Inorg. Chem. **1987**, *26*, 3447-3452

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19716

Single, Double, Triple, and Quadruple Arbuzov-like Demethylation of $[Pt[P(OMe)_3]_4]^{2+}$

Q.-B. Bao and T. B. Brill*

Received May 11, 1987

The multiple Arbuzov-like demethylation of $[Pt[P(OMe)_3]_4]^{2+}$ to form $[Pt[P(OMe)_3]_3[P(O)(OMe)_2]]^+$, $Pt[P(OMe)_3]_2[P(O)(OMe)_2]_2$, $[Pt[P(OMe)_3][P(O)(OMe)_2]_3]^-$, and $[Pt[P(O)(OMe)_2]_4]^{2-}$ (possibly diprotonated) is described along with the Arbuzov reactions of $[ClPt[P(OMe)_3]_3]^+$ and the previously described reaction of *cis*-$Cl_2Pt[P(OMe)_3]_2$. All of the products were isolated and characterized. The cis to trans equilibration of $Pt[P(OMe)_3]_2[P(O)(OMe)_2]_2$ was also studied. The $^{31}P\{^1H\}$ and ^1H NMR patterns for Pt(II)–phosphite and Pt(II)–phosphonate complexes, about which few systematic details are known, are discussed. The effects on $\delta(^{31}P)$ and $^1J_{Pt-P}$ when a phosphite ligand is converted to a phosphonate, on $\delta(^{31}P)$ and $^1J_{Pt-P}$ of a phosphorus ligand cis to the reaction site, and on $\delta(^{31}P)$ and $^1J_{Pt-P}$ of a phosphorus ligand trans to the reaction site are described.

Introduction

Platinum(II)–phosphite complexes have been studied far less frequently than the analogous Pt(II)–phosphine complexes. One possible reason for this disparity is the fact that platinum–phosphite complexes are often very soluble in organic solvents and form oils easily.[1] Another and more probable reason is the fact that platinum phosphite complexes often decompose in the presence of nucleophiles to give platinum phosphonate complexes.[1-6] This dealkylation reaction (eq 1) is the transition-metal analogue to

$$M-P(OR)_3 + X^- \rightarrow M-P(O)(OR)_2^- + RX \qquad (1)$$

the classical Michaelis–Arbuzov reaction (also called the Arbuzov reaction), which has been reviewed recently.[7] The mechanism of the attack of a nucleophile on a coordinated phosphite ligand is now known.[8-10] Several studies purposefully dealkylating Pt(II)–phosphite complexes have been conducted.[3,6]

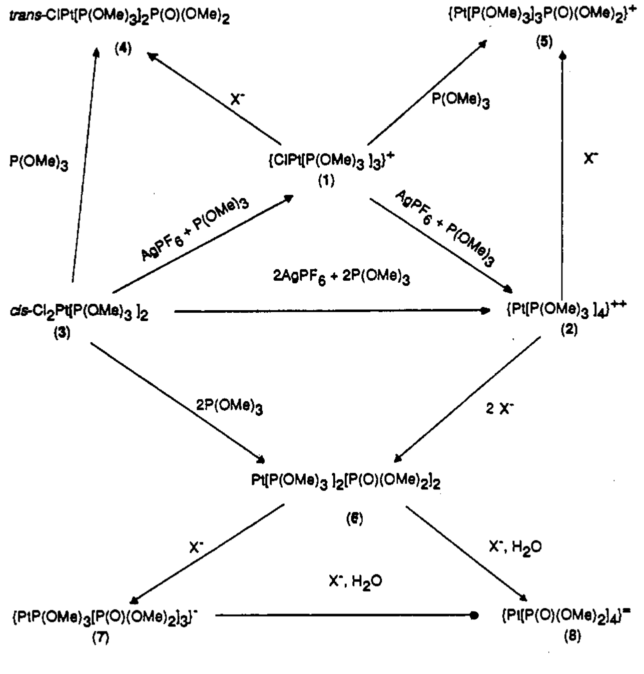
In this paper, we have investigated the systematic dealkylation of $Pt[P(OMe)_3]_4^{2+}$ by sequential single, double, triple, and quadruple Arbuzov reactions in which the phosphite ligand is converted to a phosphonate ligand. There have been no previous studies reported in which stepwise multiple Arbuzov reactions greater than three occur.[11] The $Pt[P(OMe)_3]_4^{2+}$ ion presents the opportunity to study the stepwise sequence of four. The products have been isolated in each step and also are shown to be accessible by other routes. The ^1H and $^{31}P\{^1H\}$ NMR spectra are described and permit the isomers to be distinguished. Also, a comparison of the phosphite complexes can be made to the analogous phosphine complexes of Pt(II). In the following paper, the crystal structures of many of the products are described and the correlation of the Pt–P bond distances with $^1J_{Pt-P}$ is discussed.[12]

Reactions

$[ClPt[P(OMe)_3]_3]^+$ (**1**) and $[Pt[P(OMe)_3]_4]^{2+}$ (**2**) have been reported elsewhere as BPh_4^- salts.[1] Analogous PF_6^- salts of **1** and **2** were prepared in this work according to Scheme I. **1** and **2** along with *cis*-$PtCl_2[P(OMe)_3]_2$ (**3**)[6] were useful for studying sequential multiple Arbuzov reactions.

Single Arbuzov Reactions. Single Arbuzov-like dealkylation of the neutral complex *cis*-$Cl_2Pt[P(OMe)_3]_2$, was recently reported by King and Roundhill.[6] It is generally the case that cationic phosphite complexes more easily dealkylate than do analogous neutral complexes.[6,11,13] In keeping with this, when **1** and **2** react with 1 equiv of $(n\text{-}Bu)_4NCl$ at room temperature, the transformation occurs only to single Arbuzov reaction products, $ClPt[P(OMe)_3]_2P(O)(OMe)_2$ (**4**) and $[Pt[P(OMe)_3]_3P(O)(OMe)_2]^+$ (**5**), respectively (Scheme I). No double Arbuzov reaction products were found in either reaction, indicating that the reactivities of platinum phosphite complexes toward nucleophiles are in the order of **3** ≫ **5** and **1** ≫ **4**.

Scheme I



According to the ^1H and ^{31}P NMR spectra, only the trans isomer of **4** was produced. The higher reactivity of the $P(OMe)_3$ trans to Cl than that trans to another $P(OMe)_3$ could result from the low trans influence of Cl. The resultant shorter platinum–phosphorus bond should increase the electrophilicity of the phosphite ligand, making it more reactive in the Arbuzov reaction. It will be shown momentarily that phosphonate also has a higher trans influence than phosphite, so it prefers the position trans to Cl.

