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^{1}H and ^{31}P Nuclear Magnetic Resonance Spectroscopy of Substituted Phosphinito and Phosphito Complexes of Platinum(II). Analysis of the ^{31}P Spectrum of an AA′BB′-AA′BB′X Spin System Showing Second-Order Effects in Coupling with ^{195}Pt[1]

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Dimethyl phosphite and diphenylphosphinous acid can exist in tautomeric forms where the phosphorus is either tricoordinate or tetracoordinate. In the presence of metal ions, coordination can occur via oxygen or phosphorus atoms giving the ligand ambidentate character. Both ^{1}H NMR spectroscopy and ^{31}P NMR spectroscopy have been used to investigate the coordination of metal ions to these compounds.[2,3] With platinum metal ions such as Pt(II), coordination occurs through phosphorus, and the kinetically inert complexes can be readily isolated in a pure state. This paper reports and discusses the ^{1}H and ^{31}P NMR spectra of the series of complexes $Pt[OPR_2]_2[HOPR_2]_2$ (R = OMe, OPh, Ph),[4,5] $PtX[OPR_2][HOPR_2]L$ (X = H, R = Ph, L = $PMePh_2$; X = Cl, R = OMe, L = PEt_3, PPh_3; X = Cl, R = OPh, L = PEt_3),[5-7] and $Pt[OPR_2]_2[L\text{-}L]$ (R = OMe, L-L = dppe, diars).[5,8] Finally we include NMR spectral work on complexes having BF_2 or a second metal ion coordinated through the oxygens. Details of the electronic and EPR spectra of these complexes have been previously published[9] but not our work on the ^{1}H and ^{31}P NMR spectra of these substituted phosphinito or phosphito complexes.

The ^{31}P NMR data have been measured on a Fourier transform instrument with broad-band proton decoupling. This technique allows unambiguous assignments for the chemical shifts of the separate inequivalent nuclei and also for the coupling constants ^1J(PPt) and ^2J(PPt*P*). In an earlier study of the ^{1}H and ^{31}P NMR spectra of some of these compounds using continuous-wave instrumentation, it was possible to resolve and assign some of these values, but the use of broad-band proton decoupling has allowed complete analysis of the ^{31}P NMR spectrum of a compound of type $[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2$ to be achieved for the first time. The spectrum is a composite of an AA′BB′ spin system at two-thirds of the total intensity and an AA′BB′X (X = ^{195}Pt) spin system contributing the additional one-third. The analysis has allowed evaluation of the chemical shift and coupling constant data to be made and has verified that second-order effects due to coupling with ^{195}Pt must be taken into consideration when such spectra are analyzed.

Figure 1. ^{1}H NMR spectrum of $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$.

Results and Discussion

^{1}H NMR Spectra. The compound $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$ has been prepared by Troitskaya et al. from the hydrolysis of trimethyl phosphite in the presence of salts of tetrachloroplatinate(II).[4a,b] The complex is a diprotic acid which shows two inflections in a conductivity titration against added base after the addition of first 1 and then 2 equiv of base.[9] The protons can be considered to be symmetrically bonded between paris of oxygens, and the ^{1}H NMR spectrum shows a symmetric pattern centered 3.60 ppm downfield of Me_4Si (Figure 1). The pattern is complex because of coupling to ^{31}P and ^{195}Pt and also because of virtual coupling between ^3J(POC*H*) and ^2J(*P*Pt*P*).

Complexes $PtCl[OP(OMe)_2][HOP(OMe)_2]L$ (L = PEt_3, PPh_3) show separate resonances for methoxy protons on the dimethyl phosphito-*P* group trans to chloride or phosphine. The low-field line at $\delta = 3.720$ in the triethylphosphine complex has been assigned to the dimethyl phosphite trans to the phosphine,[5,10] with the high-field line at $\delta = 3.570$ being the dimethyl phosphite ligand trans to chloride.[11] Addition of triethylamine to a solution of the compound $PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3$ causes progressive shift of the methoxy resonances to a limiting pair of $\delta = 3.685$ and 3.645. These shifts do not change on lowering the temperature to −50 °C and represent an upfield shift from the free acid for the

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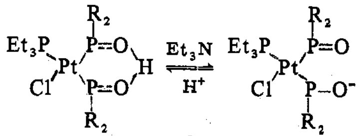
Table I. ^{1}H NMR Data for the Dimethyl Phosphito Complexes

