Organometallics **1985**, *4*, 1198–1202

Oxidative Addition of Methyl Iodide to Binuclear Complexes $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ and the Crystal Structure of a Bridged Pt(IV)–Pt(IV) Product, $[Me_3Pt(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2PtMe_3]I$

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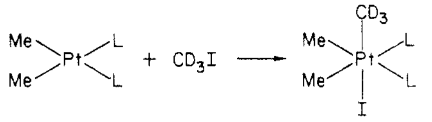
The course of reaction of methyl iodide with $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$, **1**, was found to depend on the bulk of the substituents R. When R = Me, **1a**, reaction was irreversible at room temperature and products were first $[Me_3IPt(\mu\text{-}R_2PCH_2PR_2)_2PtMe_2]$, **3a**, R = Me, and then finally $[Me_3Pt(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2PtMe_3]I$, **2**. When R = Et, **1b**, the first oxidative addition was reversible to give **3b**, R = Et, and a further very slow reaction gave $[Me_3Pt(\mu\text{-}I)(\mu\text{-}Et_2PCH_2PEt_2)_2PtMe]I$, and, when R = Ph, **1c**, no reaction with MeI occurred. The oxidative addition of CD_3I to **1a** was not stereospecific, and the reversible addition of CD_3I to **1b** led to complete exchange of all MePt groups to give CD_3Pt groups and CH_3I. The crystal structure of **2** has been determined by X-ray diffraction methods and refined to $R = 0.044$ for 2807 unique reflections with $I \geq 3\sigma(I)$. The crystals of **2** are monoclinic of space group $C2/m$ with $a = 18.396$ (5) Å, $b = 10.991$ (2) Å, $c = 14.233$ (3) Å, $\beta = 95.10$ (2)°, and $Z = 4$. The structure of the cation approximates to C_{2v} point group symmetry. It contains two *fac*-$PtMe_3$ fragments linked by an iodo bridge and by two mutually cis dmpm ligands. The Pt⋯Pt separation is extremely large [4.707 (1) Å].

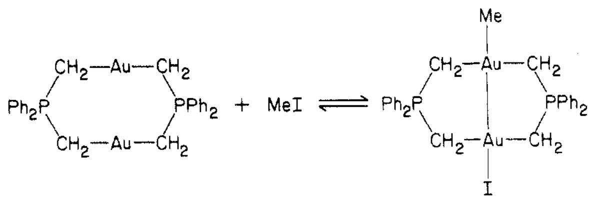
Introduction

Oxidative addition of methyl iodide to square-planar complexes occurs with trans-stereochemistry (eq 1, L = PMe_2Ph).[2,3]



(1)

Oxidative addition to binuclear complexes often occurs with metal–metal bond formation of cleavage,[4-9] and, in one case, a reversible oxidative addition has been established (eq 2).[10]



(2)

This paper describes the oxidative addition of methyl iodide to binuclear platinum(II) complexes $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$[11,12] which may be reversible (R = Et) or irreversible (R = Me), depending on the bulk of the substituents R, and the structure of a binuclear Pt(IV)–Pt(IV) complex formed by double oxidative addition. A preliminary account of part of this work has been published,[13] and this article is part of a wider study of the steric effects of ligands $R_2PCH_2PR_2$ (abbreviations: R = Me, dmpm; R = Et, depm; R = *i*-Pr, dippm; R = Ph, dppm) on the properties of bridged binuclear complexes.[11-13]

Table I. Selected Interatomic Distances and Angles in $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3][I]$