The single Arbuzov reaction products **4** and **5** also can be prepared from the reaction of 1 equiv of $P(OMe)_3$ with *cis*-$Cl_2Pt[P(OMe)_3]_2$ and **1**, respectively, as shown in Scheme I. This is, we believe, a stepwise reaction as shown in (2) and (3), involving

$$cis\text{-}Cl_2Pt[P(OMe)_3]_2 + P(OMe)_3 \rightarrow [ClPt[P(OMe)_3]_3]^+ + Cl^- \rightarrow ClPt[P(OMe)_3]_2P(O)(OMe)_2 + CH_3Cl \qquad (2)$$

$$[ClPt[P(OMe)_3]_3]^+ + P(OMe)_3 \rightarrow [Pt[P(OMe)_3]_4]^{2+} + Cl^- \rightarrow [Pt[P(OMe)_3]_3P(O)(OMe)_2]^+ + CH_3Cl \qquad (3)$$

---

[1] Couch, D. A.; Robinson, S. D. *Inorg. Chim. Acta* **1974**, *9*, 39.
[2] Grinberg, A. A.; Troitskaya, A. D. *Izv. Akad. Nauk SSSR, Ser. Khim* **1945**, 178; *Chem. Abstr.* **1945**, *39*, 1604.
[3] Mijamoto, T. *J. Organomet. Chem.* **1977**, *134*, 335.
[4] Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1977**, *60*, 1371.
[5] Solar, J. M.; Rogers, R. D.; Mason, W. R. *Inorg. Chem.* **1984**, *23*, 373.
[6] King, C.; Roundhill, D. M. *Inorg. Chem.* **1986**, *25*, 2271.
[7] Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577.
[8] Landon, S. J.; Brill, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6571.
[9] Landon, S. J.; Brill, T. B. *Inorg. Chem.* **1984**, *23*, 1266.
[10] Landon, S. J.; Brill, T. B. *Inorg. Chem.* **1984**, *23*, 4177.
[11] Klaui, W.; Otto, H.; Eberspach, W.; Buckholz, E. *Chem. Ber.* **1982**, *115*, 1922.
[12] Bao, Q.-B.; Geib, S. J.; Rheingold, A. L.; Brill, T. B. Inorg. *Chem.*, following paper in this issue.
[13] Schleman, E. V.; Brill, T. B. *J. Organomet. Chem.* **1987**, *323*, 103.

0020-1669/87/1326-3447$01.50/0

substitution followed by dealkylation, which is similar to other Arbuzov reactions that have been followed with ^{1}H NMR spectroscopy.[8-10,13] No direct spectroscopic evidence has been found for the cationic intermediates in reactions 2 and 3 because the ^{1}H NMR peaks broaden during the reaction due to fast ligand exchange. However, it was found in reaction 3 that a precipitate formed immediately after mixing **1** with $P(OMe)_3$ in $CHCl_3$ which gradually redissolved as the reaction proceeded. The precipitate is consistent with formation of the salt of $[Pt[P(OMe)_3]_4]^{2+}$, which is sparingly soluble in $CHCl_3$. The possibility of a five-coordinate intermediate, $Cl_2Pt[P(OMe)_3]_3$, in reaction 2 and $[ClPt[P(OMe)_3]_4]^+$ in reaction 3, nevertheless, cannot be excluded, because similar five-coordinate species have been found for platinum(II)–phosphine complexes.[14-16] However, consistent with the formation of the cationic intermediate in reaction 2, the trans isomer of **4** was obtained, even though *cis*-$Cl_2Pt[P(OMe)_3]_2$ was the reactant.

Double Arbuzov Reactions. Heating to 93 °C was needed to dealkylate the second phosphite ligand of the anionic complex *cis*-$[Cl_2Pt[P(OMe)_3][P(O)(OMe)_2]]^-$ (**3a**) to give the double Arbuzov reaction product $[$*cis*-$Cl_2Pt[P(O)(OMe)_2]_2H]^-$ (**3b**)[6] while we observe that the second phosphite ligand in the cationic compound **5** can be easily dealkylated in the presence of a nucleophile at room temperature to yield $Pt[P(OMe)_3]_2[P(O)(OMe)_2]_2$ (**6**). As in the single Arbuzov reaction, **6** can be prepared in other ways. Stirring **2** with 2 equiv of $(n\text{-Bu})_4NCl$ in $CHCl_3$ at room temperature gave **6** as the only product. $[PtP(OMe)_3[P(O)(OMe)_2]_3]^-$ (**7**), the product of a triple Arbuzov reaction, was not detected, indicating that the reactivity of the complexes toward dealkylation decreases in the order **5** ≫ **6**. **6** also can be synthesized by adding 2 equiv of $P(OMe)_3$ to **3** as shown in Scheme I. Two Cl ligands probably are displaced sequentially by $P(OMe)_3$ followed immediately by nucleophilic attack of Cl^- on coordinated $P(OMe)_3$ because no dicationic intermediate **2** was detected.

Cis and trans isomers are possible for **6**. Only the cis isomer was isolated as a solid, which was verified by X-ray crystallography[12] and by the ^{1}H NMR spectrum of a freshly dissolved sample. Two doublets from $^3J_{P-H}$ with a ratio of 3:2, corresponding to the methyl groups of two $P(OMe)_3$ ligands (18 H total) and two $P(O)(OMe)_2^-$ ligands (12 H total), were detected in polar solvents [e.g., $(CD_3)_2CO$ and $CDCl_3$] and in a nonpolar solvent (C_6D_6). The cis isomer gradually isomerized in solution to a cis and trans mixture. Because no excess ligand was present, it is possible that a dissociative mechanism involving a 14-electron intermediate[17] may be the pathway for this isomerization. The final cis:trans isomer ratio in the mixture depends on the polarity of the solvent. In C_6D_6, a 1:1.2 ratio of cis to trans was present in 7 h, while in a polar solvent, such as $CDCl_3$, a final ratio of 1:1 for the two isomers was obtained in the same time. In a still more polar solvent, $(CD_3)_2CO$, the ratio of cis to trans was still larger than 1 even after 3 days. The energy difference between the isomers is probably small because of the similar steric and electronic effects of the ligands, but consistent with other complexes,[18,19] the more polar cis isomer is favored in a polar solvent.

Evaporation of the solvent from a cis and trans mixture of isomers yields only the cis isomer as a solid. This can be explained by the larger dipole moment of the cis isomer compared to the trans isomer, which leads to greater intermolecular interaction in the solid state. Therefore, the cis isomer should be less soluble than the trans isomer.

