Reaction of $(np_3)Co(CH_3)$ (7) with H_2CO. A mixture of 7 (0.37 g, 0.5 mmol) and paraformaldehyde (0.1 g) in THF (20 mL) was heated under reflux for 2 h to give a yellow brown solution. Addition of butanol (30 mL) gave yellow crystals of 5 in 60% yield. The red carbonyl 6 also was obtained by adding $NaBPh_4$.

Reaction of $(np_3)CoH$ with CH_3CHO. Acetaldehyde (3 mL) was added to solution of 2 (0.36 g, 0.5 mmol) in THF (50 mL). The color of the solution changed rapidly from orange to yellow-brown and yellow–ochre crystals of $(np_3)Co(COCH_3)$ (8) began to separate after 10 min. After the mixture was left standing overnight at room temperature, the precipitation of the crystals was complete. They were collected and washed with THF and *n*-pentane; yield 70%. The same reaction can be carried out in benzene or DMF. Anal. Calcd for $C_{44}H_{45}CoNOP_3$: C, 69.93; H, 6.00; Co, 7.79; N, 1.85. Found: C, 69.67; H, 5.93; Co, 7.78; N, 1.81.

Reaction of $(np_3)CoH$ with C_2H_5CHO. Yellow crystals of $(np_3)Co(COC_2H_5)$ were obtained in 70% yield from 2 and propionaldehyde by a procedure analogous to the one above. Anal. Calcd for $C_{45}H_{47}CoNOP_3$: C, 70.21; H, 6.15; Co, 7.65; N, 1.82. Found: C, 70.09; H, 6.06; Co, 7.59; N, 1.85.

Reaction of $(np_3)Co(COCH_3)$ (18) with $LiHBEt_3$. A THF (20 mL) suspension of 8 (0.38 g, 0.5 mml) was treated with 0.75 mL of $LiHBEt_3$ (1 M in THF) at 0 °C. A fast reaction took place producing a red-orange solution. On addition of butanol (30 mL) orange crystals of 2 were formed, which were filtered and washed with ethanol and petroleum ether; yield 60%.

Reaction of $(np_3)Co(COCH_3)$ with MeLi or MeMgI. To a suspension of 8 (0.38 g, 0.5 mmol) in THF (20 mL) was added a 5% solution of MeLi (or MeMgI) in diethyl ether (0.4 mL) at room temperature which caused the solid to dissolve to give an orange solution. Addition of butanol (30 mL) gave red crystals of 7; yield 60%. Alternatively, when $NaBPh_4$ (0.34 g, 1 mmol) in butanol (20 mL) was added to the reaction mixture, red crystals of $[(np_3)Co(CH_3)]BPh_4$ were obtained in 60% yield.

Reaction of $(np_3)Co(COCH_3)$ with NaOMe. A 1 M solution of sodium methoxide in methanol (0.6 mL) was added to a suspension of 8 (0.38 g, 0.5 mmol) in THF (40 mL), and the resulting mixture was stirred magnetically for 2 days. During this time the solid dissolved to give a red solution. On addition of butanol (30 mL) red crystals of 2 were obtained in 5% yield. Addition of $NaBPh_4$ (0.34 g, 1 mmol) to the mother liquor led to the precipitation of red crystals of $[(np_3)Co(CO)]BPh_4$; yield 50%.

Reaction of $(np_3)Co(COCH_3)$ with HBF_4 or $MeOSO_2CF_3$. A THF (30 mL) suspension of 8 (0.38 g, 0.5 mmol) was reacted with a slight excess of HBF_4/diethyl ether (or $MeOSO_2CF_3$) at 0 °C. Within a few minutes a yellow-green solution was produced from which green crystals of $[(np_3)Co]BF_4$ (or SO_3CF_3) precipitated on standing; yield 90%.

Acknowledgment. This work was supported by a grant from the CNR program "Chimica Fine e Secondaria".

