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PHOSPHONATE YLIDE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II): OXIDATIVE ADDITION AND REDUCTIVE ELIMINATION, THE CRYSTAL AND MOLECULAR STRUCTURES OF *cis*- AND *trans*-[Pt(PPh$_3$)$_2$(I)(CH$_2$P(O)(OCH$_3$)$_2$)]

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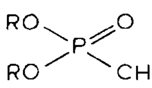
Summary

Phosphonate complexes M(PPh$_3$)$_2$(I)(CH$_2$P(O)(OR)$_2$) (M = Pd and Pt, R = Me and Et) have been prepared by the oxidative addition of ICH$_2$P(O)(OR)$_2$ to M(PPh$_3$)$_4$. While the platinum product isomerized slowly from the *cis*- to the *trans*-isomer, the palladium compound decomposed in solution. Several compounds have been identified from the decomposition reaction: ICH$_2$P(O)(OCH$_3$)$_2$, CH$_3$P(O)(OCH$_3$)$_2$, [Pd(PPh$_3$)$_2$(CH$_2$P(O)(OCH$_3$)$_2$)]I, OPPh$_3$ and [Pd(PPh$_3$)(I)(CH$_2$P(O)(OCH$_3$)$_2$)]$_2$. In air, ICH$_2$P(O)(OCH$_3$)$_2$ was the major product observed; however, in the absence of air, CH$_3$P(O)(OCH$_3$)$_2$ was the major product. A study of the reaction pathway showed that the reductive elimination proceeded via phosphine dissociation. The structures of the *trans*- and *cis*-platinum compounds were determined by X-ray diffraction, and were refined to $R_w = 0.036$ (5382 observed reflections) and 0.027 (5274 observed reflections), respectively. The bond lengths of Pt–P, Pt–C and Pt–I *trans* to various ligands clearly demonstrate the order of the *trans* influence: phosphonate > phosphine > I.

Introduction

The chemistry of phosphorus ylides with transition metals has been extensively studied in the last ten years [1]. The most widely studied phosphorus ylides are of the $R_3P^+{-}\bar{C}H_2$ type, in which R may be an alkyl or aryl group. Another class of phosphorus ylides which has been used in the Wittig reaction but has not been explored in metal complexes is the phosphonate anion $(RO)_2P(O)(CH_2)^-$ (I) [2]. Anions of this type are more reactive than the corresponding phosphoranes.

Two related systems have been reported: $[(RO)_2P(O)]_2(CH)^-$ (II) by Dixon [3] and $(Ph)_2P(S)(CH_2)^-$ (III) by Fackler [4]. In the former, it is the negatively charged carbon which bonds to the Pt metal. In the latter, the sulfur-substituted phosphonate anion III functions as a bidentate ligand with both the carbon and sulfur atoms.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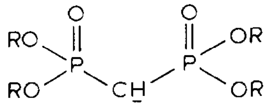
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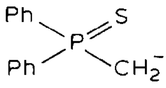

(III)

In this paper we report on the study of metal complexes of phosphonate anions. We have prepared the metal-ylide complexes by the method of oxidative addition. Although oxidative addition has long been used as a method for the preparation of metal–alkyl bonds [5], metal-ylide complexes have rarely been prepared by this method. One known example [6] is the formation of $[Pt(PPh_3)_2(CH_2PPh_3)Cl]I$ from the reaction of CH_2ClI with $Pt(PPh_3)_4$. Moss and Spiers proposed that the ylide complex was formed by the oxidative addition of $[PPh_3CH_2Cl]I$ to the Pt^0 complex.

Experimental

All chemicals and solvents were reagent grade and were used as received unless otherwise specified. $Pt(PPh_3)_4$ [7], $Pd(PPh_3)_4$ [8] and $Ir(PPh_3)_2(CO)Cl$ [7] were prepared according to the reported methods. $Pd(dppe)_2$ was prepared by following the preparation method of its analogue $Pd(PPh_3)_4$. $ICH_2P(O)(OCH_3)_2$ and $ICH_2P(O)(OC_2H_5)_2$ were prepared by the Arbuzov reaction [9] and were checked by ^1H NMR spectrometry and measurement of the refractive index.

Proton NMR spectra were recorded on a Varian EM-360 or 390 instrument. Phosphorus-31 NMR spectra were run on a Jeol FX-100 spectrometer operated at 40.37 MHz. Infrared spectra were recorded on a Beckman Acculab TMl. In all cases, samples were prepared with KBr pellets. Conductivities were measured using a WPA CMD 400 Digital Conductivity Meter. Elemental analyses were done by Chung Shung Research Center, Taiwan. The results of ^1H NMR are listed in Table 1.

trans-$Pd(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2]$. Dimethyliodomethylphosphonate (0.075 g, 0.3 mmol) in 30 ml of benzene was purged with nitrogen for 5 min. Tetrakis(triphenylphosphine)palladium (0.346 g, 0.3 mmol) was added under N_2. The resulting yellow solution turned to orange red after stirring for 4 h at room temperature. The solution was dried under reduced pressure and the residue was thoroughly washed three times with n-hexane. After air-drying, 0.2 g of the residue was collected (76% yield). Recrystallization from $CHCl_3$ and hexane gave two different types of crystals (orange crystals and light-yellow needle crystals), both having the same stoichiometry by elemental analysis. Recrystallization of either type of crystals from $CHCl_3$ gave a mixture of the two crystal types again. Anal. Found: C, 53.4; H, 4.3. $C_{39}H_{38}IO_3P_3Pd$ calcd.: C, 53.2; H, 4.3%. IR, $\nu(PO)$: 1215 cm^{-1}. If after the reaction the solution was sealed and allowed to stand for 2 days, the benzene-solvated compound $Pd(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2] \cdot C_6H_6$ was obtained as an orange crystal. Anal. Found: C, 56.0; H, 4.5. $C_{45}H_{44}IO_3P_3Pd$ calcd.: C, 56.5, H, 4.6%. IR, $\nu(PO)$: 1218 cm^{-1}.

