechanism of Reaction. The most interesting feature of the reaction 2 is the methyl transfer which accompanies oxidative addition. A method was therefore devised to determine if this methyl transfer between platinum atoms is an intramolecular or intermolecular process. The method relies on the observation that pyrolysis of **2a** occurs quantitatively to give ethane and $[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$.

First it was necessary to show that this reductive elimination was intramolecular, as expected by analogy with similar reductive eliminations from mononuclear trimethylplatinum(IV) complexes.[15] For this purpose, the complexes $[Pt_2(CD_3)_4(\mu\text{-dmpm})_2]$, **1′**, and $[Pt_2(CD_3)_4(\mu\text{-}I)(\mu\text{-dmpm})_2]I$, **2a′**, were prepared. Pyrolysis of a mixture of **2a** and **2a′**, followed by mass spectrometric analysis of the volatile products C_2D_6, CH_3CD_3, and C_2H_6 (together with background experiments described in the Experimental Section) showed that the reductive elimination was 93 ± 2% intramolecular. Next, iodine was added to a 1:1 mixture of complexes **1** and **1′**, and the relative amounts of C_2D_6, CH_3CD_3, and C_2H_6 formed on pyrolysis of this product were determined in a similar way. This showed that the methyl-transfer reaction which accompanies the oxidative addition of iodine to complex **1** occurs 92 ± 4% by intramolecular transfer, under the experimental conditions used.

Methyl-transfer reactions between mononuclear platinum complexes are usually slow.[16,17] For example, the reaction between *cis*-$[PtMe_2(PMe_2Ph)_2]$ and $[PtI_2Me_2(PMe_2Ph)_2]$ to give *trans*-$[PtIMe(PMe_2Ph)_2]$ and *fac*-$[PtIMe_3(PMe_2Ph)_2]$ takes 2 days to reach equilibrium. However, in the present reaction the methyl transfer occurs very rapidly and indicates unique reactivity of the binuclear system. The results are most simply rationalized in terms of the mechanism of Scheme I. We suggest that electrophilic attack by iodine at one platinum center is accompanied by donation of charge from the second platinum center[18,19] to give **5**, from which intramolecular methyl group transfer can occur readily. A conformational change then allows the iodide to bridge to the second platinum atom.[20] According to this mechanism, the free iodide ion formed in the initial step is prevented by steric hindrance from coordinating at the Pt^1 site of intermediate **5** to give the simple product of oxidative addition at a single platinum center. In mononuclear complexes, this situation would not arise and so simple oxidative addition is observed.[21]

Experimental Section

NMR spectra were recorded by using Varian XL100, XL200, or XL300 spectrometers. Chemical shifts are quoted with respect to internal Me_4Si (^1H), external $PO(OMe)_3$ (^{31}P), or external aqueous K_2PtCl_4 (^{195}Pt). Mass spectra were recorded by using a Varian MAT311 spectrometer.

The complexes $[Pt_2Me_4(\mu\text{-dmpm})_2]$ and $[Pt_2Me_4(\mu\text{-depm})_2]$ were prepared as described elsewhere.[12] $[Pt_2(CD_3)_4(\mu\text{-dmpm})_2]$ was prepared in the same way, but with CD_3Li in place of CH_3Li.

$[Pt_2Me_4(\mu\text{-}I)(\mu\text{-dmpm})_2]I$, Complex 2a. Complex **1** (0.078 g) was dissolved in CH_2Cl_2 (10 mL) to which an I_2/CH_2Cl_2 solution (0.028 g in 20 mL) was added dropwise. At the end of addition, a yellow solution was obtained. Solvent was then removed under vacuum. The solid was redissolved in CH_2Cl_2 (1 mL) and precipitated by adding *n*-pentane (20 mL) to give the product as a yellow crystalline solid: yield 0.102 g; decomp pt 162 °C; MS, *m/e* 931 (P − 3Me), 916 (P − 4Me). Anal. Calcd for $C_{14}H_{40}I_2P_4Pt_2$: C, 17.2; H, 4.1. found: C, 17.1; H, 4.2.