Registry No. 1, 97135-31-4; 2, 97135-32-5; 3, 97135-33-6; 4, 88440-32-8; 5, 97135-35-8; 6, 97135-37-0; 7, 97135-38-1; 8, 97149-88-7; $(np_3)Co(COC_2H_5)$, 97135-39-2; $[(np_3)CO(CH_3)]BPh_4$, 97135-41-6; $[(np_3)Co]BF_4$, 97135-43-8; $[(np_3)Co]SO_3CF_3$, 97149-89-8; formaldehyde, 50-00-0; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6.

Carbonylation of Phenylplatinum(II) Complexes Containing Bidentate Ligands

Gordon K. Anderson* and Gregg J. Lumetta

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Received December 27, 1984

A series of complexes of the type $[PtClPh(\overset{\frown}{PY})]$ ($\overset{\frown}{PY}$ = 1,2-bis(diphenylphosphino)ethane (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (appe), 1,3-bis(diphenylphosphino)propane (dppp), 1-(diphenylphosphino)-2-(methylthio)ethane (PC_2S), or 1-(diphenylphosphino)-2-(dimethylamino)ethane (PC_2N)) has been prepared and the carbonylation reactions of these complexes investigated. The corresponding benzoyl complexes have been generated by an alternative route. No reaction of $[PtClPh(\overset{\frown}{PY})]$ with CO takes place when $\overset{\frown}{PY}$ = dppe or appe, but carbonylation proceeds smoothly, albeit slowly, when $\overset{\frown}{PY}$ = dppp, PC_2S, or PC_2N. The reaction is most rapid for the dppp complex. These results are rationalized in terms of both dissociative and nondissociative reaction pathways.

Introduction

The carbonylation of organoplatinum(II) complexes of the type *trans*-$[PtXRL_2]$ (X = halide; R = alkyl or aryl; L = tertiary phosphine) has been extensively studied,[1] where the acyl or aroyl products obtained are also of trans geometry. The reaction has been shown[2,3] to proceed by two competing pathways; one involves organic group migration from the five-coordinate adduct $[PtXR(CO)L_2]$, whereas the second occurs by dissociation of L and organic group migration within the four-coordinate complex $[PtXR(CO)L]$ thus formed. The dissociative route is dominant for L = triarylphosphine, but phosphine dissociation does not occur during the carbonylation of *trans*-$[PtClPh(PMePh_2)_2]$.[3]

The involvement of cis complexes in the carbonylation scheme has been suggested,[1] but the ready isomerization of complexes of the type *cis*-$[PtXRL_2]$ renders impractical the study of their reactions with carbon monoxide. We have previously noted the lack of reactivity of [PtClPh(dppe)] and [PtClPh(appe)] (dppe = 1,2-bis(diphenylphosphino)ethane; appe = 1-(diphenylphosphino)-2-(diphenylarsino)ethane) toward carbon monoxide,[4] although their reactions were only monitored in solution by $^{31}P\{^1H\}$ NMR spectroscopy. We report here the preparation of a series of complexes of the type $[PtClPh(\overset{\frown}{PY})]$ ($\overset{\frown}{PY}$ = dppe, appe, dppp, $Ph_2PCH_2CH_2SMe$, $Ph_2PCH_2CH_2NMe_2$),

---

[1] Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

[2] Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

[3] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans*, **1980**, 1434.

[4] Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 3607.

0276-7333/85/2304-1542$01.50/0

Table I. Analytical Data for the Complexes [PtClPh($\overset{\frown}{PY}$)] and [PtCl(COPh)($\overset{\frown}{PY}$)][a]

complex	found (calcd) C	found (calcd) H
[PtClPh(dppe)]	54.13 (54.44)	3.85 (4.14)
[PtClPh(appe)]	50.93 (51.25)	3.94 (3.90)
[PtClPh(dppp)]	54.79 (55.04)	4.09 (4.34)
[PtClPh(PC_2S)]	44.12 (44.41)	3.75 (3.90)
[PtClPh(PC_2N)]	46.66 (46.77)	4.49 (4.46)
[PtCl(COPh)(dppe)]	53.71 (53.99)	3.98 (3.98)
[PtCl(COPh)(appe)]	50.76 (50.94)	3.51 (3.76)
[PtCl(COPh)(dppp)]	54.36 (54.59)	4.35 (4.18)
[PtCl(COPh)(PC_2S)]	44.10 (44.34)	3.87 (3.72)
[PtCl(COPh)(PC_2N)]	46.36 (46.59)	4.33 (4.25)

[a] The complexes decompose at temperatures in excess of 200 °C.

where the complex is constrained in a cis geometry by the chelating ligand, and the reactions of these complexes with carbon monoxide.