TABLE 1

^{1}H NMR DATA OF PHOSPHONATE COMPLEXES

Compound	Chemical shift [a] (ppm)	Assignment
$Pd(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$	0.914 (M [b], 2 [c])	$PdCH_2$
	3.08 (d [d], 6) [e]	OCH_3
$Pd(PPh_3)_2(I)(CH_2P(O)(OC_2H_5)_2)$	0.90 (*T* [f], 6) [g]	CCH_3
	0.9–1.6 (m, 2)	$PdCH_2$
	3.48 (m, 4)	OCH_2
$[Pd(PPh_3)(\mu\text{-}I)(CH_2P(O)(OCH_3)_2)]_2$	1.2–1.6 (m, 4)	$PdCH_2$
	3.35 (d, 12) [e]	OCH_3
$[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$	0.6–1.0 (m, 2)	$PdCH_2$
	3.75 (d, 6) [e]	OCH_3
$[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]BF_4$	0.6–1.0 (m, 2)	$PdCH_2$
	3.73 (d, 6) [e]	OCH_3
$[Pd(PPh_3)_2(CH_2P(O)(OC_2H_5)_2]BF_4$	0.6–1.0 (m, 2)	$PdCH_2$
	1.30 (t, 6) [g]	OCH_3
	4.10 (m, 4)	OCH_2
$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$-*cis*	1.7–2.1 (m, 2)	$PtCH_2$
	3.40 (d, 6) [h]	OCH_3
$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$-*trans*	0.8–1.4 (m, 2)	$PtCH_2$
	3.10 (d, 6) [i]	OCH_3
$[Pt(PPh_3)_2(CH_2P(O)(OCH_3)_2)]BF_4$	2.0–2.4 (m, 2)	$PtCH_2$
	3.73 (d, 6) [e]	OCH_3

[a] In $CDCl_3$ solvent downfield relative to TMS. All phenyl protons in the range between 7 and 8 ppm are not listed. [b] Multiplet. Due to the low intensity of MCH_2 signals, the coupling constants for ^2J(HP) are estimated around 13 Hz and ^3J(HP) are around 7 Hz. The *cis*-phosphine compounds are doublet of doublets and the *trans*-compounds are two overlapping triplets. [c] Relative intensities. [d] Doublet. [e] Coupling constant ^3J(HP) 13 Hz. [f] Triplet. [g] Coupling constant ^3J(HP) 7 Hz. [h] Coupling constant ^3J(HP) 13 Hz. Coupling constant ^3J(HP) 10 Hz.

$[Pd(PPh_3)(\mu\text{-}I)(CH_2P(O)(OCH_3)_2)]_2$. The *trans*-palladium compound (0.5 g, 0.6 mmol) prepared as described above was dissolved in 35 ml of $CHCl_3$ and oxygen was bubbled through the solution for 2 days. The resulting solution was then dried by vacuum pump and washed thoroughly with ether. Recrystallization from a $CHCl_3$ hexane mixture gave 0.1 g (28% yield) of a light yellow compound. Anal. Found: C, 40.4; H, 3.8, I 20.2; P, 10.3. $C_{21}H_{23}IO_3P_2Pd$ calcd.: C, 40.8; H, 3.7; I, 20.5; P, 10.1%. IR, ν(PO): 1216 cm^{-1}.

$Pd(PPh_3)_2(I)(CH_2P(O)(OC_2H_5)_2)$ and $Pd(dppe)(I)(CH_2P(O)(OCH_3)_2)$. These two compounds were prepared using a method similar to the previous one. The yields were greater than 70%. Anal. Found; C, 54.8; H, 4.6. $C_{41}H_{42}IO_3P_3Pd$ calcd.: C, 54.2; H, 4.6%. IR, ν(P=O): 1230 cm^{-1}. Anal. Found: C, 48.0; H, 4.2. $C_{29}H_{32}IO_3P_3Pd$ calcd.: C, 48.1; H, 4.1%. IR, ν(PO): 1190 cm^{-1}.

$[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]BF_4$. Since $AgBF_4$ is very hygroscopic, this salt was first dissolved in a minimum amount of distilled water. The concentration was then determined [10] before use. Aqueous $AgBF_4$ (1 mmol) was added to $Pd(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$ (0.8 g, 0.8 mmol) in 50 ml of acetone. A light yellow solid immediately precipitated. After stirring for 10 min, the solution was filtered and the filtrate was dried under vacuum. The residue was washed with copious amounts of water and was dried under vacuum at 80°C; 0.5 g of a white product was obtained (74% yield). Recrystallization from acetone gave white acetone-solvated crystals. Anal. Found: C, 55.8; H, 4.8. $C_{42}H_{44}BF_4O_4P_3Pd$ calcd.:

C, 56.1; H, 4.9%. IR, ν(PO): 1185 cm^{-1}. Molar conductivity (acetone, 2.03×10^{-5} M), 134 ohm^{-1} cm^2 mol^{-1}.

$[Pd(PPh_3)_2(CH_2P(O)(OC_2H_5)_2)]BF_4$. This compound was prepared by a method similar to that used to prepare the methyl analogue and a similar yield was obtained. Anal. Found: C, 57.7; H, 4.7. $C_{41}H_{42}BF_4O_3P_3Pd$ calcd.: C, 57.6; H, 4.8%. IR, ν(PO): 1160 cm^{-1}. Molar conductivity (acetone, 2.01×10^{-5} M), 123 ohm^{-1} cm^2 mol^{-1}.

$[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$. A large excess of NaI was added to the acetone solution of $[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]BF_4$. This was stirred for more than 4 h, and the solvent was evaporated to dryness. The residue was washed several times with water, and the product was dried under vacuum. The yield was almost quantitative. Anal. Found: C, 52.8; H, 4.4. $C_{39}H_{38}IO_3P_3Pd$ calcd.: C, 53.2; H, 4.3%. IR, ν(PO): 1185 cm^{-1}. Molar conductivity (acetone, 1.05×10^{-4} M), 90 ohm^{-1} cm^2 mol^{-1}.

cis- and trans-$[Pt(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2]]$. Dimethyliodomethylphosphonate (0.08 g, 0.3 mmol) in 10 ml of benzene was added dropwise to $Pt(PPh_3)_4$ (0.40 g, 3.2 mmol) dissolved in 20 ml of benzene under an inert atmosphere. After stirring for 3 h, the pale yellow solution turned golden yellow. The volume of the solvent was reduced to 10 ml by vacuum and 50 ml of hexane was then added. The precipitate was filtered and washed several times with n-hexane. After drying in air, 0.6 g (84% yield) of product was collected. Recrystallization from acetone gave pale yellow crystals analyzed to be *cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2 \cdot H_2O$ and a small amount of yellow crystals analyzed to be *trans*-Pt $(PPh_3)_2(I)(CH_2)P(O)(OCH_3)_2) \cdot (CH_3)_2CO$. Anal. Found: C, 47.5; H, 4.1. *cis*-$C_{39}H_{40}IO_4P_3Pt$ calcd.: C, 47.4; H, 4.1%. Found: C, 49.1; H, 4.5. *trans*-$C_{42}H_{44}IO_3P_3Pt$ calcd.: C, 49.1; H, 4.3%. IR, ν(PO): *cis* 1220 cm^{-1}; *trans* 1225 cm^{-1}, m.p. *cis*, 180°C; *trans*, 203°C.