$[Pt_2Me_4(\mu\text{-}I)(\mu\text{-dmpm})_2][PF_6]$. Complex **2a** (0.022 g) was dissolved in CH_2Cl_2 (8 mL), to which a solution of NH_4PF_6 (0.074 g) in methanol (5 mL) was added while being stirred. Solvent was then removed on the rotary evaporator to give an orange solid. This solid was washed with CH_2Cl_2 (20 mL) and then concentrated by evaporation (1.5 mL), and the product was obtained from this solution as an orange solid when *n*-pentane (20 mL) was added;

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[15] Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

[16] Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1810; **1977**, 1219

[17] Puddephatt, R. J.; Thompson, P. J. *J. Organomet. Chem.* **1979**, *166*, 251.

[18] It is not clear at what stage this Pt–Pt interaction would occur. If it occurs at an early stage, it could lead to anchimeric assistance.[4,11] Electrophilic attack by I_2 leading to oxidative addition has been established in other systems. Schmidt, S. P.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 1308.

[19] Evidence for a methyl group either bridging between or rapidly migrating between two platinum atoms has been published. Archer, D. P.; Bennett, M. A.; McLaughlin, G. M.; Robertson, G. B.; Whittacker, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, *32*.

[20] This step is probably preceded by a cis → trans stereochemical change of the Pt^2P_2 unit, which is expected to be rapid in the 14-electron intermediate. Conformational changes of dmpm ligands are also rapid.[12]

[21] Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2801.

yield 0.011 g. The ^{1}H and ^{31}P NMR spectra were identical with those of **2a**. Anal. Calcd for $C_{14}H_{40}F_6IP_5Pt_2$: C, 16.9; H, 4.0. Found: C, 16.9; H, 3.8.

[Pt$_2$Me$_4$(μ-I)(μ-depm)$_2$]I, Complex 2d. A solution of I_2 (0.032 g) in CH_2Cl_2 (20 mL) was added to [Pt$_2$Me$_4$(μ-depm)$_2$] (0.050 g) in CH_2Cl_2 (10 mL). After 30 min, the volume was reduced to 10 mL and *n*-pentane was added to precipitate the product (0.024 g). Anal. Calcd for $C_{22}H_{56}I_2P_4Pt_2$: C, 24.3; H, 5.2. Found: C, 24.0; H, 5.1.

[Pt$_2$IMe$_4$(μ-dmpm)$_2$]I$_3$, Complex 3. A solution of I_2 (0.043 g) in CH_2Cl_2 (6 mL) was added to a solution of complex **2a** (0.060 g) (12 mL) while being stirred. At the end of addition, a dark brown precipitate was obtained along with a brown solution. The precipitate was isolated by filtration and washed with *n*-pentane (10 mL): yield 0.073 g; decomp pt 160 °C. Anal. Calcd for $C_{14}H_{40}P_4I_4Pt_2$: C, 13.7; H, 3.2; I, 41.3. Found: C, 13.7; H, 3.2; I, 40.9. The ^{1}H and ^{31}P NMR data are identical with those of **2a**.

Pt$_2$IMe$_3$(μ-I)(μ-dmpm)$_2$]I$_3$, Complex 4. To a stirred solution of *fac,trans*-[Pt$_2$Me$_4$(μ-I)(μ-dmpm)$_2$]I$_3$ (0.094 g) in acetone (20 mL) was added a solution of I_2 (0.040 g) in acetone (20 mL). A dark brown solution was obtained, and after solvent was removed under vacuum, a black solid appeared. The solid was washed with *n*-pentane (30 mL) to remove excess I_2. The product was dried in vacuo and was identified by its ^{1}H and ^{31}P{^{1}H} NMR spectra: yield 0.089 g; decomp pt 166 °C. Anal. Calcd for $C_{13}H_{37}P_4I_5Pt_2$: C, 11.6; H, 2.8; I, 47.3. Found: C, 10.9; H, 2.6; I, 48.4.

