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Reactivity of Platinum Diolefin Complexes. 2. Reactions with Bulky and Chelating Group 5B Ligands and Studies Relating to Carbonyl Insertion[1]

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Reactions of [PtXY(cod)] (X = Y = Cl, Me, Ph; X = Cl, Y = Ph, COPh) with bulky monodentate and chelating group 5B ligands have been examined by $^{31}P\{^1H\}$ NMR spectroscopy. The molecularity of the products is a function of steric bulk with monodentate ligands and a function of "chelate bite" with bidentate ligands. The geometry of the products is controlled largely by the trans influence of both neutral and anionic groups. Where the steric constraints involved in nucleophilic attack of the complexes by bulky ligands are dominant, olefin displacement can be prevented entirely. Reactions of $[PtXYL_2]$ (X = Y = Ph, Cl; X = Ph, Y = Cl; L = monodentate ligand, L_2 = bidentate ligand) with carbon monoxide have been studied by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR and infrared spectroscopies. The mechanism of carbonyl insertion at platinum(II) is discussed in terms of the chelate effect and the trans influence of the anionic ligands.

Introduction

Olefin complexes of platinum(II) have proved to be invaluable starting materials in organometallic synthesis;[2] for example, we have recently reported[1] the diversity of reaction which may be observed between [PtXY(cod)] (X = Y = Cl, Me, Ph; X = Cl, Y = Me, Ph; cod = 1,5-cyclooctadiene) and two different incoming nucleophiles. Initially we observed that carbon monoxide will react to form either a charge-transfer complex (X = Y = Cl), a product formed by olefin displacement (X = Y = Me, Ph), or a product formed by insertion of carbon monoxide into a platinum–carbon σ bond (X = Cl, Y = Me, Ph). Subsequent reaction with tertiary phosphines led to the formation of *cis*-$[PtX_2(CO)(PR_3)]$ (X = Cl), *cis*-$[PtX_2(PR_3)_2]$ (X = Me, Ph), or *trans*-$[PtX(COY)(PR_3)_2]$ (X = Cl, Y = Me, Ph) in high yield.

In this paper we report the results of spectroscopic studies on the reactions of [PtXY(cod)] with bulky monodentate tertiary phosphines and with chelating group 5B ligands. $^{31}P\{^1H\}$ NMR spectroscopy has been employed to identify the species formed in solution and, particularly, to differentiate between possible molecularities of oligomeric products and geometrical arrangements of unsymmetrical species. Results of our studies on the insertion of carbon monoxide into platinum–carbon σ bonds are also described.

Experimental Section

The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 15.1 and 24.3 MHz, respectively, on a Bruker WP-60 spectrometer operating in the Fourier transform mode. ^{13}C chemical shifts are relative to Me_4Si (internal) and ^{31}P chemical shifts are relative to H_3PO_4 (external), more positive values representing deshielding. Infrared spectra were measured in solution with use of NaCl cells of 0.1-mm path length or as Nujol mulls between CsI plates and were recorded on a Perkin-Elmer 180 spectrometer. Conductivities were measured with use of a 10-mm cell equipped with platinized electrodes and a Beckman RC-18A bridge and are corrected for the inherent conductivity of the solvent.

Carbon-13 labeled carbon monoxide (90% enriched) was obtained from Prochem. Phosphine ligands were obtained from Strem Chemicals and Orgmet, Inc. Silver triflate ($AgOSO_2CF_3$) was obtained from Aldrich.

The complexes [PtXY(cod)] (X = Y = Cl, Me, Ph; X = Cl, Y = Me, Ph, COPh) were prepared by reported methods.[1,3] Reactions with monodentate ligands are described.

Reactions of $[PtCl_2(cod)]$ were performed as follows.

(1) $PMePh_2$. A solution of $PMePh_2$ (1 equiv) in $CDCl_3$ (1 mL) was added to the complex (ca. 30 mg) as a suspension in $CDCl_3$ (2 mL) and stirred for 30 min. Examination by $^{31}P\{^1H\}$ NMR showed formation of *cis*-$[PtCl_2(PMePh_2)_2]$ only.

(2) PCy_3. A solution of PCy_3 (1 equiv) in benzene (50 mL) was added dropwise over 30 min to a solution of the complex (ca. 30 mg) in benzene (50 mL). After stirring for 30 min, the solution was reduced to dryness in vacuo and the residue taken up in $CDCl_3$. Examination by $^{31}P\{^1H\}$ NMR showed formation of both *trans*-$[PtCl_2(PCy_3)_2]$ and $[Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2]$.

(3) P(*o*-tolyl)$_3$ and P(mesityl)$_3$. The solid ligand (1 equiv) was added to a benzene solution of the complex (ca. 30 mg in 25 mL) and stirred for 24 h. The solvent was removed in vacuo, and the solids were taken up in $CDCl_3$. Examination by $^{31}P\{^1H\}$ NMR showed no reaction in either case. Heating the $CDCl_3$ solutions to reflux for 1 h did not cause any reaction to occur.