	Bond Lengths (Å)		
Pt(1)–I(1)	2.745 (2)	Pt(2)–I(1)	2.746(1)
Pt(1)–P(2)	2.378(3)	Pt(2)–P(1)	2.374 (3)
Pt(1)–C(1)	2.075 (16)	Pt(2)–C(3)	2.094 (12)
Pt(1)–C(2)	2.145 (11)	Pt(2)–C(4)	2.104 (18)
P(1)–C(7)	1.835 (10)	P(2)–C(5)	1.825 (13)
P(1)–C(8)	1.856 (11)	P(2)–C(6)	1.813 (11)
P(1)–C(9)	1.790 (11)	P(2)–C(7)	1.823 (10)
	Bond Angles (deg)		
I(1)–Pt(1)–P(2)	91.8 (1)	I(1)–Pt(2)–P(1)	92.9 (1)
I(1)–Pt((1)–C(1)	172.2 (5)	I(1)–Pt(2)–C(3)	88.5 (4)
I(1)–Pt(1)–C(2)	89.2 (4)	I(1)–Pt(2)–C(4)	171.7 (6)
P(2)–Pt(1)–C(1)	93.3 (4)	P(1)–Pt(2)–C(3)	89.2 (4)
P(2)–Pt(1)–C(2)	88.6 (3)	P(1)–Pt(2)–C(4)	92.7 (4)
P(2)–Pt(1)–P(2′)[a]	97.5 (1)	P(1)–Pt(2)–P(1′)	96.4 (1)
P(2)–Pt(1)–C(2′)	173.7 (4)	P(1)–Pt(2)–C(3′)	174.1 (4)
C(1)–Pt(1)–C(2)	85.1 (5)	C(3)–Pt(2)–C(4)	85.4 (5)
C(2)–Pt(1)–C(2′)	85.2 (5)	C(3)–Pt(2)–C(3′)	85.1 (5)
Pt(1)–I(1)–Pt(2)	118.0 (1)	P(1)–C(7)–P(2)	125.8 (5)
Pt(2)–P(1)–C(7)	121.9 (4)	Pt(1)–P(2)–C(5)	114.7 (5)
Pt(2)–P(1)–C(8)	116.0 (5)	Pt(1)–P(2)–C(6)	115.1 (4)
Pt(2)–P(1)–C(9)	115.8 (5)	Pt(1)–P(2)–C(7)	122.3 (4)
C(7)–P(1)–C(8)	97.0 (5)	C(5)–P(2)–C(6)	100.6 (6)
C(7)–P(1)–C(9)	103.3 (6)	C(5)–P(2)–C(7)	96.7 (5)
C(8)–P(1)–C(9)	99.0 (6)	C(6)–P(2)–C(7)	104.0 (5)

[a] Primed atoms are derived from the corresponding unprimed atoms by applying the transformation $x, \bar{y}, z$ to the coordinates in Table III.

Results and Discussion

Characterization of the Pt(IV)–Pt(IV) Product 2. Reaction of a colorless solution of **1a** in dichloromethane

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(1) (a) University of Western Ontario. (b) University of Glasgow.

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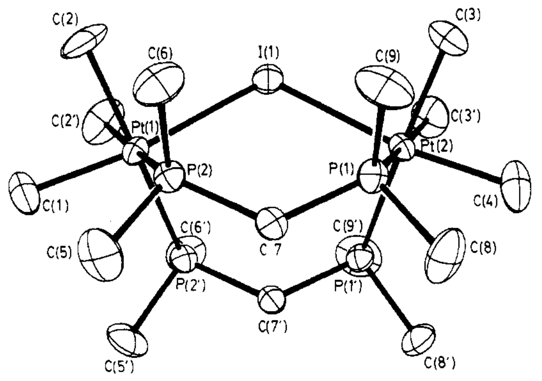
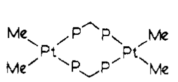


Figure 1. A perspective view of the structure of $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3]^+$, showing 50% probability of vibrational ellipsoids. A crystallographic mirror plane runs through the atoms Pt(1), Pt(2), I(1), C(1), and C(4) and maps primed atoms onto the corresponding unprimed ones (see also Tables I–III).

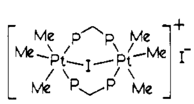
solution with excess methyl iodide gave an instant yellow coloration which then faded slowly as the colorless product **2** precipitated. The structure of **2** could not be deduced from spectroscopic data and so an X-ray structure analysis was completed (Figure 1).

In the crystal structure of **2** interionic contacts are consistent with van der Waals distances. Both anions, I(2), and the cation [atoms Pt(1), Pt(2), I(1), C(1), and C(4)] lie on a crystallographic mirror plane. The point group symmetry of the cation, however, approximates closely to C_{2v}, the noncrystallographic diad axis passing through I(1) and the centroid of the Pt(1) → Pt(2) vector.

The structure of **2** (Figure 1, Table I) shows that the oxidative addition of MeI to **1a**, which has also been characterized crystallographically,[11,12] occurs with conversion of square-planar coordination geometry of platinum(II) into octahedral geometry of platinum(IV) and the formation of an iodo bridge between the metal centers. The *cis*-bis(diphosphinomethane) configuration of **1a** is retained in **2** but in the latter each platinum atom is bonded to three *facial* methyl groups. In **2** the mean Pt–C bond length [2.11 (2) Å] differs little from the corresponding value in **1a** [2.16 (2) Å]. The Pt–P bonds, however, show a lengthening of ca. 0.1 Å [2.275 (4) in **1a** and 2.376 (2) Å in **2**], which is characteristic of the change in the oxidation state of platinum.[14]