[Pt$_2$Me$_4$(μ-Br)(μ-dmpm)$_2$]Br, Complex 2b. A Br_2/CCl_4 solution (0.096 M, 1.0 mL) was added to a stirred solution of complex 1 (0.069 g) in CH_2Cl_2 (17 mL). The solution turned bright yellow, and after solvent was removed under vacuum, the product was isolated as a yellow solid and washed with *n*-pentane (10 mL): yield 0.066 g; decomp pt 161 °C. Anal. Calcd for $C_{14}H_{40}Br_2P_4Pt_2$: C, 19.1; H, 4.6. Found: C, 18.6; H, 4.3.

[Pt$_2$Me$_4$(μ-Cl)(μ-dmpm)$_2$]Cl, Complex 2c. A Cl_2/CCl_4 solution (0.046 M, 1 mL) was added to a solution of complex 1 (0.067 g) in CH_2Cl_2 (25 mL). A pale yellow solid was obtained as the product after solvent was removed under vacuum, and the yield after being washed with *n*-pentane (10 mL) was 0.058 g; decomp pt 185 °C.

Analysis of C_2D_6, CD_3CH_3, and C_2H_6. Pyrolyses of complex **2a** and deuterated derivatives were carried out in small evacuated glass bulbs, and volatiles were admitted via the gas inlet system to the mass spectrometer. Corrections were made to allow for background, fragmentation of C_2D_6, and incomplete deuteration of **2a′** by comparison of mass spectra of ethane samples formed by pyrolysis of **2a** and **2a′** and also by analysis of ethane formed by pyrolysis of equal amounts of **2a** and **2a′** in separate bulbs, followed by combination of the ethane samples and analysis by MS as above. The percent of intramolecular reductive elimination was then determined by pyrolysis of equal amounts of **2a** and **2a′**, intimately mixed in the *same* bulb. Finally, the percent of intramolecular methyl transfer was determined by comparison of this result with that obtained when equal mixtures of 1 and 1′ were treated with I_2 and then pyrolyzed.

X-ray Structure Determination

Collection and Reduction of X-ray Data. Crystals were grown by slow diffusion of hexane into a solution of **2a** in dichloromethane. A photographic examination showed orthorhombic symmetry, and preliminary cell constants were obtained. Systematic absences of 0*kl*, *k* + *l* odd, *h*01, *h* odd, and 00*l*, *l* odd, suggest space groups *Pna*2$_1$, No. 33, or *Pnam*, an alternative setting of *Pnma*, No. 62.[22a] The density was determined by flotation in a mixture of bromoform and carbon tetrachloride and corresponds to four formula units per cell. No crystallographic site symmetry is imposed in space group *Pna*2$_1$, but either *m* or 1 symmetry for all species is required in *Pnma*. Space group *Pna*2$_1$ was originally chosen.

A crystal of equant habit was mounted in a thin-walled glass capillary to minimize loss of the solvate molecule. ω-Scans of several intense, low-angle reflections using a wide open counter had an average width at base of 0.97°.[23] Intensity data were recorded at variable scan speeds within a maximum time per datum of 60 s. Background estimations were made by extending the scan by 25% on each side. Standard reflections showed some decay, though no significant variation in crystal orientation was observed. A total of 2861 reflections was measured, of which 54 were standards, and these were processed by using the Enraf-Nonius SDP package running on a PDP 11/23+ computer.[24] Standard deviations were assigned and a starting value of 0.04 chosen for *p*.[25] A linear decay correction was applied. Psi scans[23] were made of nine reflections and used as the basis for an empirical absorption correction.[26] A total of 1716 unique data with $I > 2\sigma(I)$ were available for the analysis. Crystal data and experimental details are given in Table IV.

Table IV. Crystal Data and Experimental Conditions

compd	$Pt_2I_2P_4Cl_2C_{15}H_{42}$
fw	1061.3
temp, °C	20
unit cell dimens	
a, Å	29.412 (4)
b, Å	11.773 (2)
c, Å	8.783 (1)
cell vol	3041 (1)
Z	4
d(obsd), g cm^{-3}	2.44 (1)
d(calcd), g cm^{-3}	2.318
space group	orthorhombic, *Pnma*
radiatn	Mo Kα, λ = 0.71093 Å
monochromator	graphite, θ = 12.16°
cryst dimens, mm^3	0.24 × 0.23 × 0.19
abs coeff, cm^{-1}	116.9
transmiss coeff	0.595–0.986
detector aperture, mm (vert)	4
(horiz)	4.00 + 0.35 tan θ
crystal-detector dist, mm	205
scan, deg min^{-1}	$\theta - 2\theta$, at 1.7–4.0
scan range	0.90 + 0.35 tan θ
data collected	$0 < \theta < 25°$, $0 \leq h \leq 35$; $0 \leq k \leq 10$, $0 \leq l \leq 14$
std reflctns	040, 006, 800 every 167 min