Experimental Section

The $^{31}P\{^1H\}$ NMR spectra were recorded at 40.25 MHz on a JEOL FX-100 Fourier transform NMR spectrometer. The chemical shifts are relative to external 85% H_3PO_4, more positive shifts representing deshielding. Spectra were obtained for $CDCl_3$ solutions at ambient temperature. Infrared spectra were recorded for KBr pellets by using a Perkin-Elmer 337 spectrophotometer. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

1,2-Bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and 1-(diphenylphosphino)-2-(diphenylarsino)ethane (appe) were obtained from Alfa Products and used without further purification. The preparations of $Ph_2PCH_2CH_2SMe$ (PC_2S) and $Ph_2PCH_2CH_2NMe_2$(PC_2N) have been described previously.[5] [$PtCl_2$ (cod)][6] and [PtClPh(cod)][7] were prepared according to established procedures. The following reactions were carried out under a nitrogen atmosphere, except where indicated.

Preparation of [PtClPh(dppe)]. A chloroform solution of [PtClPh(cod)] (0.69 g, 1.65 mmol) was added to a solution of dppe (0.66 g, 1.65 mmol) in chloroform, and the mixture was stirred for 1.5 h. The almost colorless solution was concentrated to ca. 2 mL on a rotary evaporator, and ether was added to precipitate the product. The solid was filtered, washed with ether, and dried by suction to give [PtClPh(dppe)] as a white powder (0.98 g, 86%).

The complexes [PtClPh($\overset{\frown}{PY}$)] ($\overset{\frown}{PY}$ = appe, dppp, PC_2S, or PC_2N) were prepared similarly.

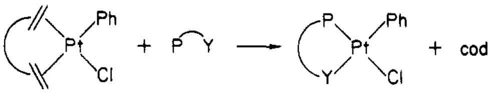
Preparation of [PtCl(COPh)(cod)]. The procedure used was similar to that previously reported,[8] with some minor modifications. [PtClPh(cod)] (1.75 g, 4.20 mmol) was dissolved in dichloromethane (10 mL) in a large Pyrex reaction vessel. The latter was connected to a vacuum line, and the solution was degassed by means of three freeze–pump–thaw cycles. Carbon monoxide (1 atm) was then introduced. After being stirred overnight, the black reaction mixture was treated with activated charcoal and filtered to give a greenish solution. This was reduced to ca. 5 mL, and ether was added to cause precipitation. The product was filtered, washed with ether, and dried by suction to leave [PtCl(COPh)(cod)] as an off-white solid (1.55 g, 83%); ν(CO) 1635 cm^{-1}.

Preparation of [PtCl(COPh)(dppe)]. A chloroform solution of [PtCl(COPh)(cod)] (0.56 g, 1.26 mmol) and dppe (0.50 g, 1.26 mmol) was stirred for 1.5 h. The solution was concentrated to 10 mL on a rotary evaporator, and ether was added slowly until precipitation commenced. This initial precipitate (apparently [$PtCl_2$(dppe)]) was removed by filtration through a Buchner funnel packed with activated charcoal. The filtrate was concentrated to 5 mL, and ether addition caused precipitation of the product. The latter was filtered, washed with ether, and dried by suction to give [PtCl(COPh)(dppe)] as a yellow solid (0.51 g, 55%).

Carbonylation of the [PtClPh($\overset{\frown}{PY}$)] Complexes. The [PtClPh($\overset{\frown}{PY}$)] complexes were dissolved in chloroform, degassed, and treated with carbon monoxide in the same manner as described for the preparation of [PtCl(COPh)(cod)].