Table I. ^{1}H NMR Spectral Data

	$P(OMe)_3$		$P(O)(OMe)_2^-$	
complex	δ^d	$^3J_{P-H}$, Hz	δ^d	$^3J_{P-H}$, Hz
1	3.98 (t)^{a,f}	12.7^e		
	3.97 (d)^g	12.9		
	3.92 (t)^{b,f}	12.7^e		
	3.86 (d)^g	13.1		
2	4.12 (t)^a	12.4^e		
3	3.86 (d)^a	12.6^e		
4	3.88 (t)^b	12.6^e	3.63 (d)	12.0
5	3.95 (b)^a		3.65 (d)	11.5
	3.88 (b)^b		3.68 (d)	11.3
cis-**6**	3.82 (d)^a	12.5	3.56 (d)	11.5
	3.80 (d)^b	12.4	3.68 (d)	11.6
	3.54 (d)^c	12.2	3.83 (d)	11.5
trans-**6**	3.83 (t)^a	12.8^e	3.52 (t)	11.2^e
	3.86 (t)^b	12.8^e	3.61 (t)	11.4^e
	3.67 (t)^c	12.4^e	3.66 (t)	11.2^e
7	3.71 (d)^a	12.5	3.47 (d)^f	11.2
			3.45 (t)^h	11.4^e
	3.80 (d)^b	12.6	3.57 (d)^f	11.6
			3.58 (t)^h	11.5^e
8			3.63 (t)	12.0^e

[a] Spectra taken in $(CD_3)_2CO$. [b] Spectra taken in $CDCl_3$. [c] Spectra taken in C_6D_6. [d] Key: d, doublet; t, triplet; b, broad. [e] Second-order spectrum; the coupling constant is $|^3J_{P-H}+^5J_{P-H}|$. [f] Trans to $P(OMe)_3$. [g] Trans to Cl. [h] Cis to $P(OMe)_3$.

Triple Arbuzov Reaction. As expected, the third scission of an oxygen–carbon bond of the neutral double Arbuzov reaction product **6** is less facile than the single and double scissions from cationic complexes. Mild heat (60 °C) for a period of 5 h was required to dealkylate the third phosphite ligand of **6** in the presence of Ph_4AsCl. At this temperature, no quadruple Arbuzov reaction product was detected, which indicates that the fourth phosphite ligand is even more difficult to dealkylate. The product anion, $\{PtP(OMe)_3[P(O)(OMe)_2]_3\}^-$ (**7**), precipitated as the tetraphenylarsonium salt, was fully characterized by its ^{1}H and ^{31}P NMR spectra.

The fact that a longer reaction time is needed to dealkylate **6** (5 h) than **3** (25 min) could be ascribed to the effect of replacing two low-trans-influence ligands (Cl^-) by two high-trans-influence ligands ($P(O)(OMe)_2^-$), which weakens the Pt–$P(OMe)_3$ bond and thus reduces the reactivity of the phosphite toward dealkylation.

Quadruple Arbuzov Reaction. Heating **6** or **7** with Ph_4AsCl did not afford the quadruple Arbuzov reaction product, $[Pt[P(O)(OMe)_2]_4]^{2-}$ (**8**), because decomposition occurred above 70 °C. However, **8** can be obtained probably as the diprotonated form by stirring **7** and excess $(n\text{-Bu})_4NBr$ in CH_2Cl_2/H_2O. Two phases separated after several minutes. The CH_2Cl_2 phase contained the desired product, **8**, and $(n\text{-Bu})_4NBr$. Should this product be specifically sought, the alternate route of Troitskaya et al.,[20] beginning with $PtCl_4^{2-}$ and improved by Sperline and Roundhill,[21] may be preferred. The crystal structure of the diprotonated form of **8**, $Pt[P(O)(OMe)_2]_2[P(OH)(OMe)_2]$, has been determined.[5]

The sequential multiple Arbuzov reaction of square-planar Pt(II) complexes is not difficult to control because the reactivity difference between any two consecutive dealkylated products is relatively large. The multiplicity of the Arbuzov reaction is, in most cases, limited by the decrease in electrophilicity of the complex as neutral phosphite ligands are sequentially converted to anionic phosphonate ligands. A cationic metal phosphite is usually easily dealkylated to form the metal phosphonate complex, while a high reaction temperature is normally required to convert a neutral metal phosphite complex by the Arbuzov reaction to an anionic metal phosphonate complex. The reactivity of a monoanionic metal phosphite complex toward Arbuzov-like dealkylation is generally low. High reaction temperatures sometimes produce the reaction. An alternate way to produce a multiple Arbuzov reaction involving an anionic metal complex containing phosphite and phosphonate ligands is to reduce the negative charge

---

(14) Romeo, R.; Minniti, D.; Trozzi, M. *Inorg. Chim. Acta* **1975**, *14*, L15.
(15) Romeo, R.; Minniti, D.; Trozzi, M. *Inorg. Chem.* **1976**, *15*, 1134.
(16) Romeo, R. *Inorg. Chem.* **1978**, *17*, 2040.
(17) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.
(18) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770.
(19) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.
(20) Troitskaya, A. D.; Itskovich, T. B. *Tr. Kazan Khim.-Tekhnol. Inst.* **1953**, *18*, 59.
(21) Sperline, R. P.; Roundhill, D. M. *Inorg. Synth.* **1979**, *19*, 1998.

Table II. ^{31}P NMR Spectral Data

complex	$P(OMe)_3$			$P(O)(OMe)_2^-$		
	δ[c]	$^2J_{P-P}$, Hz	$^1J_{Pt-P}$, Hz	δ[c]	$^2J_{P-P}$, Hz	$^1J_{Pt-P}$, Hz
1	99.5 (d)[a,e]	29.3	3911			
	75.5 (t)[f]	29.3	5569			
	97.9 (d)[b,e]	29.3	3909			
	74.5 (t)[f]	29.3	5588			
2	94.4 (s)[a]		3908			
3	75.9 (s)[a]		5671			
3a	82.0[a]	19	6608	30.4	19	5020[k]
3b				60.0[a]		5422[k]
4	106.2 (d)[b]	23.6	4464	32.6 (t)	23.2	4886
5	101.8 (d of d)[b,g]	52[i]	4293	57.9 (t of d)	741 (trans)	3488
		34[j]			34 (cis)	
	114.2 (t of d)[h]	741 (trans)				
		52 (cis)				
cis-**6**	123.2[a]	704 (trans)[d]	3260	64.4	704 (trans)[d]	3971
trans-**6**	110.8 (t)[a]	44.3	4481	77.2 (t)	44.3	3011
7	126.7 (t of d)[a]	782 (trans)	3485	83.1 (d of d)[h]	48[i]	3336
		48 (*cis*)			39[j]	
				72.5 (t of d)[g]	782 (trans)	4264
					39 (cis)	
8				91.9 (s)[a]		3446
				90		3455

[a] Spectra taken in $(CD_3)_2CO$. [b] Spectra taken in $CDCl_3$. [c] Key: s, singlet; d, doublet; t, triplet. [d] Second-order spectrum. [e] Phosphorus cis to Cl. [f] Phosphorus trans to Cl. [g] Phosphorus trans to $P(OMe)_3$. [h] Phosphorus cis to $P(OMe)_3$. [i] Coupled to $P(OMe)_3$. [j] Coupled to $P(O)(OMe)_2^-$. [k] Data from ref 6.

by supplying positively charged ions, such as H^+ or metal ions, to form the oxygen chelated species.