Reactions of [PtClPh(cod)] were performed as follows.

(4) $PMePh_2$. The procedure is as that for reaction 1. $^{31}P\{^1H\}$ NMR showed formation of *trans*-$[PtClPh(PPh_2Me)_2]$ only.

(5) PCy_3. The procedure is as that for reaction 2. $^{31}P\{^1H\}$ NMR showed formation of $[Pt_2(\mu\text{-}Cl)_2(Ph)_2(PCy_3)_2]$ only. Addition of a further equivalent of solid PCy_3 to the $CDCl_3$ solution caused further reaction, the product being identified as *trans*-$[PtClPh(PCy_3)_2]$ by $^{31}P\{^1H\}$ NMR.

(6) P(*o*-tolyl)$_3$ and P(mesityl)$_3$. The procedure is as that for reaction 3. $^{31}P\{^1H\}$ NMR showed no reaction with P(mesityl)$_3$ but formation of two isomers of $\{Pt_2(\mu\text{-}Cl)_2Ph_2[P(o\text{-tolyl})_3]_2\}$ and *trans*-$\{PtClPh[P(o\text{-tolyl})_3]_2\}$ with P(*o*-tolyl)$_3$. Addition of a further equivalent of this latter ligand as a solid to the $CDCl_3$ solution caused complete conversion to the mononuclear product.

Reactions of [PtCl(COPh)(cod)] were performed as follows.

(7) $PMePh_2$. The procedure is as that for reaction 1. $^{31}P\{^1H\}$ NMR showed formation of *trans*-$[PtCl(COPh)(PMePh_2)_2]$ only.

(8) PCy_3. The procedure is as that for reaction 2. $^{31}P\{^1H\}$ NMR showed formation of both $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PCy_3)_2]$ and $[PtClPh(CO)(PCy_3)]$. Addition of a second equivalent of PCy_3 as a solid caused further reaction, the product being identified by $^{31}P\{^1H\}$ NMR as *trans*-$[PtCl(COPh)(PCy_3)_2]$.

(9) P(*o*-tolyl)$_3$ and P(mesityl)$_3$. The procedure is as that for reaction 3. $^{31}P\{^1H\}$ NMR showed no reaction with P(mesityl)$_3$ but formation of $\{PtClPh(CO)[P(o\text{-tolyl})_3]\}$ with P(*o*-tolyl)$_3$. Addition of a further equivalent of P(*o*-tolyl)$_3$ as a solid to the $CDCl_3$ solution, followed by stirring for 48 h, caused no further reaction. Heating the solution at reflux for 7 h also had no effect.

Reactions of $[PtR_2(cod)]$ were performed as follows.

(10). The complex (ca. 30 mg) was dissolved in benzene (25 mL) and the ligand added (R = Ph, ligand = $PMePh_2$, PCy_3, P(*o*-tolyl)$_3$, P(mesityl)$_3$; R = Me, ligand = P(*o*-tolyl)$_3$). The solution was stirred for 48 h and the solvent removed in vacuo. The solids were dissolved in $CDCl_3$ and examined by $^{31}P\{^1H\}$ NMR. Only $PMePh_2$ reacted, to produce *cis*-$[PtPh_2(PMePh_2)_2]$.

Reactions with bidentate ligands were performed as follows.

(11) $[PtX_2(cod)] + \widehat{L\,L}$ (X = Cl, Ph; $\widehat{L\,L}$ = dppm, dppe, appe). The complex (ca. 30 mg) was dissolved in $CDCl_3$ and the ligand (1 equiv) added as a solid. After being stirred for 30 min, the solution was examined by $^{31}P\{^1H\}$ NMR which showed formation of $[PtX_2(LL)]$ in all cases.

(12) $[PtXY(cod)] + \widehat{L\,L}$ (X = Cl, Y = Ph, COPh; $\widehat{L\,L}$ = dppe, appe). The procedure is as that for reaction 11. $^{31}P\{^1H\}$ NMR showed

(1) For part 1 of this series see G. K. Anderson, H. C. Clark, and J. A. Davies, *Inorg. Chem.*, **20**, 1636 (1981).
(2) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, London, 1973, Chapter 13.
(3) H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, **59**, 411 (1973).

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Table I. $^{31}P\{^1H\}$ NMR Spectral Data of $[PtXY(PR_3)_2]$ Complexes[a]

complex	δ(P)	^1J(Pt,P), Hz
cis-$[PtCl_2(PMePh_2)_2]$	−1.2	3621
trans-$[PtCl_2(PCy_3)_2]$	16.3	2400
trans-$[PtClPh(PMePh_2)_2]$	8.4	3010
trans-$[PtClPh(PCy_3)_2]$	16.7	2796
trans-$\{PtClPh[P(o\text{-tolyl})_3]_2\}$	22.5	3150
trans-$[PtCl(COPh)(PMePh_2)_2]$	4.8	3215
trans-$[PtCl(COPh)(PCy_3)_2]$	17.7	3042
cis-$[PtPh_2(PMePh_2)_2]$	0.9	1760
trans-$[PtCl(COPh)(PPh_3)_2]$	19.6	3384

[a] Spectra were obtained for $CDCl_3$ solutions.

formation of [PtXY(L̂L)]. With appe, the geometry of the product has P trans to Cl in both cases.