$[Pt(PPh_3)_2(CH_2P(O)(OCH_3)_2)]BF_4$. This compound can be prepared in the same way as the palladium analogue. When first isolated, the compound was analysed to be the 1/1 acetone-solvated species. The solvent was removed under vacuum from the pulverized compound. Anal. Found: C, 50.2; H, 4.0. $C_{39}H_{38}BF_4O_3P_3Pt$ calcd.: C, 50.4; H, 4.1%. IR, ν(PO): 1185 cm^{-1}, m.p. 105°C. Molar conductivity (acetone, 1.50×10^{-5} M), 130 ohm^{-1} cm^2 mol^{-1}.

$Ir(PPh_3)_2(CO)(I)(Cl)(CH_2P(O)(OCH_3)_2)$. A mixture of an equal molar ratio of $Ir(PPh_3)_2(CO)Cl$ and $ICH_2P(O)(OCH_3)_2$ was dissolved in benzene under nitrogen atmosphere. The resulting solution was heated between 55 and 65°C for 12 h. It was then cooled to room temperature. After standing for 2 h, the precipitated white solid was filtered and washed with hexane (50% yield). Anal. Found: C, 46.5; H, 3.9. $C_{40}H_{38}ClIrO_4P_3$ calcd.: C, 46.6; H, 3.7%. IR, ν(CO): 2020 cm^{-1}; ν(PO): 1228 cm^{-1}.

Structure determination and refinement of trans- and cis-$[Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)]$. The diffraction data were collected on a Kappa geometry CAD4 diffractometer at room temperature. The experimental details are given in Table 2. Both structures were solved by the heavy atom method, with Pt and I atoms located in the Patterson map. All the non-hydrogen atoms were located in the subsequent Fourier map. Full matrix and block diagonal least-squares methods were used in the refinement process. The minimized quantity is $\Sigma W_i \mid F_0 - F_c \mid_i^2$, where $W_i = 1/\sigma_i^2(F_0)$, and $\sigma_i^2(F_0)$ was calculated from counting statistic $\sigma_c(I)$. Absorption corrections were applied to both structures according to experimental ψ rotations;

TABLE 2

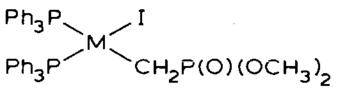
CRYSTAL DATA FOR *trans*- AND *cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$

	trans-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)\cdot(CH_3)_2CO$	*cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)\cdot H_2O$
Mol. wt.	987	1027
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.678(2)	16.981(3)
b (Å)	19.664(4)	12.870(3)
c (Å)	18.788(4)	17.309(3)
β (°)	107.36(1)	90.71(1)
Volume (Å^3)	4117.9	3782.7
Cell parameter determination	25 reflections at $22 < 2\theta < 26°$	25 reflections at $23 < 2\theta < 30°$
Z	4	4
D_m, D_c	1.65(5), 1.66	1.72(5), 1.70
Colour	yellow	light yellow
Crystal size (mm)	0.45×0.4×0.3	0.5×0.5×0.3
μ (cm^{-1})	43.37	47.18
Normalized transmission coeff.	0.74–1.00	0.60–1.00
λ (radiation)	Mo-K_α	Mo-K_α
$\theta/2\theta$ range	$1.6+0.7\tan\theta$	$1.4+0.7\tan\theta$
$2\theta_{max}$	50°	50°
Normal refinement ($I \geqslant 3\sigma(I)$)	7241, (5382)	6650, (5274)
Final shift/error	0.66	0.36
R, R_w	0.034, 0.036	0.032, 0.026
$h\,k\,l$	$0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 23$, $-22 \leqslant l \leqslant 22$	$0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 16$, $-21 \leqslant l \leqslant 21$

the range of transmission coefficients is given in Table 2. A secondary isotropic extinction correction was made during the anisotropic refinement of all non-hydrogen atoms. All the hydrogen atoms were either found in the difference Fourier map or calculated according to ideal geometry and then were kept fixed during the refinement process. The refinement finally converged to an R_w value of 0.036, 0.027 for the *trans*- and *cis*-isomer, respectively. Final difference Fourier maps were computed for both structures; no details were found in either structure. The procedure and computing program used are presented elsewhere [11]. The scattering factors and anomalous terms were applied according to the International Tables for Crystallography, Vol. IV.

Results and discussion

Preparation and characterization. The oxidative addition of iodophosphonate, $ICH_2P(O)(OCH_3)_2$, to $M(PPh_3)_4$ (M = Pd and Pt) gave good yields of phosphonate complexes IV and V, with reasonable stability in air. Using this method the major platinum compound isolated was the *cis*-isomer IV, while the palladium



(IV, M = Pt; *cis* or *trans*
V, M = Pd; *cis* or *trans*)

compound gave the *trans*-isomer V. During recrystallization from chloroform, the *cis*-platinum compound IV isomerized slowly to the *trans*-isomer. It is clear that the *cis*-isomer IV is the kinetically controlled product while the *trans*-isomer is the thermodynamically stable isomer.

These compounds are non-conductive as demonstrated by the conductivity measurements in various solvents. The coupling of methylene protons to the two phosphine phosphorus atoms observed in the ^{1}H NMR spectra suggests that like II, it is the phosphonate carbon that bonds to metals. The IR spectra of these compounds show a strong absorption frequency at ~ 1220 cm^{-1} assignable to the stretching frequencies of PO [12]. This evidence suggests that the phosphonate behaves as a monodentate ligand, as shown in IV and V.

The assignment of the *cis*- and *trans*-isomers was done by ^{31}P NMR spectroscopy, in which the *cis*-isomer shows an ABX-type pattern while the *trans*-isomer shows an A_2X-type pattern. The *trans*-palladium compound V has a phosphine ^{31}P signal at 25.4 ppm and a phosphonate ^{31}P signal at 39.0 ppm. The ^{31}P proton decoupled NMR spectrum of the *cis*-isomer IV is shown in Fig. 1. The different phosphorus signals were labelled P^A (13.6 ppm), P^B (17.1 ppm) and P^X (41.4 ppm); the coupling constants are $^{3}J(P^A-P^X)$ 10 Hz, $^{2}J(P^A-P^B)$ 17 Hz. Those signals without labels are satellites due to the coupling between ^{31}P and ^{195} Pt (I 1/2, 33% abundance). The coupling constant of ^{195}Pt–$^{31}P^B$ (4044 Hz) is much greater than that of ^{195}Pt–$^{31}P^A$ (2026 Hz), and the ^{196}Pt–C–$^{31}P^X$ (90 Hz) coupling constant is the smallest. The *trans*-platinum isomer has a phosphine ^{31}P signal at 21.6 ppm (^{2}J(Pt–P) 2910 Hz) and a phosphonate ^{31}P signal at 37.5 ppm (^{3}J(Pt–P) 141 Hz), Assuming that the relative coupling constants between ^{31}P and ^{195}Pt indicate the strength of the *trans* infuence [13], the observed order of coupling constants