Compound	Q[a]	n	δ(OMe)	δ(OMe)
$\{PtCl[OP(OMe)_2]_2PEt_3\}_nQ$	H	1	3.720	3.570
	BF_2	1	3.545	3.475
	UO_2	2	3.770	3.736
	Th	4[b]	3.715	3.680
	Zn	2[b]	3.600	3.545
$\{PtCl[OP(OMe)_2]_2PPh_3\}_nQ$	H	1	3.730	3.150
	Th	4	3.720	3.115
			δ(OMe)	
$[\{Pt[OP(OMe)_2]_2dppe\}_nQ]$-$[ClO_4]_{2n-2}$		1	3.160	
	Zn	2	3.238	
$Pt[OP(OMe)_2]_2diars$		1	3.680	

[a] Q is bonded to the oxygens. [b] Solutions prepared with this stoichiometry.

dimethyl phosphite-*P* trans to phosphine (P^z) and a downfield shift for the dimethyl phosphite-*P* trans to chloride (P^y).



R = OMe

Interestingly, inverse shifts cause the environments of the methoxy protons to become closely equivalent on addition of base. From these data we tentatively suggest that the canonical form for the anion with the charge opposite triethylphosphine is preferred over the second tautomer with the charge trans to chloride. In Table I are shown the ^{1}H NMR data obtained in the methoxy region for a series of compounds. Comparative data are collected for compounds having either H, BF_2, or a metal ion between the oxygens. For the moieties BF_2 and Zn in compounds $\{PtCl[OP(OMe)_2]_2PEt_3\}_nQ$ (n = 1, Q = BF_2; n = 2, Q = Zn) both methoxy groups show an upfield shift. The opposite effect is found with the uranyl ion, however, where each resonance is downfield shifted. This shift direction in the latter case correlates with the one found previously for a series of organo phosphite uranyl complexes.[2]

Although we have been unable to isolate and characterize polymeric materials from the diprotic acid $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$, the ^{1}H NMR spectra do show evidence for coordination of the uranyl ion. Addition of 1 equiv of uranyl chloride splits out two doublets centered at δ 3.83 ($^3J(POCH)$ = 10 Hz) and δ = 4.00 ($^3J(POCH)$ = 13 Hz), respectively, from the original symmetrical multiplet centered at δ = 3.60. This inequivalence possibly results from the distribution of protons and uranyl ions between the coordination sites on the compounds, since when 20 equiv of uranyl chloride is added, the doublets at δ = 4.02 and δ = 4.04 ($^3J(POCH)$ = 12.5 Hz) are essentially coincident. The intensity of the signal at δ = 3.60 has decreased significantly during this addition.

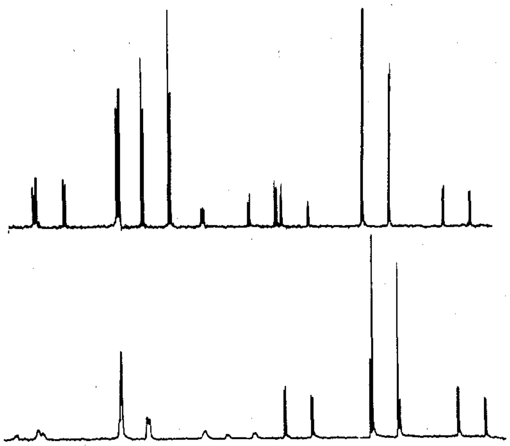
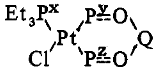
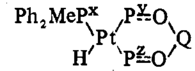
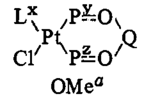


Figure 2. ^{31}P NMR spectra of $PtH[OPPh_2][QOPPh_2]PMePh_2$. The upper spectrum is for Q = H and the lower one is for Q = BF_2.