Structure Solution and Refinement. The structure was solved by direct methods[27] and refined by full-matrix least squares on *F*, minimizing the function $\sum\omega(||F_o - F_c||)^2$, where the weight *w* is given by $4F_o/\sigma^2(F_o)$. Scattering factors for neutral, non-hydrogen atoms were taken from ref 22b, while those for H were from Stewart et al.[28] Real and imaginary corrections for anomalous dispersion were included for all non-hydrogen atoms.[22b] With anisotropic thermal parameters, refinement converged at $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2} = 0.054$. An inspection of the atomic parameters showed that the correct space group was *Pnma*, a result confirmed by the intensity statistics, so the data were transformed into this setting with the transformation matrix [1,0,0], [0,0,1], [0,–1,0]. The new model converged at agreement factors R_1 = 0.041 and R_2 = 0.050 with a *p* value of 0.05.

All but two of the 22 hydrogen atoms were radily located in a difference fourier synthesis with peak heights varying from 0.5 (2) to 0.3 (2) e Å^{-3} and included with isotropic thermal parameters 10% greater than those of the bonded atoms. Idealised coordinates were used, assuming sp^3 hybridization and a C–H distance of 0.95 Å, and for the methyl H atoms the best fit was achieved by a least-squares procedure. As the refinement proceeded the H atom positions were recalculated. An extinction parameter was refined to 1.3 (3) × 10^{-8}, and three reflections were given a zero

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Table V. Atomic Positional (× 10^4) and Thermal (× 10^3) Parameters[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
Pt1	32027 (2)	2500	8604 (8)	422 (2)
Pt2	41770 (3)	2500	38994 (7)	434 (2)
I1	32216 (4)	2500	39114 (13)	561 (4)
I2	6880 (5)	2500	46750 (19)	648 (4)
Cl1	3885 (4)	7500	4427 (12)	138 (4)
Cl2	3014 (3)	7500	5878 (13)	176 (5)
P1	3259 (1)	4444 (3)	907 (4)	49.3 (9)
P2	4238 (1)	4056 (3)	2185 (4)	44.6 (9)
C1	3132 (7)	2500	−1498 (22)	56 (6)
C2	3343 (6)	5164 (13)	−876 (16)	69 (5)
C3	2768 (5)	5199 (14)	1705 (21)	86 (6)
C4	3720 (4)	4944 (12)	2093 (15)	50 (4)
C5	4399 (5)	3892 (13)	204 (13)	52 (4)
C6	4656 (5)	5084 (13)	2793 (18)	74 (5)
C7	4881 (7)	2500	4164 (21)	64 (6)
C8	4134 (5)	3707 (15)	5660 (14)	67 (5)
C9	3579 (14)	7500	6021 (30)	167 (17)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^1/_6\pi^2[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Positional parameters for Pt and I atoms (× 10^5). Values without estimated standard deviations were fixed in the refinement. Thermal parameters for Pt and I atoms (× 10^4).

weight, due to systematic error. The final cycles of refinement included 128 variables, a *p* value of 0.07, used 1646 unique observations with $I > 3\sigma$, and converged at agreement factors of $R_1 = 0.035$ and $R_2 = 0.048$. The largest parameter shift in the final cycle was 0.01σ. In a total difference Fourier synthesis the top 10 peaks (ranging from 1.2 (2) to 0.8 (2) e Å^{-3}) were all within 1.2 Å of the Pt and I atoms. The error in an observation of unit weight is 1.04 e, and an analysis of R_2 in terms of the magnitude of F_o, $\lambda^{-1}\sin\theta$, and various combinations of Miller indices showed no unusual trends. Final positional and *U*(equiv) thermal parameters are given in Table V for all non-hydrogen atoms. Anisotropic thermal parameters, hydrogen atom parameters, root-mean-square amplitudes of vibration, supplementary bond distances and angles, weighted least-squares planes, torsion angles, and structure amplitudes have been deposited.[29]