(13) [PtXY(cod)] + L̂L (X = Cl, Y = Ph, COPh; L̂L = dppm). The complex (ca. 70 mg) was dissolved in $CHCl_3$ (15 mL) and dppm (1 equiv) dissolved in $CHCl_3$ (15 mL) added dropwise over 45 min. The solution was stirred for 15 min and reduced to dryness in vacuo. The product was washed with diethyl ether and recrystallized from benzene–petroleum ether. Examination by $^{31}P\{^1H\}$ NMR showed formation of $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2R_2][Cl]$ (R = COPh) but both this dimeric product and [PtClR(dppm)] for R = Ph. Reaction of silver triflate (1 equiv) with $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2(COPh)_2][Cl]$ produced a white precipitate of AgCl but did not alter the $^{31}P\{^1H\}$ NMR spectrum of the product. Conductivity measurements in acetonitrile[4] solution gave a value of $\Lambda_0 - \Lambda_E/c^{1/2} = 544\ \Omega^{-1}\ L^{1/2}\ equiv^{-1/2}$ (where Λ_E = conductance at concentration c, Λ_0 = conductance at infinite dilution), although some deviation from linearity was apparent. $^{31}P\{^1H\}$ NMR spectra (Table VI) of $CDCl_3$ and MeCN-d_3 solutions of this product were virtually identical.

Reactions with CO and ^{13}CO were performed as follows.

(14). $[PtX_2L_2]$ (X = Ph, L = $PMePh_2$, PPh_3; L_2 = dppm, dppe, appe) and [PtXYL$_2$] (X = Cl, Y = Ph; L = $PMePh_2$, PPh_3; L_2 = dppm, dppe, appe) were dissolved in $CDCl_3$ (30 mg in 3 mL) and degassed by freeze–thawing in vacuo. The solutions were saturated with CO and stirred under a CO atmosphere for 72 h. Examination by $^{31}P\{^1H\}$ NMR showed that no reaction occurred for complexes of bidentate ligands while insertion to yield *trans*-[PtCl(COPh)L$_2$] occurred with phenylchloro complexes of monodentate ligands and phosphine displacement to yield *cis*-$[PtPh_2L(CO)]$ with diphenyl complexes of monodentate ligands.

(15) $[PtPh_2L_2]$ (L = $PMePh_2$, PPh_3) with ^{13}CO. The procedure is as that for reaction 14. $^{13}C\{^1H\}$ NMR confirmed the products to be *cis*-$[PtPh_2L(CO)]$. Removal of solvent in vacuo and reexamination of the product in $CDCl_3$ solution showed that the reaction was reversible and that $[PtPh_2L_2]$ was regenerated.

Results and Discussion

Reactions with Bulky Monodentate Phosphines. Our initial interest in the reactions of bulky phosphine ligands[5] with platinum(II) diolefin complexes arose when $^{31}P\{^1H\}$ NMR studies showed that the complex $[PtCl_2(cod)]$ reacted with 1 equiv of $PMePh_2$ to yield *cis*-$[PtCl_2(PMePh_2)_2]$[1] as the only phosphine-containing product but that a comparable reaction with PCy_3 yielded both *trans*-$[PtCl_2(PCy_3)_2]$[6] and a small amount of the halide-bridged dimer $[Pt_2(\mu\text{-Cl})_2Cl_2(PCy_3)_2]$ (Tables I and II). The nature of the dimeric product was confirmed by comparison with the $^{31}P\{^1H\}$ NMR spectrum of an authentic sample prepared by the reported method.[6]

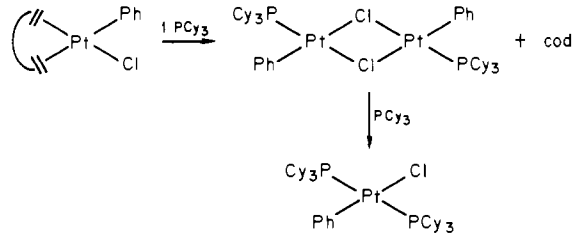
The cone-angle data of Tolman[7] allow some comparisons of relative ligand steric effects to be made and demonstrate that the PCy_3 ligand (170°) is far more sterically demanding than $PMePh_2$ (136°). The possibility that electronic effects alter the course of the reaction cannot be ignored, and indeed,

Table II. $^{31}P\{^1H\}$ NMR Spectral Data of $[Pt_2(\mu\text{-Cl})_2X_2(PR_3)_2]$ Complexes[a]

complex	δ(P)	^1J(Pt,P), Hz
$[Pt_2(\mu\text{-Cl})_2Cl_2(PCy_3)_2]$	20.2	3875
$[Pt_2(\mu\text{-Cl})_2Ph_2(PCy_3)_2]$	16.7	4761
$\{Pt_2(\mu\text{-Cl})_2Ph_2[P(o\text{-tolyl})_3]_2\}$[b]	9.4	5090
	11.1	5117
$[Pt_2(\mu\text{-Cl})_2(COPh)_2(PCy_3)_2]$	21.5	5115