1a, PP = dmpm
b, PP = depm
c, PP = dppm



2, PP = dmpm

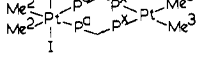
The conformation of the dmpm ligands, and hence of the eight-membered $Pt_2P_4C_2$ dimetallacycles, is also different in the two compounds. In **1a** each dmpm ligand displays two Pt–P–C–P torsion angles of the same sign and nearly equal size, giving the mean value of 44 (1)°. Such a conformation, characterized by approximate C_2 symmetry, is extremely rare among diphosphinomethane ligands, and in **1a** it yields a twist-chair eight-membered ring of C_{2h} symmetry.[11,12] In **2** the dmpm ligands adopt the more usual C_s conformation, with Pt–P–C–P torsion angles across the respective C(7)–P(1) and C(7)–P(2) bonds of −63.2 (6) and +65.2 (6)°. Here the $Pt_2P_4C_2$ ring shows C_{2v} symmetry concordant with the mean internal torsion angles across the P–C and Pt–P bonds of $|\omega_1| = 64\ (1)°$ and $|\omega_2| = 43\ (2)°$, respectively. The conformation of this ring can be considered derived by small distortions of a boat-boat arrangement of D_{2d} symmetry, such as that found in cyclooctane where $|\omega_1| = |\omega_2| = 52.5°$.[15] Such a conformation permits insertion of an iodo bridge between the two platinum atoms.

Steric overcrowding, present in **1a**,[11,12] is even more severe in **2**, where near eclipsing of the Pt–Me and P–Me bonds leads to short intramolecular contacts: C(1)···C(5) = 3.35 (2), C(2)···C(6) = 3.16 (2), C(3)···C(9) = 3.18 (2), and C(4)···C(8) = 3.38 (2) Å. The C(6)···C(9) and C(7)···C(7′) nonbonding distances of 3.42 (2) and 3.52 (2) Å are also short. The resulting steric strain is apparently balanced by some large angular distortions. Thus the local environments of the metal atoms display considerable deviations from ideal octahedral geometry as is particularly evident from the bond angles C–Pt–C = 85.1 (5)–85.4 (5), P–Pt–P = 96.4 (1)–97.5 (1), and C–Pt–L (L = P or I) = 171.7 (6)–174.1 (4)° (Table I). The Pt–P–CH_2 and P–CH_2–P angles of 121.9 (4)–122.3 (4) and 125.8 (5)°, respectively, are extremely large in comparison with the tetrahedral value. They result in the largest P···P bite, 3.257 (3) Å, and the longest Pt···Pt distance, 4.707 (1) Å, so far observed in dmpm- and dppm-bridged complexes.

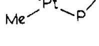
The Pt···Pt separation in **2** is much too long to indicate a bonding interaction.[16] It shows that in oxidative addition of **1a**, in which a $d^8 \rightarrow d^6$ conversion of the electronic configuration and a concomitant increase in the coordination number occur at both metal centers, the metal–metal separation increases by ca. 0.5 Å.

The ^1H NMR spectrum of **2** is fully consistent with the structure of Figure 1. Two MePt resonances are observed, with a 2:1 intensity ratio and with coupling constants typical of the *fac*-$[PtIMe_3P_2]$ coordination shell.[2,3] The CH_2P_2 protons give an AB quartet in the $^1H\{^{31}P\}$ NMR spectrum as expected. However, the ^{31}P NMR spectrum of **2** gave a singlet with singlet satellites due to coupling to ^{195}Pt, whereas all other $Pt_2(\mu\text{-dmpm})$ complexes which we have studied have given multiplet satellite signals.[11-13,17] This is evidently due to the stretched conformation of the μ-dmpm ligands in **2** (Figure 1), which must lead to the coupling constant $^2J(PP)$ being negligibly small. The ^{31}P chemical shift of **2** was −44.7 ppm ($\Delta\delta$ = 12.5 ppm from free dmpm), in the range expected for μ-dmpm complexes but, to make sure that rearrangement to monomeric *fac*-$[PtIMe_3(dmpm)]$, **5a**, did not occur in solution, an independent synthesis of **5a** was carried out by reaction of $[(PtIMe_3)_4]$ with dmpm. The ^{31}P chemical shift for **5a** was −80.7 ppm ($\Delta\delta$ = −23.5 ppm), and the high field shift is typical of chelate $R_2PCH_2PR_2$ complexes.[17] The solid-state structure of **2** (Figure 1) is clearly maintained in solution.