^{31}P NMR Spectra. Following the early work on ^{31}P NMR spectroscopy of dialkyl phosphite complexes, a number of papers have appeared correlating chemical shift and coupling constant data with bonding parameters in transition-metal compounds. Pidcock has published a very useful correlation of ^{31}P NMR spectral data on substituted phosphite complexes,[5] and Grim has also made some important investigations on substituted phosphine and phosphite complexes of the nickel triad.[12] Much of this work has been tabulated in review form, and in some cases detailed correlation has been made with theory.[13,14]

The ^{31}P NMR spectral data on our new[6,9] diphenylphosphinito and dimethyl phosphito complexes of platinum(II) are shown in Table II. Included along with these data, for comparative purposes, are some of the previously published data of Dixon[7] and Pidcock.[5] Complexes $PtH[OPPh_2][QOPPh_2]PMePh_2$ (Q = H, BF_2)[6] (Figure 2) show a downfield shift of 34 ppm for P^x (see Table II for the P^x, P^y, P^z designations) from its uncoordinated position of 28.0 ppm.[13] This magnitude and direction of shift for P^x is reflected in all the data in Table II. The chemical shift and coupling constant data for P^z are similar to those for complexes $PtCl[OPPh_2][QOPPh_2]PEt_3$ (Q = H, BF_2, $SiMe_3$), but P^y is considerably downfield shifted because of the high trans influence of the hydride ligand.[15] This effect is also apparent in the value of $^1J(PPt)$ for the hydride complexes where the value for coupling with P^y is considerably reduced from the value found by Dixon for the chloro complexes. The Pople–Santry theory of coupling constants stresses the importance of the Fermi contact interaction between nuclear moments and

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

	L	Q	X[b]	Y[b]	Z[b]	PtX[c]	PtY[c]	PtZ[c]	XY[d]	YZ[d]	XZ[d]	Ref
 Ph[a]		H	−12.0	−58.3	−76.5	2129	3833	2726	17	21	397	15
		BF_2	−14.0	−67.7	−81.7	2139	3882	2654	17		393	15
		$SiMe_3$	−14.5	−58.8	−82.6	2151	3960	2766	19	21	412	15
 Ph[a]		H	−5.8	−93.2	−80.2	2224	2302	2907	17	28	371	
		BF_2	−5.6			2390			17		368	
 OMe[a]	PEt_3	H	−18.9	−55.4	−94.9	2144	5276	3872	25	35	542	
			(−17.9)	(−55.1)	(−93.1)	(2173)	(5260)	(3895)	(−)	(−)	(547)	5
	PEt_3	BF_2	−19.2	−58.0	−88.6	2103	5520	3880	24	41	545	
	PPh_3	H	−29.1	−60.1	−89.4	2179	5209	4110	25	36	567	
	PEt_3	Th	−19.4	−45.9	−82.6	2034	5624	3701	24	32	560	
OPh[a]	PEt_3	H	−18.1	−48.2	−87.2	2217	5469	3818	23	37	547	

[a] Substituent on P^y and P^z. [b] Chemical shift from 85% H_3PO_4. [c] Values of ^1J. [d] Values of ^3J.

electron spins in s orbitals, and in square-planar complexes this theory is integrated with concepts of trans influence.[16] Both σ and π components of the metal–phosphorus bond have been assumed to be important in the interpretation of $^1J(\mathrm{PPt})$ values. For the compound $\mathrm{PtH[OPPh_2][HOPPh_2]PMePh_2}$ it appears that the low value of $^1J(\mathrm{P^yPt})$ is due to σ effects. From symmetry considerations both Cl and $\mathrm{P^y}$ will bond to the same d_π orbitals. Since a hydride ligand will have negligible d_π component in its bond to platinum(II), it follows that the bond $\mathrm{Pt{-}P^y}$ will have greater π character (and hence less σ character) when trans to hydride. From our data on $^1J(\mathrm{P^yPt})$ it appears that this decrease in σ character causes a simultaneous decrease in $^1J(\mathrm{P^yPt})$. From Figure 2 it is apparent that replacement of the acidic hydrogen (Q = H) by $\mathrm{BF_2}$ causes a broadening of the resonances for $\mathrm{P^y}$ and $\mathrm{P^z}$ due to interaction with the $^{10}\mathrm{B}$ and $^{11}\mathrm{B}$ ($I = 3$ and $^3/_2$, respectively) quadrupoles. There is some slight effect over four bonds to $\mathrm{P^x}$, but the coupling is strong over two bonds to $\mathrm{P^y}$ and $\mathrm{P^z}$.