Results and Discussion

When a chloroform solution of [PtClPh(cod)] is treated with 1 molar equiv of one of the bidentate ligands, $\overset{\frown}{PY}$, displacement of 1,5-cyclooctadiene occurs according to eq 1. Where the bidentate ligand is dppe or dppp, the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of nonequivalent phosphorus nuclei, that trans to Cl exhibiting a large one-bond platinum–phosphorus coupling constant, whereas the ^1J(Pt,P) values are 1640 and 1535 Hz for the P atom trans to Ph in [PtClPh(dppe)] and [PtClPh(dppp)], respectively. The dppp complex exhibits the expected spectrum for the ABX spin system with ^2J(P,P) = 24 Hz, but with [PtClPh(dppe)] the two-bond coupling is too small to be observed.



(1)

For appe, PC_2S, or PC_2N the complex [PtClPh($\overset{\frown}{PY}$)] could exist as either or both of two geometric isomers, but in each case only that isomer in which the diphenylphosphino group is trans to Cl is formed, as evidenced by the large ^1J(Pt,P) values. This is exactly what would be expected in terms of the relative trans influences of the ligating groups involved, namely, an arrangement in which the two highest trans influence ligands (Ph and P) are in mutually trans positions is unfavorable.[4,9] The formation of [PtClPh(PC_2N)] contrasts with the reaction of PC_2N with [$PtCl_2$(cod)], in which only [$PtCl(PC_2N)_2$]Cl is formed.[5]

The δ(P) values for the dppe, appe, PC_2S, and PC_2N complexes of the type [PtClPh($\overset{\frown}{PY}$)] are large and positive, such downfield shifts being typical of a phosphino group incorporated in a five-membered chelate ring.[10] In contrast, [PtClPh(dppp)] exhibits two resonances in its $^{31}P\{^1H\}$ NMR spectrum, both with slightly negative chemical shifts.

The complexes [PtClPh($\overset{\frown}{PY}$)] presented us with the possibility of investigating the carbonylation reaction as a function of the nature of the donor atom Y and the size of the chelate ring. (It was not possible to extend this series to include dppm, because this ligand causes formation of dimeric "A-frame" compounds of the form [$Pt_2(\mu\text{-}Cl)R_2(\mu\text{-dppm})_2$]Cl (R = Me, Ph, COPh).[11,12]) Since we have previously shown[8] that [PtCl(COPh)(cod)] may be generated by carbonylation of its phenyl analogue, we were able to prepare independently the expected products of the carbonylation reaction. Thus, treatment of a chloroform solution of [PtCl(COPh)(cod)] with the appropriate ligand provides [PtCl(COPh)($\overset{\frown}{PY}$)]. Each of these complexes is characterized by an intense band in the range 1609–1618 cm^{-1} in its infrared spectrum due to the aroyl moiety. The $^{31}P\{^1H\}$ NMR spectra of the benzoyl

---

(5) Anderson, G. K.; Kumar, R. *Inorg. Chem.* **1984**, *23*, 4064.

(6) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(7) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357.

(8) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 1636.

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

(10) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(11) Anderson, G. K.; Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *210*, 135.

(12) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374.

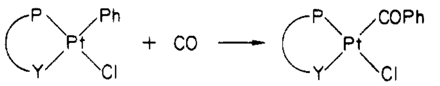
Table II. $^{31}P\{^1H\}$ **NMR and Infrared Spectroscopic Data for the Complexes [PtClPh(P⌒Y)] and [PtCl(COPh)(P⌒Y)]**

complex	δ(P)	^1J(Pt,P), Hz	ν(CO), cm^{-1}
[PtClPh(dppe)][a]	37.4[b]	4200	
	39.2[c]	1640	
[PtClPh(appe)]	38.3	4225	
[PtClPh(dppp)][d]	−0.3[b]	4110	
	−3.1[c]	1535	
[PtClPh(PC_2S)]	33.6	4445	
[PtClPh(PC_2N)]	22.4	4705	
[PtCl(COPh)(dppe)][a]	30.3[b]	4315	1609
	32.2[c]	1490	
[PtCl(COPh)(appe)]	31.1	4385	1618
[PtCl(COPh)(dppp)][e]	−6.1[b]	4275	1614
	−4.5[c]	1405	
[PtCl(COPh)(PC_2S)]	26.8	4600	1612
[PtCl(COPh)(PC_2N)]	18.8	4825	1616