Characterization of the Intermediate 3a. The intermediate, responsible for the initial coloration, in the reaction of **1a** with methyl iodide has been characterized by NMR spectroscopy as **3a**. Using excess CH_3I and



3a, PP = dmpm
b, PP = depm



4a, PP = dppm
b, PP = dippm

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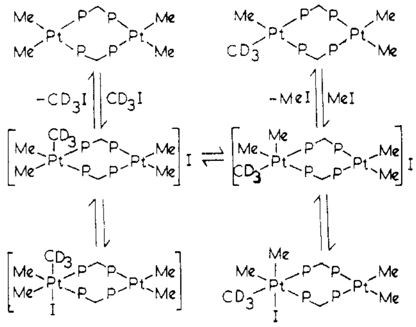
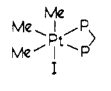
Scheme I

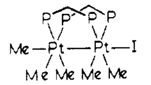


PP = dmpm or depm.

monitoring the reactions by ^1H and ^{31}P NMR, it was found that resonances due to **1a** decayed over a period of 10–20 min. In the ^{31}P NMR spectra, two new peaks grew [δ −52.1 ($^1J(PtP)$ = 1160 Hz), −22.6 ($^1J(PtP)$ = 1688 Hz)] and, from the values of $^1J(PtP)$,[18,19] were assigned as P^A and P^X, respectively, of **3a**. After about 1 h, these peaks had in turn decayed and the spectrum of **2** was observed. Similarly, in the ^1H NMR spectra, signals due to the three types of methylplatinum groups in **3a** were identified [δ 0.87 (t, $^2J(PtH)$ = 73 Hz, Me^1), 1.10 (m, $^2J(PtH)$ = 57 Hz, Me^2), 0.52 (m, $^2J(PtH)$ = 66 Hz, Me^3)] with the expected forms[20] and coupling constants,[2,3] and these signals decayed as further reaction to give **2** occurred. The spectra are not consistent with the structure **6**, considered possible by analogy with earlier work.[4-10]



5a, PP = dmpm
b, PP = dppm
c, PP = dippm



6, PP = dmpm

In order to determine the stereochemistry of oxidative addition, the reaction of **1a** with CD_3I was studied by using ^1H and ^2H NMR spectroscopy. In the ^2H NMR spectrum of intermediate **3a** signals corresponding to both Me^1 and Me^2 groups were observed, but there was no signal due to Me^3. In the ^1H NMR spectrum signals due to Me^1 and Me^2 decreased in intensity, compared to the corresponding spectrum with CH_3I as reagent, but the Me^3 signal intensity did not decrease. These data show that scrambling of the CD_3 label between the Me^1 and Me^2 positions occurs. This scrambling was not expected since most such oxidative additions occur trans (eq 1), which would give CD_3 only in the Me^1 position of **3a**. This can be rationalized by assuming that the expected ionic intermediate $[Me_3Pt(\mu\text{-dmpm})_2PtMe_2]^+I^-$ has a longer lifetime than in mononuclear complexes and scrambling of groups within the five-coordinate Me_3Pt^{IV} unit occurs before the iodide coordinates to give **3a** (see Scheme I).[21]

Reversible Oxidative Addition of MeI to 1b. Reaction of excess methyl iodide with complex **1b** gave a yellow coloration, and monitoring by NMR showed that reaction to give **3b** was complete after several hours at room temperature (Figure 2). However, on removal of the solvent under vacuum, complex **1b** was recovered in quantitative yield. The oxidative addition of methyl iodide to **1b** is therefore reversible; this is a rare phenomenon.[10]

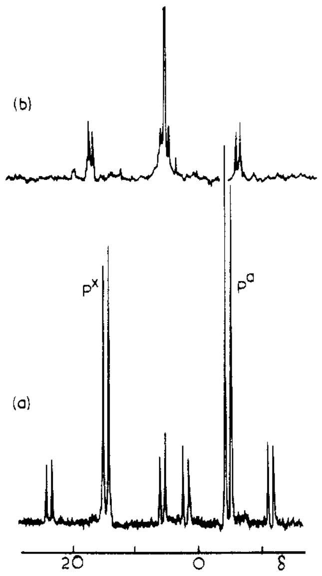
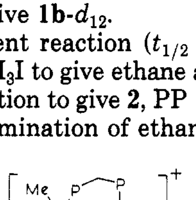


Figure 2. $^{31}P\{^1H\}$ NMR spectra (82 MHz) of (a) complex **3b**, in the reaction mixture of **1b** with excess MeI, (b) complex **1b**, formed by evaporation of the above solution followed by dissolution of the product in the absence of excess MeI.