[a] Spectra were obtained for $CDCl_3$ solutions. [b] Both symmetric and unsymmetric isomers present.[10]

Scheme I



Tolman's electronic parameters[7] for PCy_3 (2056.4) and $PMePh_2$ (2066.6) are quite different. Accordingly, we investigated the reaction of P(*o*-tolyl)$_3$ with $[PtCl_2(cod)]$ as this ligand has a very large cone angle (194°) and yet is electronically very similar to $PMePh_2$, with an electronic parameter of 2067.0. Under our standard conditions, no reaction between $[PtCl_2(cod)]$ and P(*o*-tolyl)$_3$ was observed, and even prolonged refluxing in chloroform solution had no effect. Thus, although olefin ligands are normally regarded as excellent leaving groups, displacement by a phosphorus(III) donor can be prevented if the steric constraints involved in formation of an activated transition state by nucleophilic attack of the bulky phosphine on the diolefin complex dominate the reaction pathway. Indeed, the P(mesityl)$_3$ ligand with a cone angle[7] of 212° also does not react with $[PtCl_2(cod)]$. The observation of some dimeric product in the reaction with PCy_3 suggests that such species may be formed initially but that bridge cleavage to the mononuclear product occurs, the latter step being rapid for $PMePh_2$ but slow for PCy_3. It has previously been observed that cleavage of such dimeric species is indeed a sterically controlled process.[6] It is also pertinent to note that, while $[PtCl_2(cod)]$ does not react with P(*o*-tolyl)$_3$, the norbornadiene analogue has been reported to do so,[8] suggesting that the cyclooctadiene ligand is more sensitive to steric constraints during nucleophilic attack by bulky ligands.

The reactions of the analogous phenylplatinum complex, [PtClPh(cod)], with these ligands provides further evidence that a dimeric species is initially formed. Thus, while $PMePh_2$ reacted to form only *trans*-$[PtClPh(PMePh_2)_2]$[1] (Table I), addition of 1 equiv of PCy_3 to [PtClPh(cod)] yielded the dimer $[Pt_2(\mu\text{-Cl})_2Ph_2(PCy_3)_2]$ exclusively (Scheme I); it was identified by its characteristic $^{31}P\{^1H\}$ NMR spectrum (Table II). Addition of a further equivalent of PCy_3 resulted in bridge cleavage to yield the expected product[9] *trans*-$[PtClPh(PCy_3)_2]$ (Table I).

The reaction with P(*o*-tolyl)$_3$ appears to proceed in an analogous fashion. Addition of 1 equiv of the phosphine to [PtClPh(cod)] yielded three phosphine-containing species, assigned on the basis of their $^{31}P\{^1H\}$ NMR spectra as the symmetrical and unsymmetrical isomers[10] of the dimer $\{Pt_2$-

(4) J. A. Davies, F. R. Hartley, and S. G. Murray, *Inorg. Chim. Acta*, **43**, 69 (1980).
(5) H. C. Clark, *Isr. J. Chem.*, **15**, 210 (1976–1977).
(6) G. K. Anderson, H. C. Clark, and J. A. Davies, *Inorg. Chem.*, **20**, 944 (1981).
(7) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
(8) G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 712 (1980).
(9) G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1434 (1980).
(10) G. K. Anderson, R. J. Cross, L. M. Muir, K. W. Muir, and T. Solomon, *J. Organomet. Chem.*, **170**, 385 (1979).

Scheme II

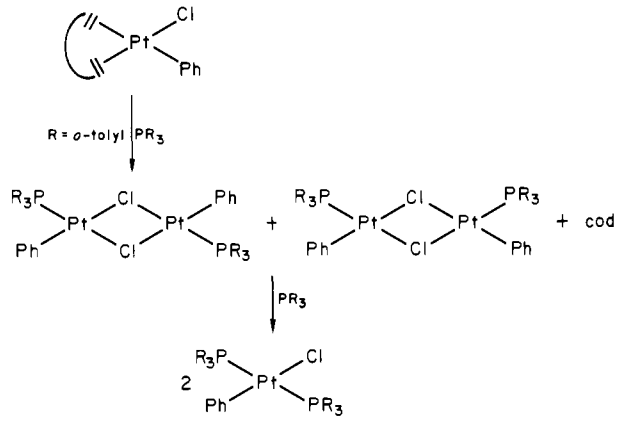
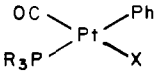


Table III. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR Spectral Data of the Complexes[a]



X	PR_3	δ(P)	^1J(Pt,P), Hz	δ(CO)	^1J(Pt,C), Hz	^2J(P,C), Hz
Cl	PCy_3	30.0	1409			
Cl	P(*o*-tolyl)$_3$	17.8	1363			
Ph	$PMePh_2$	2.1	1604	180.6	979	5
Ph	PPh_3	15.7	1621	180.7	971	5

[a] Spectra were obtained for $CDCl_3$ solutions.