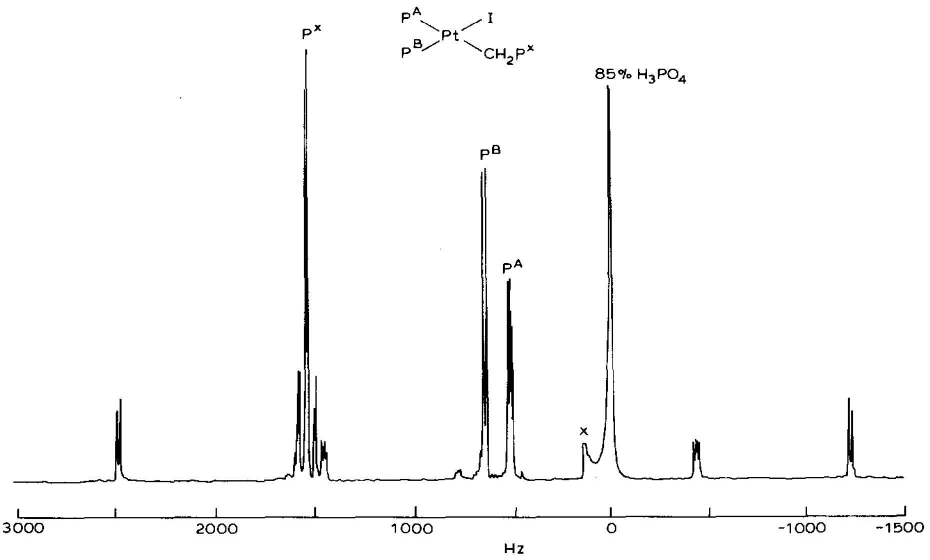
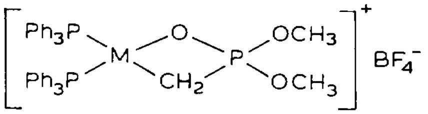


Fig. 1. ^{31}P{^{1}H} NMR spectrum of *cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$ in $CDCl_3$, 40.37 MHz, 85% H_3PO_4 standard. The different phosphorus atoms are labelled. The signal marked X is due to some unidentified impurity.

suggests the order of *trans* influence to be: phosphonate > PPh_3 > I. This order is consistent with the previously reported trans influence [14] and our X-ray structural results, which will be discussed later.

The reactions of IV and V with $AgBF_4$ in acetone gave ionic compounds VI, which are believed to be bidentate phosphonate ligands as shown in VI. The shift of



(VI, M = Pd and Pt)

the PO stretching frequency from 1220 to 1185 cm^{-1} and the conductivity measurements (~ 130 ohm^{-1} cm^2 mol^{-1}) support our conclusion that the PO oxygen is coordinated to M [15]. The bonding mode is similar to that in III. In contrast to the ease for formation of the bidentate of III, in the absence of silver ion, the formation of ionic $[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$ from V is very limited. This difference may result from the hard-soft ligand–metal interaction [16]. Attempts to use different counter-anions in various solvents in order to obtain a crystal suitable for single-crystal X-ray analysis have so far been unsuccessful.

Crystal and molecular structures of $Pt(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2]$. The atomic labelling scheme and the structures of both *trans*- and *cis*-IV are shown in Fig. 2. The atomic coordinates and bond distances and bond angles are listed in Tables 3 and 4. The bond lengths of Pt–P *trans* to phosphonate, triphenylphosphine and iodide are 2.331(2), 2.308(2) (average of 2.312 and 2.305) and 2.257(2) Å, respectively. The trend clearly demonstrates the order of the *trans* influence as phosphonate > PPh_3 > I. The same trend is also apparent in the bond lengths of Pt–C and Pt–I. The Pt–C bond lengths *trans* to PPh_3 and I are 2.124(6) and 2.080(8) Å, respectively, and the Pt–I bond lengths *trans* to phosphonate and PPh_3 are 2.6774(7) and 2.6561(7) Å. While phosphonate exhibits a relatively strong *trans* influence, the $CH(PPh_2O)_2$ ligand, reported by Dixon and co-workers [3], only shows a modest *trans* influence with Pt–P distance of 2.25(1) Å. The bond angles of L–Pt–L′ from the four ligands around the Pt atom of the *cis*-isomer are more distorted from the regular 90° (i.e. 86°, 85°, 98°, 91°) than those of the *trans*-isomer (90°, 88°, 93°, 91°). This probably results from the steric hindrance between the two neighbouring bulky PPh_3 groups. The phosphonate P=O distance (1.472 Å average) and P–C distance (1.757 Å average) are within the normal double and single bond ranges reported in II [3]. The non-bonding distance between the Pt atom and O(3) atom in the *trans*-isomer is substantially longer than that in the *cis*-isomer (3.497(6) vs. 3.450(4) Å). Both structures contain solvent molecules; the *trans*-isomer has an acetone molecule, and the *cis*-isomer has weak hydrogen bonding between water solvent O(s) atoms and the O(3) atoms of P=O groups in phosphonate, with O · · · O distances of 2.936(7) and 2.952(6) Å as shown in Fig. 3. Each *cis*-complex is hydrogen-bonded to two water molecules, and forms and infinite chain throughout the crystal. Such a hydrogen bond is slightly weaker than those in oxalic acid dihydrates, which have O · · · O distances of 2.882 and 2.868 Å [17] *.

(Continued on p. 235)

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* Full tables of atomic coordinates and thermal parameters, bond lengths, bond angles and structure factors can be obtained from the authors.