Since it was shown that addition of CD_3I to **1a** was not stereospecific, the reversible reaction of CD_3I with **1b** should lead to exchange of methyl groups as shown in Scheme I (which indicates only how the first CH_3 for CD_3 exchange is believed to occur). This was indeed the case. Reaction of excess CD_3I with **1b** gave after 1 day essentially complete exchange to give CH_3I and **3b**-d_{15} as monitored by ^1H NMR spectroscopy, and evaporation of the solvent at this stage will give **1b**-d_{12}.

A slow subsequent reaction ($t_{1/2} \approx$ 3 days) occurred between **3b** and CH_3I to give ethane and **7**. This presumably occurs by reaction to give **2**, PP = depm, followed by rapid reductive elimination of ethane to give **7**.[22,23]



7, PP = depm

The differences in reactivity between **1a** and **1b** are clearly due to increased steric hindrance in **1b**. We have shown previously that complex **1c**, with still bulkier phenyl substituents, does not react at all with methyl iodide.[24] This great sensitivity to steric effects is not observed in reactions of the monomers **4**. Thus, both **4a** and **4b**, with bulky phenyl and isopropyl substituents, respectively, react readily with methyl iodide to give **5b** or **5c**, respectively. This is because the substituents in **4** are directed away from the open sites above and below the square-planar platinum center, whereas in the dimers **1** there is much

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(18) Coupling constants in Pt(IV) complexes are often about $^2/_3$ the values for similar Pt(II) complexes, provided that the trans groups are common to both.[19] Note that $^1J(PtP^X)$ in **3a** is close to the value for **1a**, but $^1J(PtP^A)$ is about $^2/_3$ of this value.

(19) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Complexes"; Springer-Verlag: Berlin, 1979.

(20) The signals due to Me^2 and Me^3 have a very characteristic appearance seen for *cis*-$[PtMe_2P_2]$ coordination. It arises from a second-order $A_3A'_3XX'$ spin system.[2,3]

(21) Scrambling of methyl groups within five-coordinate Me_3Pt^{IV} units is known.[2] The longer lifetime could be due to steric hindrance to coordination of I^- or due to a weak donor–acceptor Pt → Pt interaction in the proposed ionic intermediate.

(22) Complex **7** is also formed by reaction of **1b** with iodine and its characterization has been described elsewhere.[23]

(23) Ling, S. S. M.; Payne, N. C.; Puddephatt, R. J., submitted for publication in Organometallics.

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greater steric hindrance to attack at these sites.[11]

It is clear that complexes **1** are more reactive toward oxidative addition than are the corresponding complexes **3**. This is probably due largely to increased steric hindrance in **3**, but it is possible that electronic effects may also be significant.

Experimental Section

NMR spectra were recorded by using Varian XL100, XL200, and XL300 spectrometers. The complexes $[Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2]$ were prepared by the literature method.[11]

$[Pt_2Me_6(\mu\text{-}I)(\mu\text{-dmpm})_2]I$, 2. Iodomethane (0.1 mL) was added to a stirred solution of complex **1a** (0.06 g) in CH_2Cl_2 (12 mL). A white suspension was observed after 30 min, and the mixture was allowed to stand for 10 h to give the product as a white precipitate. The product was washed with *n*-pentane (4 mL) and then dried in vacuo: yield 0.071 g; decomp pt 280 °C. MS: *m/e* 931 (P − 5Me), 916 (P − 6Me). NMR in $CDCl_3$: ^1H, δ 0.93 [t, $^3J(PH)$ = 8 Hz, $^2J(PtH)$ = 70 Hz, *Me*Pt trans to I], 0.96 [m, $^2J(PtH)$ = 55 Hz, *Me*Pt trans to P], 1.52–1.86 [m, *Me*P], 2.79 and 3.15 [m, $^2J(H^aH^b)$ = 8 Hz, $CH^aH^bP_2$]; ^{31}P, δ −44.7 [s, $^1J(PtP)$ = 1186 Hz, $\Delta\delta$ = 12.5 ppm, *P*Pt]. Anal. Calcd for $C_{16}H_{46}I_2P_4Pt_2$: C, 19.1; H, 4.6. Found: C, 19.2; H, 4.6.