[a] ^2J(P,P) not observed. [b] Trans to Cl. [c] Cis to Cl. [d] ^2J(P,P) = 24 Hz. [e] ^2J(P,P) = 29 Hz.

complexes are similar to those of their phenyl analogues, the complexes with appe, PC_2S, or PC_2N existing only as the isomer with the diphenylphosphino moiety trans to Cl. The ^1J(Pt,P) values for the P atom trans to COPh in [PtCl(COPh)(dppe)] and [PtCl(COPh)(dppp)] are smaller than those for the corresponding phenyl compounds, indicating that the aroyl group has a higher trans influence.

The carbonylation reactions were carried out by stirring chloroform solutions of the phenylplatinum(II) complexes under an atmosphere of carbon monoxide. As has been noted previously,[4] the dppe and appe complexes are unreactive toward CO, and no change in the $^{31}P\{^1H\}$ NMR spectrum could be detected in either case after stirring under a blanket of CO for 72 h at ambient temperature. The complexes [PtClPh(P⌒Y)] (P⌒Y = dppp, PC_2S, PC_2N) do react with CO under these conditions, according to eq 2, although the reactions are slow. In the case of [PtClPh(dppp)] the carbonylation reaction requires 48 h to reach completion, whereas the reaction of [PtClPh(PC_2S)] with CO is incomplete even after 6 days. Carbonylation of the PC_2N complex is very slow; after 3 days only a small amount of [PtCl(COPh)(PC_2N)] is detected in the $^{31}P\{^1H\}$ NMR spectrum, although the ν(CO) band is quite evident in the infrared spectrum. In each case the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of the phenyl and benzoyl complexes only, and solution infrared studies do not reveal the presence of intermediate species containing terminal carbonyls.[13] Although the reactions are slow, a qualitative order of reactivity of the complexes [PtClPh(P⌒Y)] toward CO is as follows:

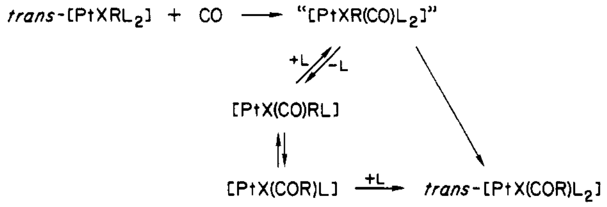


(2)

$$\text{dppp} > PC_2S > PC_2N >> \text{dppe, appe}$$

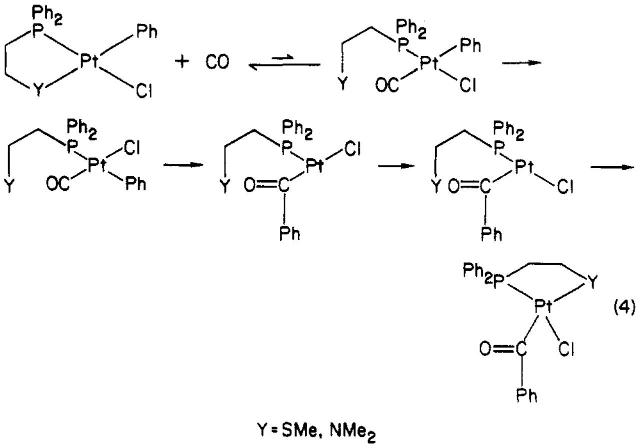
Carbonylation of complexes of the type *trans*-[$PtXRL_2$] is also slow under these conditions.[2,3]