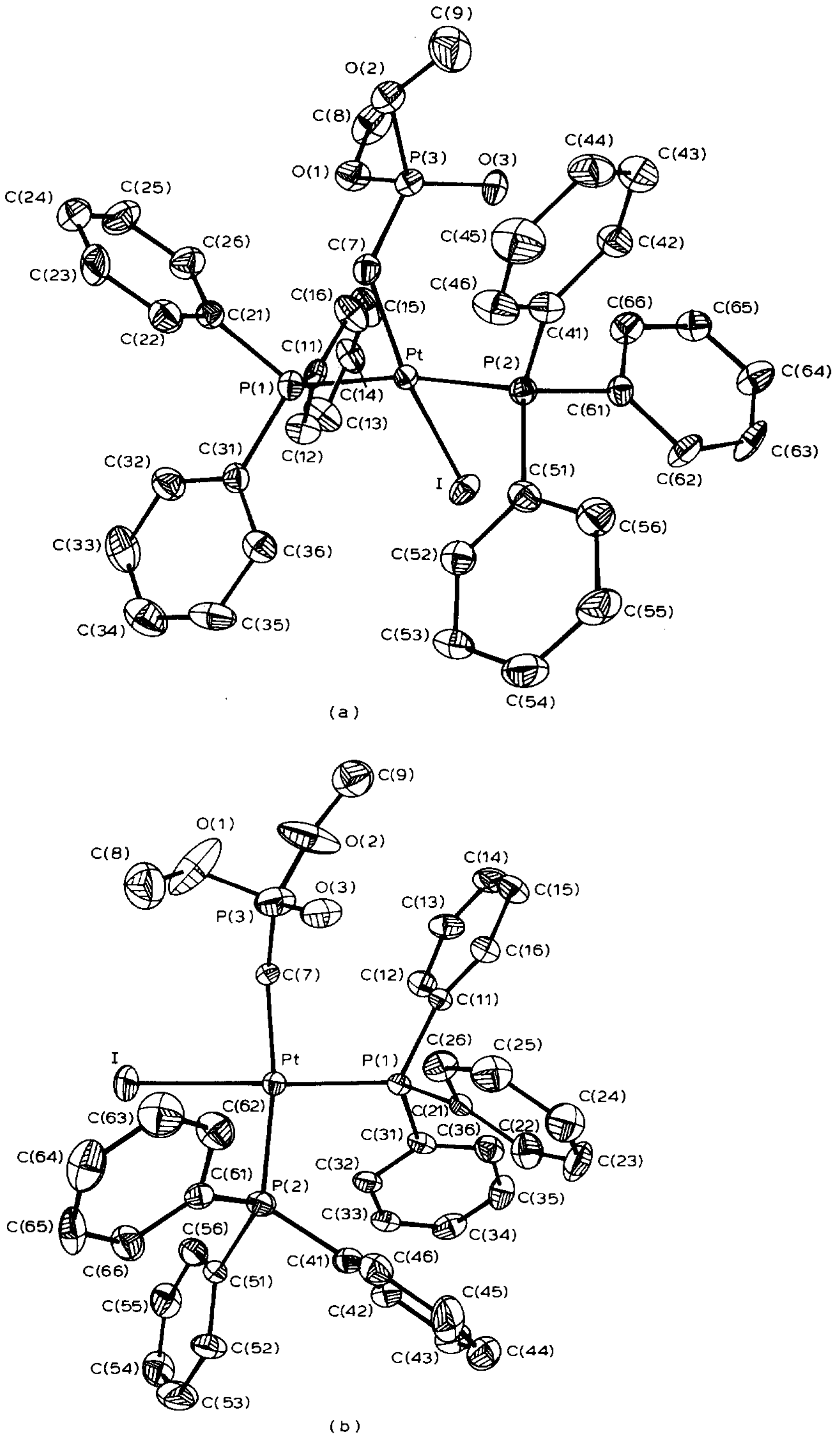


Fig. 2. Molecular structures of $Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$; (a) *trans*; (b) *cis*.

TABLE 3a

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR *trans*-$Pt(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2]\cdot$acetone

Atom	x	y	z	B_{iso}
Pt	0.01411(3)	0.24821(2)	0.15025(2)	2.30(1)
I	0.17019(6)	0.15979(3)	0.12290(4)	3.95(4)
P(1)	−0.1081(2)	0.1581(1)	0.1576(1)	2.7(1)
P(2)	0.1572(2)	0.3319(1)	0.1609(1)	2.5(1)
P(3)	−0.1949(2)	0.3466(1)	0.0608(1)	3.4(1)
C(11)	−0.1448(7)	0.1037(4)	0.0759(5)	2.9(4)
C(12)	−0.1153(9)	0.0352(5)	0.0795(5)	4.5(6)
C(13)	−0.1402(10)	−0.0030(5)	0.0126(6)	5.6(8)
C(14)	−0.1982(9)	0.0270(5)	−0.0547(6)	5.0(6)
C(15)	−0.2247(10)	0.0962(5)	−0.0582(5)	5.0(7)
C(16)	−0.1975(9)	0.1351(5)	0.0064(5)	4.5(7)
C(21)	−0.2526(7)	0.1773(4)	0.1729(5)	3.1(5)
C(22)	−0.2482(9)	0.2104(5)	0.2399(5)	4.3(5)
C(23)	−0.3543(10)	0.2247(5)	0.2553(6)	6.7(7)
C(24)	−0.4629(9)	0.2048(6)	0.2070(6)	6.2(7)
C(25)	−0.4665(9)	0.1721(6)	0.1444(6)	5.9(7)
C(26)	−0.3617(8)	0.1578(5)	0.1251(5)	4.4(6)
C(31)	−0.0471(8)	0.1007(4)	0.2373(5)	3.2(5)
C(32)	−0.1217(9)	0.0502(5)	0.2524(6)	5.2(6)
C(33)	−0.0784(11)	0.0051(5)	0.3107(6)	6.5(8)
C(34)	0.0381(10)	0.0112(5)	0.3555(5)	5.7(8)
C(35)	0.1087(10)	0.0600(6)	0.3437(5)	5.5(7)
C(36)	0.0685(9)	0.1038(5)	0.2829(5)	4.3(6)
C(41)	0.1166(7)	0.4204(4)	0.1672(4)	2.6(4)
C(42)	0.1024(8)	0.4669(4)	0.1101(5)	3.3(5)
C(43)	0.0739(9)	0.5352(5)	0.1183(5)	4.6(6)
C(44)	0.0621(9)	0.5562(5)	0.1854(6)	4.9(6)
C(45)	0.0728(10)	0.5111(5)	0.2433(5)	4.8(7)
C(46)	0.0999(9)	0.4432(5)	0.2348(5)	4.0(6)
C(51)	0.2827(7)	0.3224(4)	0.2483(4)	2.8(4)
C(52)	0.2870(7)	0.2667(4)	0.2941(4)	3.0(4)
C(53)	0.3837(8)	0.2603(5)	0.3605(4)	4.0(3)
C(54)	0.4702(8)	0.3086(5)	0.3794(5)	4.0(5)
C(55)	0.4652(8)	0.3647(5)	0.3343(5)	4.0(5)
C(56)	0.3719(8)	0.3725(4)	0.2686(5)	3.3(5)
C(61)	0.2244(7)	0.3334(4)	0.0845(4)	2.9(4)
C(62)	0.3505(7)	0.3356(5)	0.0964(5)	3.6(5)
C(63)	0.3932(8)	0.3385(5)	0.0347(5)	5.1(6)
C(64)	0.3146(9)	0.3388(5)	−0.0364(5)	5.1(6)
C(65)	0.1940(8)	0.3362(5)	−0.0473(5)	4.0(5)
C(66)	0.1468(7)	0.3333(5)	0.0119(4)	3.3(5)
C(7)	−0.1157(8)	0.3203(4)	0.1514(5)	3.2(4)
C(8)	−0.3682(9)	0.2897(6)	−0.0426(6)	5.7(7)
C(9)	−0.2428(11)	0.4765(5)	0.0609(6)	6.6(8)
O(1)	−0.2920(5)	0.2893(3)	0.0329(3)	3.9(3)
O(2)	−0.2784(6)	0.4088(3)	0.0691(4)	4.9(4)
O(3)	−0.1267(5)	0.3629(3)	0.0091(3)	4.2(4)
O [a]	0.9578	0.3417	0.3621	7.9
C(1s) [a]	0.8958	0.3741	0.3816	7.9
C(2s) [a]	0.8374	0.3517	0.4353	7.9
C(3s) [a]	0.9282	0.4513	0.4112	7.9

[a] Acetone solvent.