$[PtIMe_3(dmpm)]$. To a stirred solution of $[\{PtIMe_3\}_4]$ (0.082 g) in benzene (20 mL) was added dmpm (0.037 mL). The solution was allowed to stir for 30 min, then benzene was removed under vacuum, and the product was obtained as a white solid, which was washed with two portions of *n*-pentane (5 mL): yield 0.070 g; decomp pt 177 °C. NMR in $CDCl_3$: ^1H, δ 0.93 [m, $^2J(PtH)$ = 61 Hz, *Me*Pt trans to P], 1.06 [t, $^3J(PH)$ = 8 Hz, $^2J(PtH)$ = 73 Hz, *Me*Pt trans to I], 1.36 [d, $^2J + {}^4J(PH)$ = 13 Hz, $^3J(PtH)$ = 10 Hz, *Me*P], 1.83 [d, $^2J + {}^4J(PH)$ = 11 Hz $^3J(PtH)$ = 9 Hz, *Me*P], 3.58 [m, $^2J(H^aH^b)$ = 15 Hz, $^2J(PH)$ = 11 Hz, $CH^aH^bP_2$], 3.83 [m, $^2J(H^aH^b)$ = 15 Hz, $^2J(PH)$ = 9 Hz, $^3J(PtH)$ = 9 Hz, $CH^aH^bP_2$]; ^{31}P, δ −80.7 [s, $^1J(PtP)$ = 987 Hz, −$\Delta\delta$ = −23.5, *P*Pt]. Anal. Calcd for $C_8H_{23}P_2IPt$: C, 19.1; H, 4.6. Found: C, 19.0; H, 4.5.

Complex 1a with CH_3I. To a saturated solution of complex **1a** (5 mg) in $CDCl_3$ (0.5 mL) in an NMR tube was added excess CH_3I (20 μL). The reaction was monitored by ^1H, $^1H\{^{31}P\}$, and ^{31}P NMR spectroscopies. In each case, an initial spectrum was taken before the CH_3I was added and then spectra were taken at 10-min intervals after addition until no further change occurred (1 h). Reaction of **1a** with CD_3I was studied similarly, but $^2H\{^1H\}$ NMR spectra were also recorded at the reaction proceeded. NMR of **3a** in $CDCl_3$: ^1H, δ 0.52 [m, $^2J(PtH)$ = 66 Hz, Me^3Pt], 0.87 [t, $^3J(PH)$ = 7 Hz, $^2J(PtH)$ = 73 Hz, Me^1Pt], 1.10 [m, $^2J(PtH)$ = 57 Hz, Me^2Pt], 1.56–1.78 [m, *Me*P]; ^{31}P, −52.1 [s, $^1J(PtP)$ = 1160 Hz, $^3J(PtP)$ = 11 Hz, $\Delta\delta$ = 5.1 ppm P^aPt], −22.6 [s, $^1J(PtP)$ = 1688 Hz, $\Delta\delta$ = 34.6 Hz, P^xPt].

Complex 1b with CH_3I or CD_3I. To a solution of **1b** (5 mg) in $CDCl_3$ (0.25 mL) in an NMR tube was added CH_3I (0.10 mL). The solution became yellow in color. After 1 h, reaction to give **3b** was complete, as monitored by ^1H and ^{31}P NMR. The solvent was evaporated under vacuum to give a white solid identified as pure **1b** by the ^1H and ^{31}P NMR spectra.

Reaction of **1b** with CD_3I was carried out in the same way and occurred at about the same rate. However, the exchange of *Me*Pt for CD_3I groups was also monitored by the growth of the CH_3I resonance in the ^1H NMR spectra. This exchange was slower than the oxidative addition and was complete in about 1 day at room temperature. NMR of **3b** in $CDCl_3$: ^1H, δ 1.43 [m, $^2J(PtH)$ = 66 Hz, Me^3Pt], 1.6–2.6 [complex, CH_3C + Me^1, Me^2], 3.8 and 4.9 [m, CH_2Me], ^{31}P, δ −5.0 [d, $^2J(PP)$ = 71 Hz, $^1J(PtP)$ = 1102 Hz, $^3J(PtP)$ = 15 Hz, $\Delta\delta$ = 23.6 Hz, P^aPt], 14.46 [d, $^2J(PP)$ = 71 Hz, $^1J(PtP)$ = 1464 Hz, $\Delta\delta$ = 43.1, P^xPt].