^{1}H and ^{31}P NMR Spectroscopy

^{1}H and ^{31}P NMR spectra were obtained on the new platinum phosphite and phosphonate complexes (see Tables I and II) and are useful for determining the geometry and bonding features. The similarities and differences of the ^{1}H and ^{31}P NMR spectra of platinum phosphite and phosphonate compounds compared to the well documented analogous platinum phosphine compounds will be noted where applicable.

^{1}H NMR Results. The ^{1}H NMR spectrum of **3** has been calculated.[22] An intense doublet for **3** was assigned to the combination of $^3J_{P-H}$ and $^5J_{P-H}$ with a separation of $|^3J_{P-H} + {}^5J_{P-H}|$. Generally, a coordinated $P(OMe)_3$ or $P(O)(OMe)_2^-$ ligand has a $^3J_{P-H}$ value of about 9–12 Hz.[7] The ^{1}H NMR pattern for the different methyl groups depends on both the interligand coupling $^2J_{P-P}$, and the chemical shift difference of the coupled phosphorus ligands $\Delta = (\delta_P - \delta_{P'})$. If $^2J_{P-P'} \ll \Delta$, then a doublet without perturbation is observed. If $^2J_{P-P'} = \Delta$, then a perturbation occurs. If $^2J_{P-P'} \gg \Delta$, then an apparent triplet would be produced in the proton spectrum.[23] In square-planar Pt(II) complexes, $^2J_{P-P'}$ is on the order of tens of hertz for the ligands in the cis position, while it is in the order of hundreds of hertz for ligands in the trans position. Therefore, a "virtual" triplet is common for two equivalent phosphorus ligands in the trans position and a doublet is common for the two equivalent ligands in the cis position. The separation of these peaks is $|^3J_{P-H} + {}^5J_{P'-H}|$.

The ^{1}H NMR spectrum of **1** in $(CD_3)_2CO$ was reported before[17] to be a singlet at $\delta = 3.84$. The absence of coupling was attributed to rapid ligand exchange because some excess ligand remained. Similar absence of interligand phosphorus–hydrogen coupling in the ^{1}H NMR spectrum has also been found for square-planar nickel(II) and platinum(II) methylphosphine derivatives.[24] The ^{1}H NMR spectrum of **1** in $(CD_3)_2CO$ was found in this work to be a multiplet as a result of the $^3J_{P-H}$ and $^5J_{P-H}$ coupling. A "virtual" triplet with relative intensity of 1:2:1 and a doublet were observed at room temperature, which results from the two different types of phosphito ligands. The triplet results from the two $P(OMe)_3$ cis to Cl assuming square-planar geometry, while the doublet corresponds to the $P(OMe)_3$ trans to Cl. The ligands in **1** are not labile on the NMR time scale at room temperature when no excess $P(OMe)_3$ is present. The absence of intra- and interligand coupling observed previously[17] must be caused by excess free ligand because it has been proven that the rate of ligand exchange depends on the concentration of free ligand.[25] The loss of coupling by ligand exchange is also observed in the ^{1}H spectrum of **2** as will be discussed momentarily.

In a solvent of low polarity ($CDCl_3$), the salt of **1** is less dissociated into its component ions. Hence, all of the phosphite protons are more shielded, but to an extent different for the two sets of phosphite ligands. Coincidence of the signals results in a spectrum with only four resolved peaks having a relative intensity of 1:2:2:1. If a comparison is made of the separation of the four peaks with the coupling constants measured for **1** in $(CD_3)_2CO$, it can be reasoned that one of the center peaks is the overlap of one side peak from a triplet and half of the doublet. For **1** in $CDCl_3$ the coupling constant for the triplet is 12.7 Hz and that for the doublet is 13.1 Hz, which are comparable to those in $(CD_3)_2CO$ of 12.7 and 12.9 Hz, respectively.

Complex **4** has coupling similar to **1**. However, the triplet for the two phosphito ligands and doublet for the phosphonato ligand trans to Cl due to the spin system of $AX_9A'X'_9BX_6$ were well resolved in the ^{1}H NMR spectrum. In this case, the ^{1}H NMR spectrum along with the ^{31}P NMR spectrum specifies the geometry of the complex. If the cis isomer were formed instead of the trans isomer, a doublet could still be possible for $P(O)(OMe)_2^-$ because of the absence of virtual coupling with the two nonequivalent trans phosphorus ligands. However, a pattern involving two doublets from two different $P(OMe)_3$ ligands should occur instead of a single triplet.

The complexes **2** and **8** belong to the coupling system $[A]_4[X]_4$. A singlet flanked by two pairs of satellites is observed for these two complexes. This pattern has been observed for other complexes with the same coupling system, e.g., $[RhL_4]^+$ (L = $P(OMe)_2Ph$, $P(OMe)Ph_2$],[26] and *trans*-$Rh[P(OMe)_3]_4XY^+$ (X = Y = Br; X = H, Y = Br; X = CH_3, Y = I).[26,27] In all of these complexes the four phosphorus ligands are square planar about the metal atom. With a small amount of $P(OMe)_3$ added to a $(CD_3)_2CO$ solution of **2**, no free $P(OMe)_3$ was detected and only a broad singlet shifted upfield from the original position centered

---

(22) Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, *21*, 2220.
(23) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.
(24) Cherwinski, W. J.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1511.
(25) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenback, D. *Inorg. Chem.* **1980**, *19*, 1356.
(26) Haines, L. M. *Inorg. Chem.* **1971**, *10*, 1693.
(27) Haines, L. M. *J. Organomet. Chem.* **1970**, *25*, C85.