TABLE 3b

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR *cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)\cdot H_2O$

Atom	x	y	z	B_{iso}
Pt	0.10595(1)	0.20931(2)	0.22948(1)	2.60(1)
I	0.17008(3)	0.09027(5)	0.33868(3)	5.45(4)
P(1)	0.0664(1)	0.3266(1)	0.1403(1)	2.6(1)
P(2)	−0.0034(1)	0.2185(2)	0.3093(1)	3.0(1)
P(3)	0.1910(1)	0.0722(2)	0.0979(1)	4.6(1)
O(1)	0.2286(3)	−0.0284(5)	0.1308(4)	9.9(6)
O(2)	0.2534(3)	0.1005(6)	0.0326(3)	10.2(7)
O(3)	0.1112(2)	0.0574(4)	0.0657(2)	4.4(3)
C(7)	0.2077(3)	0.1727(5)	0.1646(3)	3.1(4)
C(8)	0.1852(5)	−0.1072(7)	0.1670(4)	7.3(6)
C(9)	0.2487(5)	0.0760(7)	−0.0404(4)	6.7(6)
C(11)	0.1271(3)	0.3425(5)	0.0533(3)	2.8(3)
C(12)	0.2003(4)	0.3903(5)	0.0620(3)	3.5(4)
C(13)	0.2495(4)	0.4020(6)	0.0000(4)	4.7(4)
C(14)	0.2253(4)	0.3656(6)	−0.0703(3)	4.7(4)
C(15)	0.1531(4)	0.3187(6)	−0.0814(3)	4.5(5)
C(16)	0.1034(4)	0.3054(5)	−0.0181(3)	3.6(4)
C(21)	−0.0318(3)	0.3031(5)	0.0994(3)	2.5(3)
C(22)	−0.0868(4)	0.3784(5)	0.0835(3)	3.5(4)
C(23)	−0.1577(4)	0.3515(6)	0.0483(4)	4.6(5)
C(24)	−0.1724(4)	0.2508(6)	0.0284(4)	5.0(5)
C(25)	−0.1182(4)	0.1749(6)	0.0451(4)	4.5(4)
C(26)	−0.0484(3)	0.2007(5)	0.0810(3)	3.3(4)
C(31)	0.0700(3)	0.4578(5)	0.1783(3)	2.8(4)
C(32)	0.0943(3)	0.4741(5)	0.2530(3)	3.1(4)
C(33)	0.0985(4)	0.5741(6)	0.2828(3)	4.0(5)
C(34)	0.0782(4)	0.6594(6)	0.2386(4)	4.6(4)
C(35)	0.0564(4)	0.6446(6)	0.1629(4)	4.9(4)
C(36)	0.0531(4)	0.5451(5)	0.1320(3)	3.7(4)
C(41)	−0.0928(3)	0.2882(5)	0.2797(3)	3.2(4)
C(42)	−0.0945(4)	0.3953(6)	0.2879(3)	4.1(4)
C(43)	−0.1609(4)	0.4514(6)	0.2677(4)	5.4(5)
C(44)	−0.2261(4)	0.4012(7)	0.2390(4)	5.8(6)
C(45)	−0.2257(4)	0.2961(7)	0.2309(4)	5.6(6)
C(46)	−0.1579(4)	0.2393(6)	0.2506(3)	4.1(4)
C(51)	0.0112(4)	0.2769(5)	0.4050(3)	3.3(4)
C(52)	−0.0532(4)	0.2869(6)	0.4534(3)	4.6(5)
C(53)	−0.0437(4)	0.3334(7)	0.5250(4)	5.9(6)
C(54)	0.0279(5)	0.3704(6)	0.5470(4)	5.8(5)
C(55)	0.0925(4)	0.3630(6)	0.5002(4)	5.2(5)
C(56)	0.0837(4)	0.3147(6)	0.4292(3)	4.0(4)
C(61)	−0.0369(3)	0.0848(5)	0.3248(3)	3.4(4)
C(62)	−0.0397(4)	0.0189(6)	0.2615(3)	4.2(4)
C(63)	−0.0576(4)	−0.0840(6)	0.2704(4)	5.1(4)
C(64)	−0.0719(4)	−0.1248(6)	0.3421(4)	5.4(5)
C(65)	−0.0694(4)	−0.0619(6)	0.4058(4)	5.3(5)
C(66)	−0.0520(4)	0.0421(6)	0.3981(3)	4.3(4)
O(s) [a]	0.5247(3)	0.4184(4)	0.4178(3)	6.4(1)

[a] Water oxygen atom.