Table IV. Infrared Spectral Data of Carbonyl and Aroyl Complexes[a]

complex	ν(CO), cm^{-1}	ν(COPh), cm^{-1}
trans-[PtCl(COPh)$(PCy_3)_2$]		1630
cis-[$PtPh_2$(CO)$(PMePh_2)$]	2048	
cis-[$PtPh_2$(CO)(PPh_3)]	2050	

[a] Spectra were obtained for $CDCl_3$ solutions.

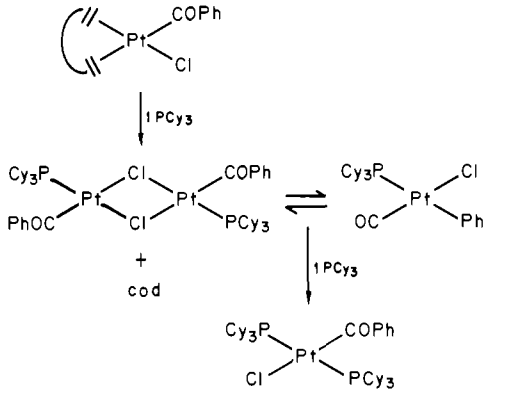
$(\mu\text{-Cl})_2Ph_2[P(o\text{-tolyl})_3]_2\}$ (Table II) and the monomer *trans*-{PtClPh$[P(o\text{-tolyl})_3]_2$} (Table I). Addition of a further equivalent of phosphine resulted in total conversion to the mononuclear product, although the reaction was slow and heating was required to obtain complete cleavage (see Scheme II). The very bulky P(mesityl)$_3$ ligand did not react with [PtClPh(cod)] over a period of 24 h at room temperature.

The degree of steric control in cyclooctadiene displacement by tertiary phosphines is exemplified in the reactions of the aroyl complex [PtCl(COPh)(cod)]. The reaction with $PMePh_2$ yielded *trans*-[PtCl(COPh)$(PMePh_2)_2$][1] as the sole phosphine-containing product (Table I), while reaction with 1 equiv of PCy_3 yielded the known complex $[Pt_2(\mu\text{-Cl})_2(COPh)_2(PCy_3)_2]$[8] (Table II) and its equilibration product [PtClPh(CO)(PCy_3)] (Table III). Reaction with further phosphine resulted in complete conversion to the mononuclear species *trans*-[PtCl(COPh)$(PCy_3)_2$], identified by its $^{31}P\{^1H\}$ NMR (Table I) and infrared (Table IV) spectra. See Scheme III.

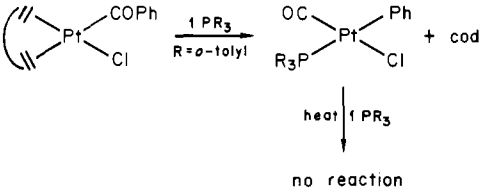
In contrast, P(*o*-tolyl)$_3$ reacted to produce only the terminal carbonyl complex (Table III), resulting from rapid equilibration of the dimer. No further reaction could be induced upon addition of further P(*o*-tolyl)$_3$, even with prolonged heating (Scheme IV).

Displacement of cyclooctadiene from $[PtPh_2(cod)]$ by $PMePh_2$ yielded the complex *cis*-$[PtPh_2(PMePh_2)_2]$[1] (Table I). Attempts to perform similar displacement reactions with PCy_3, P(*o*-tolyl)$_3$, or P(mesityl)$_3$ were unsuccessful, a result expected from consideration of the possible product geometries. Thus, it seems likely that two bulky ligands will be unable to

Scheme III



Scheme IV



adopt a cis configuration, while the two high trans influence[11] organo groups will be unwilling to form a complex of trans geometry. Similarly, no reaction between $[PtMe_2(cod)]$ and P(*o*-tolyl)$_3$ could be detected spectroscopically.

In summary, $PMePh_2$ reacts via cyclooctadiene displacement to yield mononuclear products, of either cis or trans geometry, in all cases; PCy_3 reacts to form detectable dimeric species, if bridging ligands are available, which are cleaved by further phosphine to form trans-mononuclear products. Similarly, P(*o*-tolyl)$_3$ yields dimeric species, or their equilibration products, but these react reluctantly, if at all, to form monomeric complexes while P(mesityl)$_3$ does not react under any conditions we have examined with platinum(II) cyclooctadiene complexes.

Reactions with Bidentate Group 5B Ligands. Bennett and co-workers have used platinum(II) diolefin complexes as precursors in the synthesis of complexes containing chelating diphosphines and have shown that the molecularity of the products is sensitive to the chelate bite of the ligand.[12] Thus, reaction of [PtClMe(cod)] with the ligands $Ph_2P\{CH_2\}_nPPh_2$ yields mononuclear products for n = 2 and 3 but both monomeric and oligomeric products for n = 1. NMR data obtained by INDOR and molecular weight measurements characterized the oligomer (n = 1) in terms of a trimeric structure.