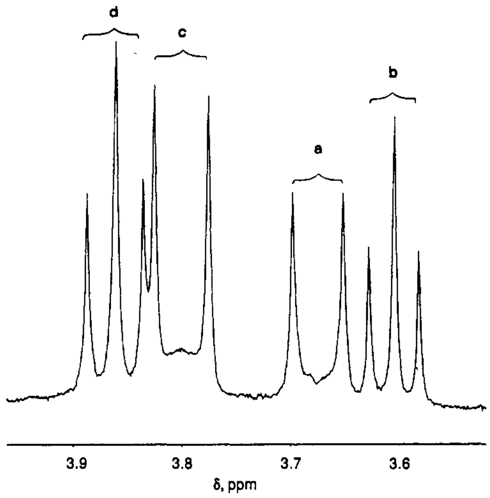


Figure 1. ^{1}H NMR spectrum of an equilibrium solution of *cis*- and *trans*-Pt[P(OMe)$_3$]$_2$[P(O)(OMe)$_2$]$_2$ in CDCl$_3$: a = cis phosphonate; c = cis phosphite; b = trans phosphonate; d = trans phosphite.

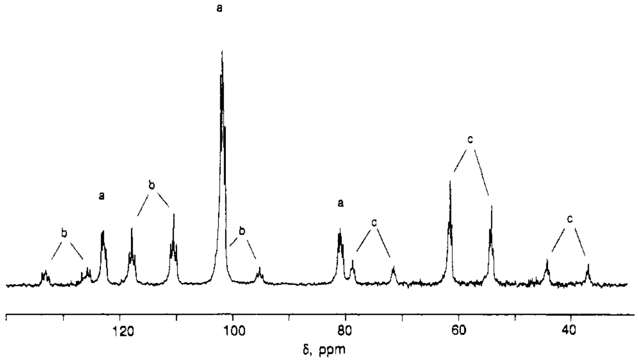


Figure 2. ^{31}P{^{1}H} NMR spectrum of [Pt[P(OMe)$_3$]$_3$P(O)(OMe)$_2$]$^+$: a = the two *trans*-P(OMe)$_3$ ligands; b = the P(OMe)$_3$ ligand trans to P(O)(OMe)$_2^-$; c = the P(O)(OMe)$_2^-$ ligand trans to P(OMe)$_3$.

at δ = 4.12 appears. The extent of this shift depends on the amount of P(OMe)$_3$ added, which indicates that fast ligand exchange occurs and that the broad peak is the average chemical shift of coordinated and free P(OMe)$_3$.

The $AX_nBX_mB'X'_mCX_m$ coupling system describes **5** and **7**. If all of the ^{1}H signals are resolved, there should be a triplet for the two equivalent trans ligands owing to virtual coupling, and two doublets for the nonequivalent trans ligands. This is exactly what is found for **7**. A doublet and a triplet for the three phosphonato ligands occur in the same region, but are well resolved and separated from the doublet for the phosphito ligand. The doublet and the triplet for the three phosphito ligands of **5** overlap, giving only a broad peak at 3.88 ppm with little resolution. The doublet for P(O)(OMe)$_2^-$ at 3.68 ppm is well separated from this broad peak.

Cis and trans isomers are possible for **6**. The ^{1}H NMR spectrum should be a $AX_nA'X'_nBX_mB'X'_m$ spin system. In freshly dissolved **6**, two intense doublets with a relative intensity of 3:2 are present. The lower field doublet corresponds to the two phosphito ligands while the doublet at higher field resulted from the two phosphonato ligands of the cis isomer. However, two weak triplets from a trace of the trans isomer can also be detected when the complex is freshly dissolved in CDCl$_3$. The intensity of two triplets grows while the intensity of the doublets decreases with time as a result of slow cis to trans isomerization. The final ratio of doublets to triplets is about 1:1 in CDCl$_3$, as seen in Figure 1, and is not affected significantly by the temperature between 0 and 50 °C. Similar spectra but with different isomer ratios were also obtained in the more polar solvent (CD$_3$)$_2$CO and the nonpolar solvent C$_6$D$_6$.

^{31}P NMR Results. Extensive ^{31}P NMR spectra have been reported for platinum–phosphine complexes.[28-31] The two coupling constants, $^1J_{Pt-P}$ and $^2J_{P-P}$, are especially useful. The former is helpful for indirectly investigating the trans and cis influence of ligands in square-planar complexes.[32] The latter has been widely used to distinguish cis and trans isomers because the P–P coupling is weak in *cis*-bis(phosphorus) complexes and fairly strong in *trans*-bis(phosphorus) complexes.[28] $^1J_{P-P}$ in square-planar tertiary phosphine–platinum(II) complexes also provides information about platinum–phosphorus bonds.[23,33-35] Although the initial correlations of Pt–P bond distances with $^1J_{Pt-P}$ appeared promising,[36] further examination of this relationship in square-planar Pt(II) complexes showed that only a qualitative correlation existed.[28] The failure of the correlation usually can be attributed to the steric and electronic effects of the cis ligands and the fact that many factors contribute to $^1J_{Pt-P}$.[37] Nevertheless, the trend of higher $^1J_{Pt-P}$ being associated with shorter Pt–P bond lengths reflects that $^1J_{Pt-P}$ and the Pt–P bond lengths are both sensitive to the s-orbital bond character.[28] Unfortunately, $\delta(^{31}P)$ in Pt–P bonds can be connected to bonding parameters only in a very qualitative way.

When phosphite displaced chloride from **3** giving **1**, both $\delta(^{31}P)$ and $^1J_{Pt-P}$ of the phosphito ligand trans to Cl changed only slightly (75.9 ppm and 5671 Hz for **3** versus 75.5 ppm and 5569 Hz for **1**) in accordance with the assumption that the cis influence on the NMR spectrum is relatively small.[31] These changes are comparable to those of the corresponding phosphine complexes (−24.9 ppm and 3489 Hz for *cis*-Cl$_2$Pt(PMe$_3$)$_2$ versus −26.8 ppm and 3368 Hz for [ClPt(PMe$_3$)$_3$]Cl) for phosphorus trans to Cl.[25] It should be pointed out that the similarity of chemical shift for the phosphorus ligand trans to Cl in the neutral and cationic complexes does not necessary imply that the electron density on the phosphorus atom is unchanged. Instead, it could result from the cancelation of opposed effects; that is, the effect of substituting a neutral P(OMe)$_3$ for an anionic Cl$^-$ should increase the Pt–P σ overlap and decrease the π back-bond, causing a downfield shift for the phosphorus ligand cis to the reaction site, whereas the better σ donor ligand P(OMe)$_3$ compared to Cl$^-$ increases the electron density on the phosphorus ligand cis to the reaction site, causing an upfield shift. A much greater change in $\delta(^{31}P)$ and $^1J_{Pt-P}$ occurs for P(OMe)$_3$ in the position trans to the reaction site in **3** compared to P(OMe)$_3$ cis to the reaction site (99.5 ppm and 3911 Hz for **1** versus 75.9 ppm and 5671 Hz for **3**). In the analogous platinum complexes of PMe$_3$ the corresponding $\delta(^{31}P)$ and $^1J_{Pt-P}$ values are −24.9 ppm and 3489 Hz for *cis*-Cl$_2$Pt(PMe$_3$)$_2$ versus −12.0 ppm and 2230 Hz for [ClPt(PMe$_3$)$_3$]Cl.[25] This decrease in $\delta(^{31}P)$ when Cl is replaced by a phosphorus ligand can be explained by the competition for the π-electron density by the two trans phosphorus ligands in **1**. The relatively small value of $^1J_{Pt-P}$ for the trans P(OMe)$_3$ ligands can be attributed to weakening of the Pt–P bonds by the high trans influence of P(OMe)$_3$. In Pt–phosphine complexes, smaller values of $^1J_{Pt-P}$ usually correspond to longer Pt–P bonds.[29] This pattern also holds for platinum–phosphite and platinum–phosphonate complexes. The ^{31}P NMR pattern of **1** is a doublet for the two P(OMe)$_3$ ligands trans to each other and a triplet for the P(OMe)$_3$ ligand trans to Cl, both with satellites from ^{195}Pt coupling. The cis $^2J_{P-P}$ is 29.1 Hz, which is larger than that for the PMe$_3$ analogue (22 Hz),[25] but still is typical of cis $^2J_{P-P}$ coupling. The larger values of $^2J_{P-P}$ in the phosphite complex