The data for complexes $\mathrm{PtCl[OP(OR)_2][HOP(OR)_2]L}$ have been compiled by first-order analysis of the spectra. Pidcock has previously analyzed the $^{31}\mathrm{P}$ NMR spectrum of the complex $\mathrm{PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3}$ by second-order analysis, but it is apparent from Table II that only a small numerical difference arises from using the simpler approach. Comparing the chemical shifts of the coordinated dimethyl phosphite ligands and the respective coupling constants $^1J(\mathrm{PPt})$ between the two complexes $\mathrm{PtCl[OP(OMe)_2][QOP(OMe)_2]PEt_3}$ (Q = H, $\mathrm{BF_2}$), it is apparent that substitution of $\mathrm{BF_2}$ for H deshields the phosphite $\mathrm{P^y}$, and shields the phosphite $\mathrm{P^z}$. Simultaneously $^1J(\mathrm{P^yPt})$ increases, but for $^1J(\mathrm{P^zPt})$ the broadening of the resonance by $\mathrm{BF_2}$ prohibits assignment of a change. If changes in chemical shift may be attributed to changes in π system electron density at phosphorus, and differences in $^1J(\mathrm{PPt})$ to changes in σ bonds between platinum and phosphorus,[13] these spectra imply that replacement of H by $\mathrm{BF_2}$ changes the electron density of oxygen on the phosphite $\mathrm{P^y}$ at the expense of that phosphorus, deshielding it.[17] Simultaneous with this effect the electron density at oxygen on the phosphite $\mathrm{P^z}$ is changed to cause an increase of electron density on that phosphorus, which is shielded. For phosphite $\mathrm{P^y}$ the inductive loss of π-electron density synergistically increases the σ donation of phosphorus which increases $^1J(\mathrm{P^yPt})$. These observations lead to the conclusion that $\mathrm{BF_2}$ shows less electron withdrawal than H and also that the $\mathrm{BF_2}$ is bonded to both oxygens.

Comparison of the complexes $\mathrm{PtCl[OP(OMe)_2][HOP(OMe)_2]PEt_3}$ and $\mathrm{\{PtCl[OP(OMe)_2]_2PEt_3\}_4Th}$ shows the effect of a strong general shielding when H is replaced by Th(IV),[17] yet $^1J(\mathrm{P^xPt})$ and $^1J(\mathrm{P^zPt})$ decrease and $^1J(\mathrm{P^yPt})$ increases. Comparison between the $^1\mathrm{H}$ spectra of the H and Th complexes shows that replacement of H for Th produces only a small shielding of the methyl protons. The implication is that a cyclic or extensive π system has been established which produces a shielding effect within the chelate ring but a deshielding effect outside the ring.

We have measured the $^{31}\mathrm{P}$ NMR spectra of the complexes $\mathrm{Pt[OPR_2]_2[HOPR_2]_2}$ (R = OMe, OPh, Ph). Complexes with R = OMe and OPh show a single resonance at $\delta = 90.7$, $^1J(\mathrm{PPt}) = 3461$ Hz, and $\delta = 79.5$, $^1J(\mathrm{PPt}) = 3628$ Hz, respectively, in agreement with the earlier results by Pidcock. The complex $\mathrm{Pt[OPPh_2]_2[HOPPh_2]_2}$, however, shows this resonance at $\delta = 72.5$, $^1J(\mathrm{PPt}) = 2467$ Hz, split into a doublet of separation 7.4 Hz. These data show that the acidic hydrogen is symmetrically bonded between a pair of oxygens,[4c,18] but it is likely that the situation is a dynamic equilibrium as implied recently by Dixon.[15] Such an exchange would resemble that found for 2,4-pentanedione where the hydrogen transfers between the two oxygens.[19] It is possible that this exchange is sufficiently slow at room temperature to lead to a small doublet splitting in the spectrum, but temperature-dependent $^{31}\mathrm{P}$ NMR data will be required to clarify this point.

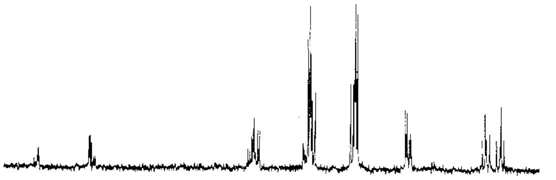


Figure 3. $^{31}\mathrm{P}$ NMR spectrum of $\mathrm{Pt[OP(OMe)_2]_2dppe}$.