$[PtIMe_3(dippm)]$. The complex $[PtMe_2(dippm)]$ (0.030 g) was dissolved in CH_2Cl_2 (2 mL), and excess MeI (0.5 mL) was added. After 6 h the solvent was removed under vacuum, and the resulting solid was washed with *n*-pentane (2 mL) and characterized as the pure product by ^1H and ^{31}P NMR spectroscopies; yield 0.012 g. NMR in $CDCl_3$: ^1H, δ 0.99 [m, $^2J(PtH)$ = 60 Hz, *Me*Pt trans to P], 0.84 [t, $^3J(PH)$ = 7 Hz, $^2J(PtH)$ = 72 Hz, *Me*Pt trans to I], 1.1–1.6 [complex, *Me*C], 2.30 [m, $^2J(HH)$ = 7 Hz, *CH*Me_2], 3.12 [m, $^2J(H^aH^b)$ = 14 Hz, $^2J(PH)$ = 10 Hz, $CH^aH^bP_2$], 4.00 [m, $^2J(H^aH^b)$ = 14 Hz, $^2J(PH)$ = 8 Hz, $^3J(PtH)$ = 18 Hz, $CH^aH^bP_2$]; ^{31}P, δ −52.0 [s, $^1J(PtP)$ = 916 Hz, $\Delta\delta$ = +45.8 ppm *P*Pt]. Anal. Calcd for $C_{16}H_{39}IP_2Pt$: C, 31.2; H, 6.3. Found: C, 31.0; H, 6.2.

Table II. Crystallographic Data for $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3][I]$

formula	$C_{16}H_{46}I_2P_4Pt_2$
fw, amu	1006.4
cryst system	monoclinic
space group	*C*2/*m*
a, Å	18.396 (5)
b, Å	10.991 (2)
c, Å	14.233 (3)
β, deg	95.10 (2)
V, Å^3	2866
Z	4
F(000), electrons	1856
d(calcd), g cm^{-3}	2.332
μ(MoKα), cm^{-1}	122.1
abs factors on *F*	0.59–1.58
intensity measurements	
scan type	$\theta/2\theta$
scan width ($\Delta\omega$), deg	1.23
max counting time, s	90
2θ range, deg	4–54
2^a	0.04
unique reflctns	3284
final refinement	
reflctns used [$I \geq 3\sigma(I)$]	2807
refined parameters	153
shift/error, max value	0.31
R^b	0.044
$R_w{}^b$	0.066
weights, *w*	$\sigma^{-2}(F_o)$

[a] Manojlović-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1974**, 2427. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table III. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3][I]$

	x/a	*y/b*	*z/c*	*U*,^{a} Å^2
Pt(1)	0.16732 (3)	0	0.13279 (3)	0.0257 (3)
Pt(2)	0.42103 (3)	0	0.21399 (3)	0.0249 (3)
I(1)	0.30629 (5)	0	0.07670 (5)	0.0358 (6)
I(2)	0.76165 (8)	0	0.43702 (7)	0.0537 (10)
P(1)	0.37065 (13)	0.16105 (21)	0.29850 (15)	0.0278 (12)
P(2)	0.19542 (13)	0.16276 (21)	0.24004 (15)	0.0267 (12)
C(1)	0.0575 (8)	0	0.1557 (12)	0.050 (10)
C(2)	0.1367 (7)	0.1320 (11)	0.0256 (7)	0.055 (9)
C(3)	0.4728 (6)	0.1289 (11)	0.1345 (8)	0.052 (7)
C(4)	0.5188 (9)	0	0.3029 (14)	0.056 (13)
C(5)	0.1278 (7)	0.1892 (12)	0.3242 (9)	0.056 (8)
C(6)	0.1988 (7)	0.3120 (9)	0.1863 (8)	0.048 (8)
C(7)	0.2750 (5)	0.1601 (8)	0.3260 (6)	0.029 (5)
C(8)	0.4121 (7)	0.1859 (12)	0.4207 (7)	0.054 (8)
C(9)	0.3821 (8)	0.3106 (9)	0.2524 (9)	0.059 (10)

[a] $U = (U_{11} + U_{22} + U_{33})/3$.

X-ray Structure Analysis of $[Me_3Pt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3][I]$ 2. The experimental and computational procedures employed are those standard in this laboratory (Glasgow) and previously fully described in ref 4. Pertinent details of this analysis are shown in Table II.

All X-ray measurements were made at 22 ± 1 °C, with a yellow, plate-like crystal of approximate dimensions 0.95 × 0.30 × 0.10 mm. Graphite-monochromated molybdenum radiation (λ = 0.71069 Å) and an Enraf-Nonius CAD4 diffractometer were used.

The unit-cell dimensions were determined by a least-squares treatment of diffractometric angles of 25 high-angle reflections. The intensities of X-ray reflections were corrected for background, Lorentz, polarization, and absorption effects. The absorption correction was made by using the empirical method of Walker and Stuart.[25] A total of 2798 reflections related by symmetry

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(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

were averaged to obtain 1365 unique structure amplitudes; they gave R (internal) of 0.138 before, and 0.046 after, absorption correction.