As mentioned earlier, the reaction of *trans*-[$PtXRL_2$] with CO proceeds by two competing pathways, as shown in eq 3.[2] One pathway involves carbonyl insertion[14] within the five-coordinate intermediate,[15] whereas the other occurs by phosphine dissociation. It has been shown[16] that carbonyl insertion only occurs from one of the three possible isomers of [PtXR(CO)L] (that in which L and R occupy mutually trans positions), and the dissociative route for carbonylation of *trans*-[$PtXRL_2$] necessitates an isomerization step before carbonyl insertion can occur.[3] Such isomerizations are much faster when L = PPh_3 than when L = $PMePh_2$, an observation which is consistent with an isomerization mechanism involving L dissociation.[15] In the case of the carbonylation of *trans*-[$PtClPh(PMePh_2)_2$], which proceeds to completion within 72 h,[4] no phosphine dissociation takes place[3] with the more nucleophilic ligand.



(3)

Let us see how these observations relate to the carbonylation of [PtClPh(P⌒Y)]. In comparing the relative reactivities of the complexes containing a five-membered chelate ring, we find the rate of aroyl product formation to decrease in the order PC_2S > PC_2N >> dppe, appe. The lack of reactivity of the dppe and appe complexes toward carbonylation may be explained in terms of the relative difficulty with which CO might displace a diphenylphosphino or diphenylarsino group, particularly when that group is part of a chelating ligand. Displacement of the thioether or amine function should occur more readily, because these moieties are less nucleophilic toward platinum(II) than are tertiary phosphines or arsines. A suggested reaction mechanism is depicted in eq 4. Since



(4)

species containing terminal carbonyls are not detected,[13] the initial equilibrium must lie to the left, as may be expected when the moiety to be displaced is part of a five-membered chelate ring. In keeping with the observed rate of isomerization of [$PtClPh(CO)(PMePh_2)$)],[16] the isomerization step is expected to be slow but, once formed, the isomer with P and Ph in mutually trans positions may rapidly undergo carbonyl insertion, a process which may be facilitated by the close proximity of the incoming thioether or amine group. The overall carbonylation process is slow, however, owing to the unfavorable equilibrium position for the initial step. It is not presently understood why the reaction of [PtClPh(PC_2S)] with CO

---

(13) The product of the reaction of [PtClPh(PC_2N)] with CO exhibited a very weak band at ca. 2100 cm^{-1} in its infrared spectrum, which is likely to be due to a species containing a terminal CO ligand but, on redissolving in chloroform, no corresponding signal could be detected in the $^{31}P\{^1H\}$ NMR spectrum.

(14) The term "insertion" is used to indicate the result of the overall change; no mechanistic significance should be attached.

(15) These have been shown[3] in certain instances to be ionic or ion-paired species.

(16) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246.

is faster than that of its PC_2N analogue.

Two possible explanations would appear to exist for the reactivity of [PtClPh(dppp)] towards CO. Assuming a large $^1J(Pt,P)$ value to be indicative of a strong Pt–P bond,[17] the smaller one-bond coupling constants in [PtClPh(dppp)], when compared with its dppe analogue, would indicate slightly weaker Pt–P bonds which ought to be more susceptible to cleavage upon CO addition. In general, six-membered chelate rings in such systems are inherently less thermodynamically stable than their five-membered counterparts. Thus, displacement of the diphenylphosphino moiety by CO could possibly occur more readily with dppp than with dppe, and a reaction mechanism similar to that shown in eq 4 might be envisioned.

Of the complexes studied the carbonylation of [PtClPh(dppp)] is most facile, and it is unlikely perhaps that the Pt–P bond trans to Ph in this complex should be more easily ruptured by CO than the Pt–S or Pt–N bond in [PtClPh($\overset{\frown}{P\;Y}$)] ($\overset{\frown}{P\;Y}$ = PC_2S, PC_2N), due to the inherent strength of Pt–P bonds. Thus, it is possible that the reactivity of the dppp complex is too great to be accounted for in terms of the dissociative pathway. An alternative explanation might be that the greater flexibility of the dppp ligand could facilitate carbonyl insertion within a five coordinate species. It was noted above that carbonylation of *trans*-[$PtClPh(PMePh_2)_2$] proceeds without phosphine dissociation,[3] and each end of the dppp (or dppe) ligand closely resembles $PMePh_2$. Whereas the coordinated dppe ligand is relatively inflexible, which may prevent the five-coordinate species from adopting the conformation necessary for carbonyl insertion, the dppp ligand may be able to span the requisite sites in the distorted trigonal-bipyramidal or square-pyramidal species which undergoes carbonyl insertion.