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Registry No. 1, 88228-39-1; **2a**, 89144-02-5; **2a**·CH_2Cl_2, 97275-72-4; **2b**, 89144-01-4; **2c**, 89144-00-3; **2d**, 96427-22-4; **3**, 89194-92-3; 4, 89144-04-7; $[Pt_2Me_4(\mu\text{-}I)(\mu\text{-dmpm})_2][PF_6]$, 89194-93-4; $[Pt_2Me_4(\mu\text{-depm})_2]$, 91491-48-4; $[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$, 97210-43-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, thermal parameters, root-mean-square amplitudes of vibration, hydrogen atom parameters, supplementary dimensions, weighted least-squares planes, torsion angles, and structure amplitudes ($10F_o$ vs. $10F_c$ in electrons) (16 pages). Ordering information is given on any current masthead page.

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[29] Supplementary material.

The Mechanism of Thermal Decomposition of *trans*-Chloroethylbis(triethylphosphine)platinum(II)[1]

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The thermal decomposition of *trans*-chloroethylbis(triethylphosphine)platinum(II) ($L_2PtEtCl$, 1) in cyclohexane solution at 158 °C yields *trans*-chlorohydridobis(triethylphosphine)platinum(II) (3) and ethylene. The most probable rate-limiting step for this reaction is dissociation of ethylene from a five-coordinate 18-electron platinum(II) intermediate, $L_2PtHCl(C_2H_4)$ (2). Three pathways might be involved in the formation of 2 from 1 (Scheme I): β-hydride elimination proceeding directly from 1 *without* prior dissociation of phosphine or chloride; phosphine dissociation, reversible β-hydride elimination, and phosphine reassociation; or chloride dissociation, reversible β-hydride elimination, and chloride reassociation. Presently available evidence does not distinguish between these three pathways. The conversion of 1 to 3 and ethylene has Arrhenius activation parameters $E_a = 34$ kcal/mol and log $A = 13$. The reaction is effectively irreversible at low to moderate conversions, when ethylene concentrations in solution are low. At high conversions, the reverse reaction (3 + ethylene → 1) is significant. The equilibrium constant for $1 \rightleftharpoons 3$ + ethylene was measured as a function of temperature giving $K_{eq}(158\ °C) = 0.69$ M, $\Delta G°(158\ °C) = 0.32$ kcal/mol, $\Delta H° = 12$ kcal/mol, and $\Delta S° = 27$ eu. The deuterium *equilibrium* isotope effect for the reaction $L_2PtClC_2H_5(D_5) \rightarrow L_2PtClH(D) + C_2H_4(D_4)$ is $K_{eq}^H/K_{eq}^D = 1.9 \pm 0.4$; the deuterium *kinetic* isotope effect on the overall rate of decomposition of $L_2PtClC_2H_5(D_5)$ under conditions in which the reverse reaction is slow is $k_H/k_D = 2.5 \pm 0.2$. The rate of reaction increases slightly with increasing concentration of phosphine and chloride ion (as benzyldimethyltetradecylammonium chloride) and with solvent polarity. Intermolecular exchange of phosphine ligands between platinum centers occurs within 30 min at room temperature in cyclohexane solution (measured by observing the NMR spectrum of mixtures of $L_2PtEtCl$ and $(L\text{-}d_{15})_2PtEtCl$); halide ion exchange between $L_2Pt(C_2H_5)Cl$ and $L_2Pt(C_2D_5)Br$ is also observed within 30 min under these conditions.

Introduction

The transformation of metal alkyls to metal hydrides and olefins by β-hydride elimination is an important process in organometallic chemistry,[3-9] but because the β-hydride elimination step is itself rarely rate limiting, this process remains incompletely understood mechanistically.

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