The availability of our series of cyclooctadiene platinum(II) precursors enabled us to investigate further displacement reactions with the chelate ligands $Ph_2P\{CH_2\}_nPPh_2$ (n = 1, 2) and $Ph_2As\{CH_2\}_2PPh_2$ (abbreviated as dppm, dppe, and appe, respectively).

The reaction of $[PtCl_2(cod)]$ with the ligands dppm, dppe, and appe (L L) yielded the expected mononuclear products $[PtCl_2(L\,L)]$ (Table V). Similar reactions of these ligands with $[PtPh_2(cod)]$ also yielded exclusively mononuclear complexes (Table V). The unsymmetrical complexes [PtClR(cod)] (R = Ph, COPh) reacted with dppe to yield mononuclear compounds with $^{31}P\{^1H\}$ NMR spectra (Table V) typical of the ABX spin system. These spectra clearly demonstrate that the value of ^1J(Pt,P) for P trans to Cl(~4200 Hz) is far

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(12) T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 439 (1976).

Table V. $^{31}P\{^1H\}$ NMR Spectral Data of $[PtXY(\overset{\frown}{L\ L})]$ Complexes[a]

complex	δ(P)	^1J(Pt,P), Hz
[$PtCl_2$(dppm)]	−64.2	3084
[$PtCl_2$(dppe)]	40.8	3616
[$PtCl_2$(appe)]	42.5	3562
[$PtPh_2$(dppm)]	−38.1	1389
[$PtPh_2$(dppe)]	40.9	1687
[$PtPh_2$(appe)]	44.4	1704
[PtClPh(dppm)]	−43.2,[b] −40.3[c]	3909,[b] 1213[c]
[PtClPh(dppe)]	36.9,[b] 38.7[c]	4192,[b] 1638[c]
[PtClPh(appe)]	38.0	4219
[PtCl(COPh)(dppe)]	30.0,[b] 31.7[c]	4319,[b] 1494[c]
[PtCl(COPh)(appe)]	30.8	4382

[a] Spectra were obtained for $CDCl_3$ solutions. [b] For P trans to Cl. [c] For P trans to R.

Table VI. $^{31}P\{^1H\}$ NMR Spectral Data of $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2(R)_2]$[Cl] Complexes

R	δ(P)	^1J(Pt,P), Hz	^3J(Pt,P), Hz	J(P,P), Hz
Ph[a]	8.4	3037	+39	29
COPh[a]	5.9	3354	+48	28
COPh[b]	6.4	3355	+49	27

[a] Spectra were obtained for $CDCl_3$ solutions. [b] Spectrum obtained for MeCN-d_3 solution.

larger than for P trans to R (~1500 Hz), and this fact, useful as a probe in geometry determinations, prompted us to investigate the reactions of appe with the [PtClR(cod)] complexes, where a mononuclear product may be of two possible geometries, I and II. The $^{31}P\{^1H\}$ NMR spectra (Table V)

of the products demonstrated that a single mononuclear product was formed in each case of geometry I (^1J(Pt,P) = 4219 Hz for R = Ph, 4382 Hz for R = COPh). These results demonstrate that the possible product with two high trans-influence ligands[11] arranged in a mutually trans geometry (II) is disfavored, a finding substantiated by previous work on the geometry of cationic $[PtCl(PR_3)(appe)]^+$ complexes.[13]

The reactions of [PtClR(cod)] with dppm yielded a single product for R = COPh but a mixture of two species for R = Ph. The $^{31}P\{^1H\}$ NMR spectrum of the aroyl complex (Table VI) was typical of the AA′A″A‴XX′ spin system[14] indicating that a dinuclear dppm-bridged product was formed.[15] The product was shown to be ionic by conductivity measurements and by reaction with silver(I) triflate, which produced a silver chloride precipitate, but did not alter the $^{31}P\{^1H\}$ NMR spectrum indicating that anion exchange had occurred. The product is accordingly formulated as the cationic "A-frame" complex $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2(COPh)_2][Cl]$ in agreement with recent results of Puddephatt on the analogous methyl complex.[16] The aryl analogue yielded both the ionic product $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2Ph_2][Cl]$ (Table VI) and the mononuclear complex [PtClPh(dppm)] (Table V) in a ratio of ~4:1.

These results show that the molecularity of the products is sensitive to the chelate bite of the bidentate ligand, while the geometry of the mononuclear species is determined by the trans influence[11] of both the neutral and anionic groups. A preliminary account of the reactions of dppm has been reported.[17]

Studies Related to Carbonyl Insertion. Our interest in insertion processes at platinum(II), particularly carbonyl insertion[1] in relation to platinum-catalyzed hydroformylation systems,[18] led us to compare the relative reactivities of $[PtPh_2L_2]$ (L = $PMePh_2$, PPh_3; L_2 = dppm, dppe, appe) and $[PtPhClL_2]$ =L = $PMePh_2$, PPh_3; L_2 = dppe, appe) toward carbon monoxide insertion into the platinum–aryl bond under ambient conditions. Previous attempts[19] to study carbonyl insertion reactions of $[PtPh_2L_2]$ complexes have been largely unsuccessful.