---

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

(29) Pidcock, A. *Adv. Chem. Ser.* **1982**, *No. 196*, 1 and references therein.

(30) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, 266.

(31) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(32) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; pp 136–140.

(33) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 346.

(34) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.

(35) Finer, E. G.; Harris, R. K. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *6*, 61.

(36) Mather, G. G.; Pidcock, A.; Rapsey, J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.

(37) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.

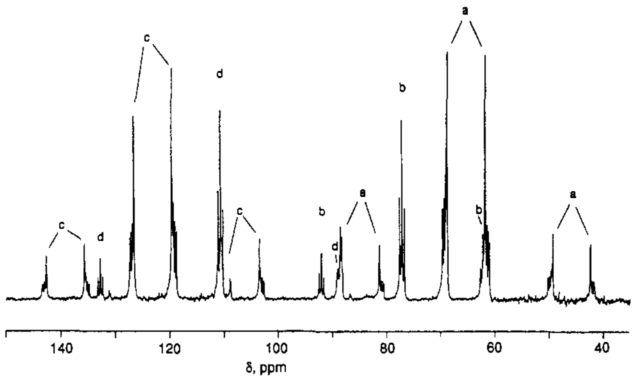


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of an equilibrium solution of *cis* and *trans*-$Pt[P(OMe)_3]_2[P(O)(OMe)_2]_2$ in $CDCl_3$: a = cis phosphonate; c = cis phosphite; b = trans phosphonate; d = trans phosphite.

as compared to those in the phosphine complex can be attributed to the increased phosphorus 3s character in the Pt–P bond orbital as the electronegativity of substituents on the phosphorus atom increases.[32]

When the Cl^- ligand of **1** was replaced by $P(OMe)_3$, yielding **2**, only a singlet with ^{195}Pt satellites was observed in the ^{31}P NMR spectrum. $^1J_{Pt-P}$ is 3908 Hz, which is almost the same as that for the trans phosphito ligands in **1** (3911 Hz). A parallel result is found for the PMe_3 analogue where $^1J_{Pt-P}$ is 2230 Hz for $[Pt(PMe_3)_4]^{2+}$ and 2230 Hz for $[ClPt(PMe_3)_3]^+$.[25]

The change of one phosphito ligand to a phosphonato ligand on going from **2** to **5** causes the ^{31}P NMR spectrum (Figure 2) to become much more complicated. The two trans phosphito ligands gave a doublet of doublets as a result of the cis coupling of the two different phosphorus atoms. Both the phosphonato and the unique phosphito ligand gave a doublet of triplets. The doublet resulted from the coupling to the nonequal phosphorus ligands in the trans position having a very large coupling constant ($^2J_{P-P}$ = 741 Hz). This doublet is then further split into triplets by the two cis phosphito ligands.

trans-$ClPt[P(OMe)_3]_2P(O)(OMe)_2$, resulting from the single Arbuzov reaction at the phosphito ligand trans to Cl, has the same ^{31}P NMR spectral pattern as **1**. This is a doublet and a triplet accompanied by ^{195}Pt satellites.

Two very different ^{31}P NMR spectra were obtained for the two isomers from the double Arbuzov reaction of **2** as shown in Figure 3. The *trans* isomer of **6** showed two triplets, "d" (phosphite) and "b" (phosphonate), accompanied by ^{195}Pt satellites for each kind of phosphorus ligand coupled to one another. The cis isomer of **6**, the signals of which are assigned as "c" and "a" for phosphite ligands and phosphonate ligand, respectively, shows a second-order ^{31}P NMR spectrum, which is consistent with an AA′BB′ spin system. A similar spectrum has been reported recently for $RuCl_2(dppm)(PMe_2Ph)_2$.[38]

When a third $P(OMe)_3$ ligand of **2** is dealkylated to produce **7**, the ^{31}P NMR spectral pattern resembles that of **5**, which has the same spin system. Finally, when the $P(OMe)_3$ ligand of **7** is dealkylated to produce **8**, a single ^{31}P signal is present at 91.9 ppm with ^{195}Pt satellites at $^1J_{Pt-P}$ = 3446 Hz. These values compare well to those from previous reports on **8** where $\delta(^{31}P)$ = 90 with $^1J_{Pt-P}$ = 3455 Hz[5] and $\delta(^{31}P)$ = 88.7 with $^1J_{Pt-P}$ = 3456 Hz[39] were found.

Because of the scarcity of information about phosphite and phosphonate ligands in platinum(II) complexes, the effect of phosphonate ligands on $\delta(^{31}P)$ and $^1J_{Pt-P}$ with themselves and the neighboring ligands was examined further. Some conclusions can be drawn when all of the spectral data are compiled for closely related complexes. At least three effects are noteworthy in the platinum–phosphite and platinum–phosphonate complexes:

Table III. Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ upon Converting a Phosphite Ligand to a Phosphonate Ligand

$P(OMe)_3$ in initial complex	$P(O)(OMe)_2^-$ in final complex	Δ^1J_{Pt-P}, Hz	$\Delta\delta$
1	**5**	−683	−42.9
2	**3**	−420	−36.4
3	**3a**	−651	−45.5[a]
3	**3a**	−651	−45.5[a]
3a	**3b**	−1186	−20.0[a]
5	*cis*-**6**	−268	−37.8
5	*trans*-**6**	−75	−37.0
cis-**6**	**7**	−76	−39.9
trans-**6**	**7**	−217	−38.3
7	**8**	−39	−34.8

[a] Data from ref 6.