In order to try to distinguish between these two possibilities, we have carried out the reaction of [PtClPh(dppp)] with CO in the presence of elemental sulfur.[18] After a chloroform solution of the complex was stirred with excess sulfur under a CO atmosphere for 48 h, the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of [PtClPh(dppp)] and [PtCl(COPh)(dppp)] only. Stirring a chloroform solution of dppp with excess sulfur for 20 h results in quantitative conversion to $Ph_2P(S)(CH_2)_3P(S)Ph_2$, as evidenced by a single resonance at δ(P) 41.4 in the $^{31}P\{^1H\}$ NMR spectrum. We interpret these results to mean that dppp (or one end thereof) does not dissociate during the carbonylation of [PtClPh(dppp)], thus favoring the idea of a distorted five-coordinate species within which carbonyl insertion occurs as the explanation of the reactivity toward CO of the dppp complex. (It is possible, however, that one end of the dppp ligand dissociates but recoordinates to platinum before reaction with sulfur can occur.)

The reverse reaction, namely, decarbonylation, has also been investigated. When chloroform solutions of [PtCl(COPh)(dppe)] or [PtCl(COPh)(appe)] are refluxed for several days, no decarbonylation occurs. With [PtCl(COPh)($\overset{\frown}{P\;Y}$)] ($\overset{\frown}{P\;Y}$ = dppp, PC_2S, PC_2N) decarbonylation does take place under these conditions to yield [PtClPh($\overset{\frown}{P\;Y}$)], but the reactions are complicated by the formation of significant amounts of [$PtCl_2(\overset{\frown}{P\;Y})$]. The latter may arise by disproportionation of the platinum(II) complexes, although the expected [$PtPh_2(\overset{\frown}{P\;Y})$] species are not detected, or by reaction with the solvent. The insolubility of the complexes in nonhalogenated solvents has so far precluded differentiation between these two possibilities.

Acknowledgment. We thank Johnson Matthey for a generous loan of platinum salts. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and thanks are expressed to Research Corp. and the University of Missouri Weldon Spring Fund for support of this work.

Registry No. dppe, 1663-45-2; appe, 23582-06-1; dppp, 6737-42-4; PC_2S, 20859-51-2; PC_2N, 29679-67-2; [PtClPh(dppe)], 27711-51-9; [PtClPh(appe)], 96806-43-8; [PtClPh(dppp)], 96806-44-9; [$PtClPh(PC_2S)$], 96806-45-0; [$PtClPh(PC_2N)$], 96806-46-1; [PtCl(COPh)(dppe)], 78064-20-7; [PtCl(COPh)(appe)], 96806-47-2; [PtCl(COPh)(dppp)], 96806-48-3; [$PtCl(COPh)(PC_2S)$], 96806-49-4; [$PtCl(COPh)(PC_2N)$], 96806-50-7; [$PtCl_2$(dppe)], 14647-25-7; [$PtCl_2$(dppp)], 59329-00-9; [$PtCl_2(PC_2S)$], 92763-60-5; [$PtCl_2(PC_2N)$], 96806-51-8; [PtClPh(cod)], 51177-65-2; [PtCl(COPh)(cod)], 76705-02-7; $Ph_2P(S)(CH_2)_3P(S)Ph$, 61894-25-5.

---

[17] Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

[18] This method was employed to show that carbonylation of *trans*-[$PtClPh(PPh_3)_2$] involves phosphine dissociation, as evidenced by the formation of Ph_3PS, whereas that of *trans*-[$PtClPh(PMePh_2)_2$] apparently does not.[3]