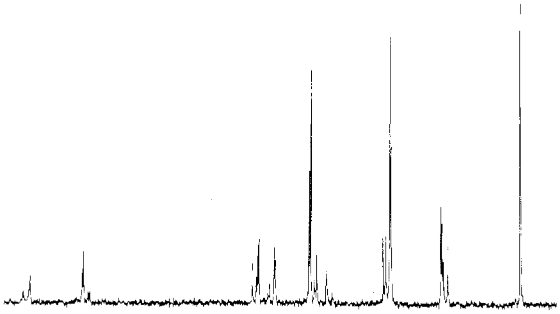


Figure 4. $^{31}\mathrm{P}$ NMR spectrum of $\mathrm{[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2}$.

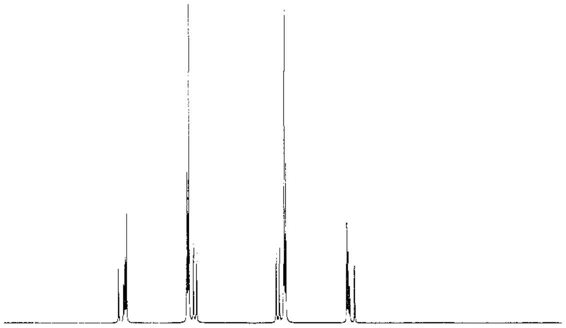
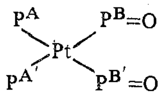


Figure 5. Calculated $^{31}\mathrm{P}$ NMR spectrum for the center line portion of Figure 4.

Table III. Chemical Shift and Coupling Constant Data for $\mathrm{[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2}$[c]



δ_A[a]	δ_B[a]	$J_\mathrm{AA'}$[b]	J_AB[b]	$J_\mathrm{AB'}$[b]	$J_\mathrm{BB'}$[b]
−50.75	−80.13	+10.15	+27.85	−488.64	+49.74

[a] Chemical shift in ppm. [b] Coupling constant in Hz. [c] $\delta_\mathrm{A'} = \delta_\mathrm{A}$; $\delta_\mathrm{B'} = \delta_\mathrm{B}$; $J_\mathrm{A'B'} = J_\mathrm{AB}$; $J_\mathrm{A'B} = J_\mathrm{AB'}$.

The $^{31}\mathrm{P}$ NMR spectra of $\mathrm{Pt[OP(OMe)_2]_2dppe}$ and $\mathrm{[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2}$ show a complex spin pattern (Figures 3 and 4) which cannot be interpreted on the basis of a first-order analysis. We have therefore carried out computer simulation calculations with a LAOCOON III program to extract the chemical shift and coupling constant data for the zinc complex (Table III). The spectrum has been analyzed as an AA′BB′ spin system superimposed with an AA′BB′X spin system for the $^{195}\mathrm{Pt}$ portion of the spectrum (Figures 5 and 6). The spectrum is a particularly interesting one since the $^{195}\mathrm{Pt}$ satellites are not symmetrically flanking the center portion of the spectrum. Second-order effects on $^1\mathrm{H}$ NMR spectra due to coupling with $^{31}\mathrm{P}$ and $^{195}\mathrm{Pt}$ have been previously reported with similar complexes,[20,21] but in this case these effects can be investigated without interference from coupling with the protons of the phosphine.[21] Our calculations show that the single line is not an impurity but is caused by

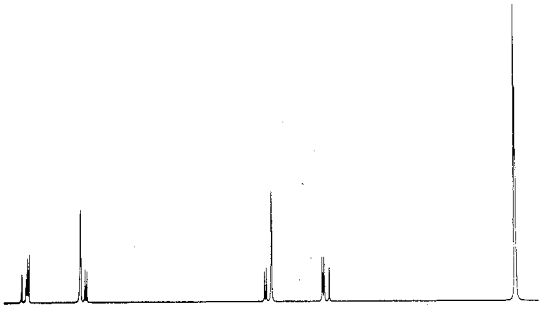


Figure 6. Calculated ^{31}P NMR spectrum for the ^{195}Pt satellite portion of Figure 4. The intensities are not scaled to accommodate the isotopic abundance of ^{195}Pt.

an accidental coincidence of the ^{195}Pt satellite multiplet. For the complex $Pt[OP(OMe)_2]_2dppe$ this coincidence is not observed and the satellite multiplet observed (Figure 3). Nevertheless even in this latter case the ^{195}Pt satellite portion of the spectrum is not symmetric, and second-order effects between ^{31}P and ^{195}Pt are apparent.