Table IV. Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ for a Phosphorus Ligand Cis to the Reaction Site When a Phosphite Ligand Is Converted to a Phosphonate Ligand

$P(OMe)_3$ in initial complex	$P(O)(OMe)_2^-$ in final complex	Δ^1J_{Pt-P}, Hz	$\Delta\delta$
1	**4**	553	7.0
2	**5**	331	7.4
3	**3a**	937	4.1[a]
3a	**3b**	402	29.6[a]
5	*cis*-**6**	174	8.8[b]
		483	6.0[c]
5	*trans*-**6**	242	9.0
cis-**6**	**7**	225	3.7[b]
		293	8.5[c]
trans-**6**	**7**	325	5.9
7	**8**	110	8.8

[a] Data from ref 6. [b] $P(OMe)_3$. [c] $P(O)(OMe)_2^-$.

(a) Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ of Converting a Phosphite Ligand to a Phosphonate Ligand. ^{59}Co NQR data[40] suggest that $P(O)(OMe)_2^-$ and $P(OMe)_3$ are electronically similar, but that $P(O)(OMe)_2^-$ is a slightly poorer π-electron acceptor and/or σ-electron donor than $P(OMe)_3$ despite the fact that $\delta(^{31}P)$ for $P(O)(OMe)_2^-$ is 40–85 ppm more shielded than $P(OMe)_3$ in analogous complexes.[7] As shown in Table III, a relatively narrow region of upfield shift in $\delta(^{31}P)$ (34.8–45.5) and widely spread but consistently decreasing values of $^1J_{Pt-P}$ (39–683 Hz, or 1.1–12.3%) occur when a phosphite on Pt(II) is dealkylated to a phosphonate ligand. The conversion of **3a** to **3b** causes an even larger change in $^1J_{Pt-P}$. This upfield shift has been interpreted to result from the negative charge of the phosphonate ligand residing primarily on the phosphorus atom.[6]

(b) Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ for a Phosphorus Ligand Cis to the Reaction Site When a Phosphite Ligand Is Changed to a Phosphonate Ligand. In contrast to the trans influence, where σ-bond effects appear to dominate, the strength of a cis metal–ligand bond is controlled by three comparably important factors: σ-bond effects, π-bond effects, and steric factors. The steric difference between $P(OMe)_3$ and $P(O)(OMe)_2^-$ is relatively small. The data in Table IV show that changing a phosphite ligand on Pt(II) to a phosphonate ligand causes an increase of both $^1J_{Pt-P}$ (110–937 Hz, or 3.3–16.5%) and $\delta(^{31}P)$ (4.1–29.6) for the cis phosphorus ligand. The increase in $^1J_{Pt-P}$ reflects the lower cis influence of $P(O)(OMe)_2^-$ compared to $P(OMe)_3$, and is also consistent with the fact that $P(O)(OMe)_2^-$ is weaker π-acceptor ligand than $P(OMe)_3$ because $^1J_{Pt-P}$ is markedly reduced by Pt–P π bonding to a cis ligand.[41] The increase in $\delta(^{31}P)$ for the cis ligand is possibly due to the weaker s-donor character of $P(O)(OMe)_2^-$ compared to $P(OMe)_3$, which results in less electron density on the Pt(II) center. In turn, the Pt–P σ-bond character increases and/or the π-back-bond character decreases in the cis Pt–P bond.

---

(38) Whinnery, L. L.; Yue, H. J.; Marsella, J. A. *Inorg. Chem.* **1986**, *25*, 4136.

(39) Allen, F. H.; Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2087.

(40) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533.

(41) Cairns, M. A.; Dixon, K. R.; Rivertt, G. A. *J. Organomet. Chem.* **1979**, *171*, 373.

Table V. Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ for a Phosphorus Ligand Trans to the Reaction Site When a Phosphite Ligand Is Converted to a Phosphonate Ligand

$P(OMe)_3$ in initial complex	$P(O)(OMe)_2^-$ in final complex	Δ^1J_{Pt-P}, Hz	$\Delta\delta$
2	**5**	−822	19.8
5	*cis*-**6**	−979	21.2
5	*trans*-**6**	−477	19.2
cis-**6**	**7**	−635	19.1
trans-**6**	**7**	−996	15.9
7	**8**	−818	19.4

(c) Effect on $\delta(^{31}P)$ and $^1J_{Pt-P}$ for a Phosphorus Ligand Trans to the Reaction Site When a Phosphite Ligand Is Changed to a Phosphonate Ligand. The position of $P(O)(OMe)_2^-$ in trans influence series has not been established previously. As shown in Table V, a large, but negative, effect on $^1J_{Pt-P}$ for the phosphorus ligand (decrease of 477–996 Hz, or 13.7–23.2%) occurs upon dealkylation of the trans $P(OMe)_3$, which is contrary to the molecular orbital prediction that a ligand with a large trans influence would produce a cis influence of comparable magnitude.[42] The large effect on $^1J_{Pt-P}$ may result from partial rehybridization of the platinum atom upon dealkylation. The chemical shift change $\Delta\delta$ also can be interpreted in the same way as in section b, and the bigger difference (15.9–21.2 ppm) indicates that the electronic effect is more easily transmitted to the trans position than to the cis position.

Experimental Section

All solvents were of reagent grade or better and used as received. $P(OMe)_3$ was purchased from Aldrich Chemical Co. and freshly distilled prior to use. Tetra-*n*-butylammonium bromide, tetra-*n*-butylammonium chloride, and tetraphenylarsonium chloride hydrate were purchased from Aldrich Chemical Co. and used as received, except for the tetraphenylarsonium chloride hydrate, which was dried under vacuum at 120 °C. *cis*-$Cl_2Pt[P(OMe)_3]_2$ was prepared by the literature method.[43] All reactions were carried out under a nitrogen atmosphere.

^1H NMR spectra were recorded on a Bruker AM-250 spectrometer, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM-250 spectrometer. $\delta(^1H)$ is reported relative to $SiMe_4$ (δ = 0.0 ppm), while $\delta(^{31}P)$ is referenced downfield to 85% H_3PO_4 (external).

All melting points were obtained by using a Melt-Temp heating block and are not corrected. Microanalyses were performed by Micro-Analysis, Wilmington, DE.