TABLE 4

SELECTED BOND DISTANCES AND BOND ANGLES OF THE Pt COORDINATIOIN SPHERE OF THE *trans*- AND *cis*-ISOMERS

trans-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$ ·acetone		*cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)\cdot H_2O$	
Bond distance (Å)			
Pt–I	2.6774(8)	Pt–I	2.6561(7)
Pt–P(1)	2.305(2)	Pt–P(1)	2.257(2)
Pt–P(2)	2.312(2)	Pt–P(2)	2.331(2)
Pt–C(7)	2.080(8)	Pt–C(7)	2.124(6)
P(1)–C(11)	1.816(8)	P(1)–C(11)	1.843(6)
P(1)–C(21)	1.833(8)	P(1)–C(21)	1.828(6)
P(1)–C(31)	1.841(9)	P(1)–C(31)	1.811(7)
P(2)–C(41)	1.816(8)	P(2)–C(41)	1.828(6)
P(2)–C(51)	1.856(8)	P(2)–C(51)	1.834(6)
P(2)–C(61)	1.830(8)	P(2)–C(61)	1.832(7)
P(3)–C(7)	1.755(9)	P(3)–O(1)	1.548(6)
P(3)–O(1)	1.573(6)	P(3)–O(2)	1.600(6)
P(3)–O(2)	1.600(6)	P(3)–O(3)	1.479(6)
P(3)–O(3)	1.465(6)	P(3)–C(7)	1.759(7)
O(1)–C(8)	1.43(1)	O(1)–C(8)	1.40(1)
O(2)–C(9)	1.42(1)	O(2)–C(9)	1.310(9)
Bond angle (°)			
I–Pt–P(1)	89.95(6)	I–Pt–P(1)	171.56(5)
I–Pt–P(2)	87.88(6)	I–Pt–P(2)	85.98(5)
I–Pt–C(7)	169.9(2)	I–Pt–C(7)	85.4(2)
P(1)–Pt–P(2)	170.69(8)	P(1)–Pt–P(2)	97.97(6)
P(1)–Pt–C(7)	93.3(2)	P(1)–Pt–C(7)	91.4(2)
P(2)–Pt–C(7)	91.4(2)	P(2)–Pt–C(7)	169.5(2)
C(7)–P(3)–O(1)	103.4(4)	O(1)–P(3)–O(2)	99.8(4)
C(7)–P(3)–O(2)	106.9(4)	O(1)–P(3)–O(3)	113.4(3)
C(7)–P(3)–O(3)	118.3(4)	O(1)–P(3)–C(7)	108.3(3)
O(1)–P(3)–O(2)	100.4(4)	O(2)–P(3)–O(3)	112.4(3)
O(1)–P(3)–O(3)	114.6(4)	O(2)–P(3)–C(7)	101.3(3)
O(2)–P(3)–O(3)	111.4(4)	O(3)–P(3)–C(7)	119.2(3)
P(3)–O(1)–C(8)	120.0(6)	P(3)–O(1)–C(8)	123.2(6)
P(3)–O(2)–C(9)	120.1(6)	P(3)–O(2)–C(9)	126.5(6)
Pt–C(7)–P(3)	111.4(4)	Pt–C(7)–P(3)	112.6(3)

Reductive elimination of iodophosphonate and other decomposition reactions. *trans*-V in $CDCl_3$ was allowed to stand in an NMR tube. After a prolonged period of time we observed the formation of $ICH_2P(O)(OCH_3)_2$ in the ^1H NMR spectrum. This means that the oxidative addition product V decomposed reversibly via a reductive elimination reaction. Since the reductive elimination reaction is, in general, an important catalytic step [18], the relative lack of attention to this reaction in the literature [19], when compared with the oxidative addition, prompted us to study this system in detail.

The decomposition reactions of *trans*-$Pd(PPh_3)_2(I)[CH_2P(O)(OCH_3)_2]$ was studied by NMR spectroscopy. The freshly prepared *trans*-isomer in $CDCl_3$ showed a sharp doublet at 3.08 ppm assignable to OCH_3 protons. When the sample was kept at 20°C under air for 24 h, the sharp doublet gradually broadened and another

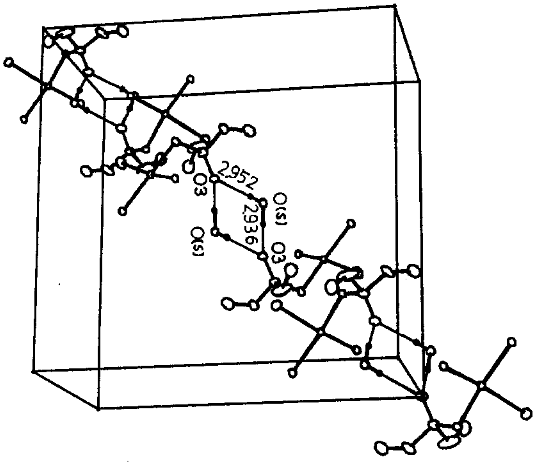


Fig. 3. Hydrogen bonding between solvent H_2O molecule and phosphonate oxygen atoms in *cis*-$Pt(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)\cdot H_2O$.

broad doublet appeared at 3.30 ppm after 2 days. Prolonged standing gave four new sets of doublets between 3 and 4 ppm while the original doublet at 3.08 ppm gradually disappeared. At 50°C a similar situation occurred except that the change was more drastic and the relative ratio of the new species was different. The four sets of OCH_3 doublets correspond to $[Pd(PPh_3)(\mu\text{-}I)(CH_2P(O)(OCH_3)_2)]_2$ (VII), $ICH_2P(O)(OCH_3)_2$, $CH_3P(O)(OCH_3)_2$ and $[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$ (Fig. 4). When the sample was sealed under vacuum and kept at 50°C for 5 days, the major decomposition product observed was $CH_3P(O)(OCH_3)_2$ and the minor product was $ICH_2P(O)(OCH_3)_3$.

The decomposition reaction product $ICH_2P(O)(OCH_3)_2$ observed in the ^1H NMR spectrum (doublet at 3.80 and 3.08 ppm, relative intensity 3/1) must come from the reductive elimination of palladium compound V. The formation of $CH_3P(O)(OCH_3)_2$ (doublet at 3.70 and 1.45 ppm, relative intensity 2/1) from the pohsphonate ligand requires a hydrogen atom either from the trace amount of water in the solvent or from the orthometallation of the phosphine phenyls. In one experiment the water peak originally observed before decomposition disappeared after reaction. In another controlled experiment in which air and moisture were excluded, $CH_3P(O)(OCH_3)_2$ was also observed. Thus hydrogen sources both from water and orthometallation of the phosphine phenyls are possible for the formation of phosphonate. The dimeric VII, which will be discussed below, displays a broad doublet at 3.30 ppm due to the exchange with V. The appearance of a small amount of ionic compound $[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$ could possibly be explained as coming from V by the displacement of the coordinated iodide by the dangling oxygen atom of PO.

After work-up on a preparative scale of the decomposed compound, yellow, white and orange-red crystalline compounds were isolated. The yellow material VII reacted with PPh_3 to give the starting compound V. Microanalysis, IR and ^1H NMR spectroscopy suggested a dimeric compound of formula $[Pd(PPh_3)(\mu\text{-}I)(CH_2P(O)(OCH_3)_2)]_2$. Upon mixing the dimeric compound VII and monomeric V, the