The complex $Pt[OP(OMe)_2]_2(diars)$ is structurally analogous. No second-order effects due to the arsenic quadrupole are observed, and the methoxy groups give rise to a single resonance at $\delta = 61.6$, $^1J(PPt) = 4753$ Hz.

Experimental Section

Complexes $PtH[OPPh_2][QOPPh_2]PMePh_2$ ($Q = H, BF_2$),[6] $PtCl[OP(OMe)_2][QOP(OMe)_2]L$ ($Q = H, BF_2, L = PEt_3$; $Q = H, L = PPh_3$),[5,9] $\{PtCl[OP(OMe)_2]_2PEt_3\}_4Th$,[9] $Pt[OPPh_2]_2[HOPPh_2]_2$,[4c,d] and $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$[22] were prepared as previously described. Nuclear magnetic resonance spectra were measured as solutions in $CDCl_3$. ^{1}H NMR spectra were measured in 5-mm sample tubes with hexamethyldisiloxane ($\delta = 0.02$) as internal reference on a Jeol MH-100 spectrometer. ^{31}P NMR spectra were measured in 10-mm spinning sample tubes with 85% H_3PO_4 as external reference on a Bruker WH-90 Fourier transform spectrometer. Broad-band decoupling of ^{1}H was employed and the nucleus resonated at 36.450 MHz in a multinuclear tunable probe. Preliminary calculations were made with a Nicolet NMRCAL program on the WH-90 computer, and final iterative fits were achieved using a LAOCOON III program.

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Registry No. $\{PtCl[OP(OMe)_2]_2PEt_3\}H$, 63264-38-0; $\{PtCl[OP(OMe)_2]_2PEt_3\}BF_2$, 63678-34-2; $\{PtCl[OP(OMe)_2]_2PEt_3\}_2UO_2$, 63239-09-8; $\{PtCl[OP(OMe)_2]_2PEt_3\}_4Th$, 66454-95-3; $\{PtCl[OP(OMe)_2]_2PEt_3\}_2Zn$, 66322-92-7; $\{PtCl[OP(OMe)_2]_2PPh_3\}H$, 63292-78-4; $\{PtCl[OP(OMe)_2]_2PPh_3\}_4Th$, 63310-65-6; $Pt[OP(OMe)_2]_2dppe$, 21657-30-7; $[\{Pt[OP(OMe)_2]_2dppe\}_2Zn][ClO_4]_2$, 63280-74-0; $Pt[OP(OMe)_2]_2diars$, 63264-39-1; $\{PtH[OPPh_2]_2PPh_2Me\}H$, 55012-58-3; $\{PtH[OPPh_2]_2PPh_2Me\}BF_2$, 55012-60-7; $\{PtCl[OP(OPh)_2]_2PEt_3\}H$, 63292-77-3; $Pt[OP(OMe)_2]_2[HOP(OMe)_2]_2$, 21794-30-9.

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Kinetic Study of Carbonyl Dissociation in $W(CO)_3(CS)(o\text{-phen})$. Labilization by the Thiocarbonyl Ligand

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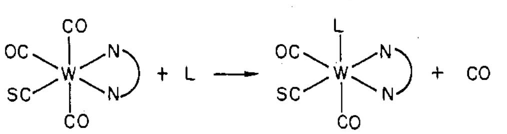
In 1967 Graham and Angelici[1] reported kinetic studies of substitution reactions of an *o*-phenanthroline complex

$$W(CO)_4(o\text{-phen}) + L \rightarrow cis\text{-}W(CO)_3(L)(o\text{-phen}) + CO \qquad (1)$$

where L was $P(n\text{-}C_4H_9)_3$, $P(OC_2H_5)_3$, $P(OCH_2)_3CCH_3$, or $P(C_6H_5)_3$. With all L ligands, the reaction proceeded by a dissociative pathway. With the more nucleophilic ligands, an associative mechanism was also detected.

We now report results of a kinetic study of the reaction of the analogous thiocarbonyl complex



(2)

where L is $P(OCH_3)_3$, $P(OCH_2CH_3)_3$, $P(C_6H_5)_3$, or $P(n\text{-}C_4H_9)_3$ and the bidentate nitrogen donor ligand is *o*-phenanthroline. The purpose of this study was to determine what effect if any, the CS group has on the mechanism and