Chlorotris(trimethyl phosphite)platinum(II) Hexafluorophosphate [1-(PF$_6$)]. $AgPF_6$ (0.550 g, 2.18 mmol) dissolved in 10 mL of acetone was slowly added to 20 mL of an acetone solution of *cis*-$Cl_2Pt[P(OMe)_3]_2$ (1.118 g, 2.18 mmol). $P(OMe)_3$ (0.270 g, 2.18 mmol) was then added. A white precipitate (AgCl) formed immediately. After being stirred for 3 h, the solution was filtered through Celite. The filtrate was removed under vacuum. The white solid was then washed with benzene, and dried under vacuum to yield **1**(PF_6) (1.440 g, 89%). Colorless crystals can be obtained by recrystallization from acetone/diethyl ether at 0 °C; mp 135–136 °C. Anal. Calcd for $C_9H_{27}ClF_6O_9P_4Pt$: C, 14.46; H, 3.64. Found: C, 14.77; H, 3.70.

Tetrakis(trimethyl phosphite)platinum(II) Hexafluorophosphate [2(PF$_6$)$_2$]. Method A. $AgPF_6$ (0.6800 g, 2.69 mmol) dissolved in 10 mL of acetone along with $P(OMe)_3$ (0.333 g, 2.69 mmol) were added slowly to 15 mL of an acetone solution of *cis*-$Cl_2Pt[P(OMe)_3]_2$ (0.6950 g, 1.35 mmol). AgCl precipitated immediately. After being stirred for 3 h, the solution was filtered through Celite. The solvent was removed under reduced pressure. After the resultant precipitate was washed with C_6H_6 (3 × 5 mL), the compound was dried under vacuum, yielding 1.23 g (93%) of **2**(PF_6)$_2$. **2**(PF_6)$_2$ was recrystallized from aceteone/ether at 0 °C giving colorless crystals; mp 201–202 °C. Anal. Calcd for $C_{12}H_{36}F_{12}O_{12}P_6Pt$: C, 14.69; H, 3.70. Found: C, 14.71; H, 3.51.

Method B. $AgPF_6$ (0.0372 g, 0.147 mmol) in acetone solution (5 mL) and $P(OMe)_3$ (0.0182 g, 0.147 mmol) were added slowly to 10 mL of an acetone solution of **1**(PF_6) (0.1100 g, 0.147 mmol). AgCl precipitated immediately. The workup followed method A, yielding 0.101 g (70%) of **2**(PF_6)$_2$.

***trans*-Chlorobis(trimethyl phosphite)(dimethyl phosphonato)platinum(II) (4). Method A.** One equivalent of $P(OMe)_3$ (0.0266 g, 0.214 mmol) was added to *cis*-$Cl_2Pt[P(OMe)_3]_2$ (0.110 g, 0.214 mmol) in 1.5 mL of $CHCl_3$. After the mixture was stirred for 8 h, the solvent was removed under vacuum, resulting in an oil. Anal. Calcd for $C_8H_{24}ClO_9P_3Pt$: C, 16.35; H, 4.12. Found: C, 16.23; H, 4.08.

Method B. 3 (1.0356 g, 1.385 mmol) and tetra-*n*-butylammonium chloride (96%) (0.3850 g, 1.385 mmol) were stirred in 10 mL of $CDCl_3$ for 24 h. After the solvent was removed under vacuum, the thick oil was extracted with C_6H_6 (2 × 4 mL). The product could not be solidified after solvent removal. The ^1H and ^{31}P NMR spectra revealed the same product as that obtained from method A.

Tris(trimethyl phosphite)(dimethyl phosphonato)platinum(II) Hexafluorophosphate [(5)PF$_6$]. $P(OMe)_3$ (62.1 mg, 0.501 mmol) was added to a solution of **1**(PF_6) (0.3745 g, 0.501 mmol) in 2 mL of $CHCl_3$. After the mixture was stirred for 1 min, a precipitate formed, which, we believe, is the intermediate complex $[Pt[P(OMe)_3]_4]^{2+}$. The precipitate was gradually redissolved as a result of its conversion to **3** by dealkylation. After 20 h, the solvent was removed under reduced pressure. The product was washed with C_6H_6 (3 × 5 mL), and then dried under vacuum; yield 0.380 g (92%). Colorless crystals can be obtained by recrystallizing from acetone/ether at 0 °C; mp 140–141 °C. Anal. Calcd for $C_{11}H_{33}F_6O_{12}P_5Pt$: C, 16.08; H, 4.05. Found: C, 16.41; H, 4.09.

***cis*- and *trans*-Bis(trimethyl phosphite)bis(dimethyl phosphonato)platinum(II) (6). Method A.** A mixture of $P(OMe)_3$ (0.1785 g, 1.44 mol) and *cis*-$Cl_2Pt[P(OMe)_3]_2$ (0.350 g, 0.68 mmol) was stirred in 3 mL of CH_3CN for 6 h. After the solvent was removed by flushing with N_2, the precipitate was washed with diethyl ether (2 × 15 mL), and dried under vacuum. The yield was 0.320 g (71%). Recrystallization from acetone/ether at 0 °C produced colorless crystals, mp 64–65 °C. Anal. Calcd. for $C_{10}H_{30}O_{12}P_4Pt$: C, 18.16; H, 4.54. Found: C, 18.42; H, 4.49.

Method B. A mixture of **2**(PF_6)$_2$ (0.7820 g, 0.797 mmol) and tetra-*n*-butylammonium bromide (0.5140 g, 1.594 mmol) was dissolved in 20 mL of $CHCl_3$. The dicationic complex **2**(PF_6)$_2$ is not very soluble in $CHCl_3$. The precipitate gradually dissolved as the reaction proceeded. The solvent was evaporated by a stream of N_2 while stirring for 18 h. The resultant oil was extracted with C_6H_6 (2 × 5 mL), and pentane was slowly added to the C_6H_6 extract until a small amount of precipitate began to form. This precipitate was removed by centrifugation, and then the solvent was evaporated to yield 0.400 g (76%) of colorless **4**.

Tetraphenylarsonium (Trimethyl phosphite)tris(dimethyl phosphonato)platinate(II) [(Ph$_4$As)7]. A 25-mL round-bottom flask fitted with a reflux condenser and containing **4** (0.100 g, 0.151 mmol) and Ph_4AsCl (0.051 g, 0.122 mmol) was placed in a water bath at 60 °C. CH_3CN (2 mL) was added. After the mixture was stirred for 5 h, the solvent was removed under vacuum. The excess of **4** was removed by extracting the mixture with C_6H_6 (4 × 5 mL) and then washing the white solid with ether. After drying under vacuum, 0.110 g (88%) of **7** was yielded. The colorless crystals of (Ph_4As)**7** can be obtained by recrystallization from acetone/ether at 0 °C; mp 173–175 °C. Anal. Calcd for $C_{33}H_{47}AsO_{12}P_4Pt$: C, 38.49; H, 4.60. Found: C, 38.97; H, 4.61.

---

(42) Zumdahl, S. S.; Drago, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 6669.

(43) Church, M. J.; Mays, M. J. *J. Inorg. Nucl. Chem.* **1971**, *33*, 253.