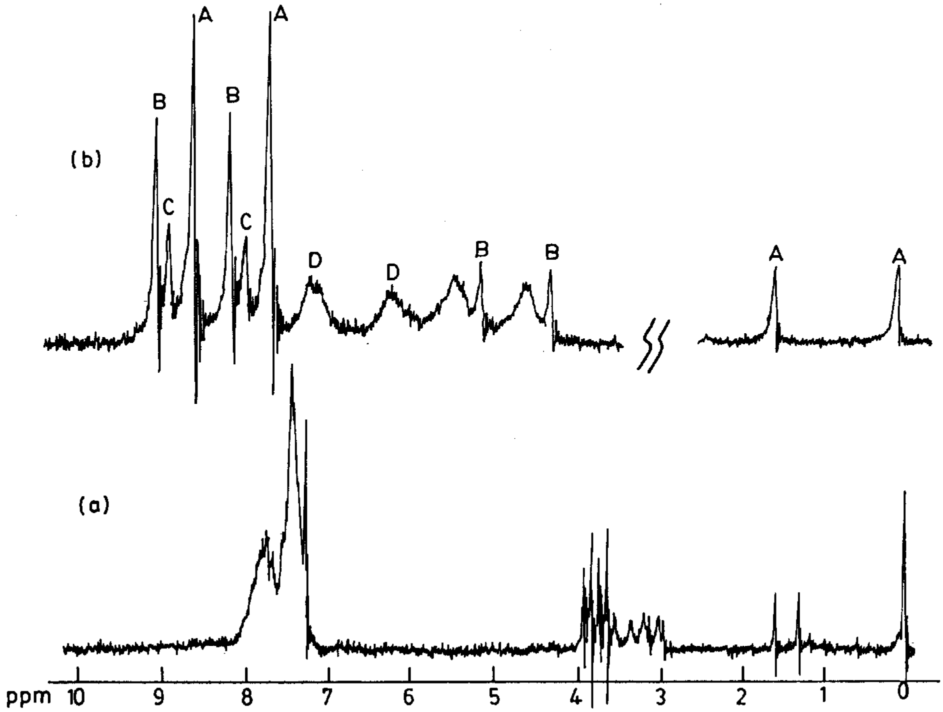
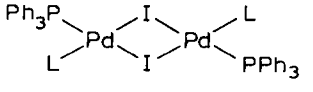


Fig. 4. (a) ^1H NMR spectrum of $Pd(PPh_3)_2(I)(CH_2P(O)(OCH_3)_2)$ in $CDCl_3$ after warming at 50°C for 8 days. (b) Enlarged portion of (a) from 1 to 4 ppm. Assignments are A, $CH_3P(O)(OCH_3)_2$; B, $ICH_2P(O)(OCH_3)_2$; C, $[Pd(PPh_3)_2(CH_2P(O)(OCH_3)_2)]I$; D, $[Pd(PPh_3)(\mu\text{-}I)(CH_2P(O)(OCH_3)_2)]_2$.

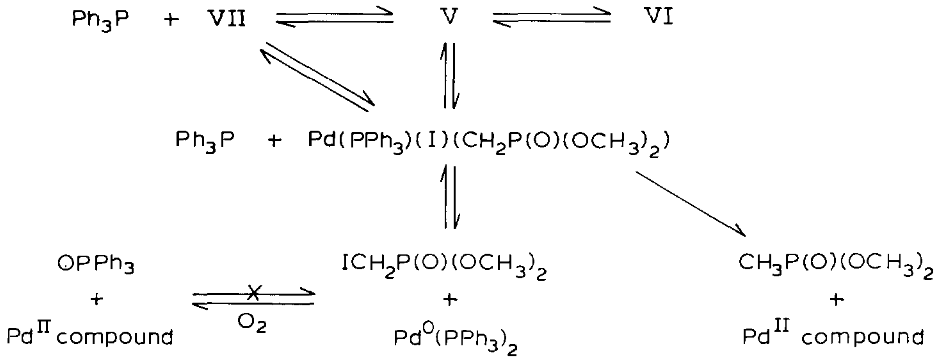
two sharp ^1H NMR doublets assignable to VII and V individually were broadened. This result suggests that the exchange rate between VII and V is comparable to the NMR time-scale.



(VII, $L = CH_2P(O)(OCH_3)_2$)

Fitton et al. [20] reported the formation of dimeric $[Pd(PPh_3)(Cl)(CH_2Ph)]_2$ from the recrystallization of a benzylpalladium compound $Pd(PPh_3)_2(Cl)(CH_2Ph)$ from chloroform and hexane. Cusumano et al. [21] also reported that prolonged photolysis of a *cis/trans* mixture of $Pd(PR_3)_2Cl_2$ yielded the dimer $[Pd(PR_3)Cl_2]_2$ and PR_3, where R = n-Pr. In all cases, phosphines dissociated to form coordinatively unsaturated species which then further dimerized.

The white crystalline material has microanalysis, m.p. ^1H NMR and IR signals identical to authentic $OPPh_3$. Triphenylphosphine oxide was always observed in high yield in the decomposition reaction in air. However, when the reaction was carried out under nitrogen atmosphere only a small amount of phosphine but no phosphine oxide was observed. This result suggests that the oxygen atom of $OPPh_3$ came from air.



SCHEME 1

The third compound has an orange-red colour. The ^1H NMR spectrum of this compound showed only phenyl signals around 7–8 ppm. Although the exact nature of this compound is not known, the phosphonate ligand is certainly lost.

To explain the above result, we propose the decomposition reactions shown in Scheme 1.

Since PPh_3 or $OPPh_3$ from the decomposition reactions has always been observed, a coordinatively unsaturated intermediate may indeed exist. To determine the relation between the phosphine dissociation and the reductive elimination of alkyl halide, several experiments were carried out. A one-tenth molar ratio of free PPh_3 was added to V in $CDCl_3$ at 20°C. An ^1H NMR spectrum taken after 3 days showed no $ICH_2P(O)(OCH_3)_2$ signal. Since the presence of free phosphine will inhibit the dissociation of the coordinated phosphine, this observation implies that the less the coordinated phosphine is dissociated, the less the reductive elimination will be observed. In order to study the effect of the bidentate chelates on the decomposition reaction we prepared a diphos chelate compound, Pd(dppe)(I)[$CH_2P(O)(OCH_3)_2$] (dppe = bis(diphenylphosphino)ethane). This compound does show greater thermal stability towards reductive elimination in comparison with the corresponding monodentate phosphine complexes (by NMR). Since the chelate diphos compound should show greater thermal stability towards phosphine dissociation, this observation supports the previous argument about the phosphine dissociation and reductive elimination. The effects of excess phosphine and a bidentate chelate on the reductive elimination have already been discussed by others [22–24]. Thus phosphine dissociation does indeed promote the reductive elimination.

After the dissociation of phosphine, the coordinated unsaturated species may undergo reductive elimination to give $Pd(PPh_3)_2$ and $ICH_2P(O)(OCH_3)_2$, or the coordinated $CH_2P(O)(OCH_3)_2$ ligand may abstract a hydrogen atom as described before to give $CH_3P(O)(OCH_3)_2$. In the absence of air, the oxidative addition of $ICH_2P(O)(OCH_3)_2$ back to $Pd(PPh_3)_2$ is reversible. On the other hand, the formation of $CH_3P(O)(OCH_3)_2$ is irreversible, hence $CH_3P(O)(OCH_3)_2$ is the major product. In the presence of air, the formation of $ICH_2P(O)(OCH_3)_2$ is also irreversible due to the oxidation of Pd(O) by air. Hence the relative amount of $CH_3P(O)(OCH_3)_2$ and $ICH_2P(O)(OCH_3)_2$ formed depends on the relative rate of formation of the individual phosphonates. The experimental results are consistent with our proposed scheme.

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