Initially we observed that $[PtPh_2(cod)]$ reacts with carbon monoxide to form $[PtPh_2(CO)_2]$[1] and that addition of a second nucleophile, either dppe or 2 equiv of $PMePh_2$, did not induce insertion but merely displaced the carbonyl ligands. Attempts to insert carbon monoxide into the platinum–carbon σ bonds of $[PtClPhL_2]$ (L_2 = dppe, appe) and $[PtPh_2L_2]$ (L_2 = dppm, dppe, appe) by stirring CO-saturated solutions of the complexes under an atmosphere of CO for 72 h were unsuccessful, and $^{31}P\{^1H\}$ NMR spectroscopy showed that no observable reaction had occurred. Identical treatment of $[PtClPhL_2]$ (L = $PMePh_2$, PPh_3) led to the formation of the insertion products *trans*-$[PtCl(COPh)L_2]$, identified by their $^{31}P\{^1H\}$ NMR spectra (Table I). Examination by $^{31}P\{^1H\}$ NMR of the reaction mixtures formed by stirring solutions of the complexes $[PtPh_2L_2]$ (L = $PMePh_2$, PPh_3) under carbon monoxide showed the presence of free phosphine[20] and the formation of a new species (Table III) with a value of ^1J(Pt,P) ≃ 1600 Hz, representing a decrease in the coupling constant of ~150 Hz from the diaryl precursors. The solution infrared spectra showed bands assigned to terminal carbonyl groups (Table IV), suggesting that phosphine displacement by carbon monoxide had occurred. The lowering in value of ^1J(Pt,P) in the $^{31}P\{^1H\}$ NMR spectra, compared with the diaryl complexes, suggested that the new species may have phosphine and carbonyl moieties coordinated in a mutually cis geometry.[21] In order to elucidate the structure of these species in solution unequivocally, we performed analogous reactions with 90% labeled ^{13}CO and obtained the $^{13}C\{^1H\}$ NMR spectra. The spectra (Table III) show that a single carbonyl-containing species is formed in each case. The low values of ^1J(Pt,C) suggest that the carbonyl moiety is trans to a group of high trans influence,[11] while the multiplicity and magnitude of ^2J(P,C) demonstrates that a single phosphine is also coordinated to platinum and is cis with respect to the carbonyl group.[22] In these systems it is thus concluded that phosphine displacement occurs to yield the complexes *cis*-$[PtPh_2(CO)(PR_3)]$ (PR_3 = PPh_3, $PMePh_2$). Although the system appears ideally suited to promote insertion,[8] as the carbonyl and organo groups are mutually cis, and a good nucleophile, in the form of free phosphine, is present in solution, no further reaction to yield an aroyl complex was observed. In fact, the phosphine displacement is itself a reversible process, and removing the solvent from the reaction system in vacuo caused displacement of carbon monoxide and

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(20) In $CDCl_3$ solution δ(P) = 29.5 ($PMePh_2$) and δ(P) = −5.2 (PPh_3).
(21) For example, values of ^1J(Pt,P) for P trans to Cl vary with the cis ligand in the complexes *cis*-$[PtCl_2(PMePh_2)_2]$ (^1J(Pt,P) = 3621 Hz) and *cis*-$[PtCl_2(CO)(PMePh_2)]$ (^1J(Pt,P) = 2946 Hz).
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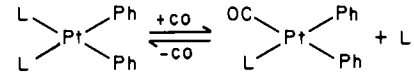
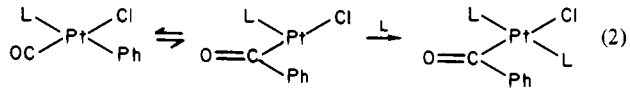
regeneration of the diaryl complex (eq 1).



$$L = PPh_2Me, PPh_3 \qquad (1)$$

The mechanism of carbonyl insertion has been investigated in depth[8,9,23–25] for complexes of the type *trans*-[PtPhClL$_2$] (L = tertiary phosphine, arsine, etc.) and shown to proceed in certain cases via initial phosphine displacement followed by phenyl migration to yield a 14-electron "T-shaped" intermediate. Reaction of the unsaturated intermediate with the displaced phosphine thus yields the product *trans*-[PtCl(COPh)L$_2$] (eq 2). The phenyl migration reaction does not



(2)

occur with the diphenylplatinum complexes; the geometry of the "T-shaped" intermediate formed by such a migration would require the phenyl and benzoyl groups to be mutually trans, a disfavored arrangement of such high trans-influence ligands.[11] The reaction thus proceeds only as far as the *cis*-[PtPh$_2$(PR$_3$)(CO)] complex, and no insertion products are formed. The lack of insertion observed with complexes of bidentate ligands can be attributed to the prevention of the initial step in the insertion process, phosphine displacement by carbon monoxide, because of the chelating ability of these ligands. Interestingly, we have recently observed[18] that platinum(II) complexes of monodentate phosphines show high catalytic activity in the homogeneous hydroformylation of olefins, in which carbonyl insertion is believed to be a fundamental step, compared with the reported activity of platinum(II) complexes of chelating phosphines.[26] All such systems, however, require the use of additives such as tin(II) halides to obtain high activity. A subsequent paper[27] will concern the effects of tin(II) halides on the stoichiometric carbonylation and decarbonylation reactions of platinum(II) phenyl derivatives.