The crystal structure was successfully solved in the space group $C2/m$ and refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The atomic scattering factors and the anomalous dispersion corrections were taken from ref 26. The positions of the platinum atoms were obtained from a Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Hydrogen atoms were not located in electron density maps nor included in structure factor calculations. An allowance was made for anisotropic thermal vibrations of all non-hydrogen atoms. In the final difference electron density map the function values were in the range ±3 e $Å^{-3}$; the extreme values, associated with the positions of platinum and iodine atoms, are likely to reflect residual absorption effects.

The final atomic coordinates are shown in Table III. The anisotropic thermal parameters of atoms and the observed and calculated structure amplitudes are listed in supplementary material.

All calculations were performed on a GOULD SEL 32/27 minicomputer, using the locally developed GX program system.[27]

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Registry No. **1a**, 88228-39-1; **1b**, 91491-48-4; **1c**, 79870-63-6; **2**, 96412-20-3; **3a**, 89144-05-8; **3b**, 96412-21-4; **4b**, 91491-49-5; **5a**, 96412-23-6; **5c**, 96412-22-5; **7**, 96427-22-4; $[\{PtIMe_3\}_4]$, 18253-26-4; MeI, 74-88-4.

Supplementary Material Available: Anisotropic thermal parameters of atoms (Table IV) and final $|F_o|$ and $|F_c|$ values (Table V) (16 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Some Ligand Substitution and Insertion Reactions in Pseudotetrahedral Ruthenium(II) Complexes

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Pseudotetrahedral (S_{Ru},R_C)-**1** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru(prophos)Cl, **1′** (where prophos is (*R*)-1,2-propanediylbis(diphenylphosphine)), react with CH_3MgBr or C_2H_5MgBr to give the alkylation products (S_{Ru},R_C)-**2** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru(prophos)R, **2′** (R = CH_3, **a**; R = C_2H_5, **b**), with stereospecific retention of configuration at the ruthenium atom. With C_2H_5MgBr also a competitive formation of the corresponding hydrides (S_{Ru},R_C)-**3** and (R_{Ru},R_C)-$(\eta$-$C_5H_5)$Ru(prophos)H, **3′**, takes place. Hydride formation is the only reaction observed when **1** or **1′** is reacted with *sec*-C_4H_9MgBr and, according to NOE experiments, takes also place with retention of configuration. Under the conditions of their formation (or even under more severe conditions) **2b** and **2b′** do not thermally decompose to **3** or **3′**. Hydride formation is therefore not a consequence of alkylation followed by β-hydrogen elimination but must arise from a different reaction pathway whose possible nature is discussed. Hydrides **3** and **3′** react with CH_2N_2 in the presence of catalytic amounts of $Pd(CH_3COO)_2$ to give the methyl derivatives **2a** and **2a′** with retention of configuration. Stereospecific retention of configuration is also observed in the formation of **3** and **3′** when **1** and **1′** are treated with CH_3ONa. By contrast, the reaction of **1** and **1′** and that of (S_{Ru},R_C)-**4** and (R_{Ru},R_C)-$[(\eta$-$C_5H_5)$Ru(prophos)$(CH_3CN)]PF_6$, **4′**, with HCOONa is stereoselective; in the first case **3** and **3′** were obtained in a 20:80 and in the second one in a 40:60 molar ratio. **1** and **1′** form from the hydrides **3** and **3′** when treated with $CDCl_3$ or CCl_4 in a stereoselective reaction. Predominant inversion of configuration is observed in the reaction of **4** and **4′** with $(C_6H_5)_4AsCl$ to give **1** and **1′**.

Soon after the first reports on homogeneous asymmetric reactions catalyzed by transition-metal complexes containing chiral ligands, the possibility was recognized that the metal can become a chirality center during catalysis.[2,3] The possible role of chiral metals in those enantioselective transformations has been discussed[4] and sometimes probably recognized.[5] Furthermore, it has been recently shown that in the stoichiometric cyclopropanation of styrene by chiral diastereomeric ethylideneiron complexes the chirality at the metal plays an overwhelming (if not exclusive) role with respect to that of the phosphine ligand in determining the stereochemical outcome of the reaction.[6]

Therefore the search for the rationalization and improvement of results of homogeneous asymmetric catalysis implies not only a better identification of the catalytic species[7] but also a more detailed knowledge of the stere-

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