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Registry No. *cis*-[PtCl$_2$(PMePh$_2$)$_2$], 16633-72-0; *trans*-[PtCl$_2$(PCy$_3$)$_2$], 60158-99-8; *trans*-[PtClPh(PMePh$_2$)$_2$], 60772-01-2; *trans*-[PtClPh(PCy$_3$)$_2$], 60750-86-9; *trans*-{PtClPh[P(*o*-tolyl)$_3$]$_2$}, 78064-13-8; *trans*-[PtCl(COPh)(PMePh$_2$)$_2$], 60742-07-6; *trans*-[PtCl(COPh)(PCy$_3$)$_2$], 78064-14-9; *cis*-[PtPh$_2$(PMePh$_2$)$_2$], 51538-76-2; *trans*-[PtCl(COPh)(PPh$_3$)$_2$], 18421-48-2; Pt$_2$(μ-Cl)$_2$Cl$_2$(PCy$_3$)$_2$, 78147-52-1; Pt$_2$(μ-Cl)$_2$Ph$_2$(PCy$_3$)$_2$, 78064-15-0; Pt$_2$(μ-Cl)$_2$Ph$_2$[P(*o*-tolyl)$_3$]$_2$ (*sym* isomer), 78064-16-1; Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PCy$_3$)$_2$, 78147-53-2; PtClPh(CO)(PCy$_3$), 78147-54-3; PtClPh(CO)[P(*o*-tolyl)$_3$], 74139-73-4; *cis*-[PtPh$_2$(CO)(PMePh$_2$)], 78088-86-5; *cis*-[PtPh$_2$(CO)(PPh$_3$)], 78064-17-2; PtCl$_2$(dppm), 52595-94-5; PtCl$_2$(dppe), 14647-25-7; PtCl$_2$(appe), 14647-20-2; PtPh$_2$(dppm), 52621-11-1; PtPh$_2$(dppe), 52595-92-3; PtPh$_2$(appe), 78064-18-3; PtClPh(dppm), 78064-19-4; PtClPh(dppe), 27711-51-9; PtClPh(appe), 78064-12-7; PtCl(COPh)(dppe), 78064-20-7; PtCl(COPh)(appe), 78064-11-6; [Pt$_2$(μ-Cl)(μ-dppm)$_2$(Ph)$_2$]Cl, 78064-21-8; [Pt$_2$(μ-Cl)(μ-dppm)$_2$(COPh)$_2$]Cl, 78064-22-9; PtCl$_2$(cod), 12080-32-9; PtClPh(cod), 51177-65-2; PtCl(COPh)(cod), 76705-02-7; PtPh$_2$(cod), 12277-88-2; PtPh$_2$(PPh$_3$)$_2$, 50988-66-4; PtClPh(PPh$_3$)$_2$, 16744-25-5; Pt$_2$(μ-Cl)$_2$Ph$_2$[P(*o*-tolyl)$_3$]$_2$ (*unsym* isomer), 78147-55-4.

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Preparation, Characterization, and Some Reactions of Tri-*tert*-butylarsine Complexes of Platinum(II) and Palladium(II) Chlorides

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As(*t*-Bu)$_3$ reacts with platinum(II) chlorides to afford either *trans*-PtCl$_2$[As(*t*-Bu)$_3$]$_2$ or the dinuclear complex Pt$_2$(μ-Cl)$_2$Cl$_2$[As(*t*-Bu)$_3$]$_2$. With palladium(II) chloride, however, only the dinuclear complex Pd$_2$(μ-Cl)$_2$Cl$_2$[As(*t*-Bu)$_3$]$_2$ is formed even in the presence of excess As(*t*-Bu)$_3$. These complexes undergo substitution and/or bridge-cleavage reactions with CO, py, AsPh$_3$, Cl$^-$, or tertiary phosphines.

Introduction

It has now been well recognized that the properties of the metal complexes of phosphorus donor ligands[2–4] are markedly affected by the electronic and the steric[4] effects of the substituents on phosphorus. However, investigations on the electronic and/or the steric effects in metal complexes of arsenic or antimony donor ligands[2] have been lacking. As part of a systematic study of the steric effects in platinum metal complexes of tertiary phosphines, arsines, and stibines, platinum and palladium complexes of tri-*tert*-butylphosphine,[5–7] -arsine,[8] and -stibine[9] have been investigated in this laboratory. Recently we reported on the stabilization of platinum(II) and palladium(II) hydride complexes[8] by tri-*tert*-butylarsine. Preparation, characterization, and some reactions of tri-

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