it is often experimentally impossible to measure both rate and equilibrium constants. However, for reaction 1 this was possible in some cases, as shown in Figures 3 and 4. Figure 4, which includes diphos and triarylphosphine nucleophiles, has a slope of 0.38, which compares favorably with that derived from Figure 3, $\partial \log k_1/\partial \log K_{eq} = \rho_1/\rho_{eq} = 0.36$. This suggests that bond formation and sp^2 to sp^3 rehybridization is approximately one-third complete in the transition state. This view is supported by the similarity noted above of the Brønsted and Hammett slopes for reaction 1 and S_N2 attack on the sp^3 carbon in C_2H_5I. A reexamination[24] of reaction 2 data also supports this view. However, recent work[5] on $P(C_6H_5)_3$ addition to $[(C_6H_6)_2M]^{2+}$ (M = Fe, Ru, Os) was interpreted in terms of a late transition state, so the intimate mechanism of reactions such as (1) and (2) remains somewhat uncertain. Phosphine addition to "organic" carbocations is being studied in this laboratory to determine the validity of Ritchie's N_+ equation[8] for phosphine nucleophiles and to provide a basis for comparison of coordinated π-hydrocarbon and carbocation electrophiles.

Acknowledgment. Discussions with Dr. S. D. Ittel and Professor J. O. Edwards are gratefully acknowledged. This work was supported in part by a grant from the National Science Foundation (No. CHE-8023964).

Registry No. I (L = CO), 43175-64-0; I (L = $P(C_6H_5)_3$), 43140-27-8; I (L = $As(C_6H_5)_3$), 43140-28-9; I (L = $Sb(C_6H_5)_3$), 43140-29-0; I (L = $P(p\text{-}C_6H_4Cl)_3$), 79200-93-4; I (L = $P(p\text{-}C_6H_4F)_3$), 79200-95-6; I (L = $P(p\text{-}C_6H_4Me)_3$), 79200-97-8; I (L = $P(p\text{-}C_6H_4OMe)_3$), 79200-99-0; I (L = $P(CH_2CH_2CN)_3$), 79201-01-7; II (L = CO, R = OBu), 79201-02-8; II (L = $P(C_6H_5)_3$, R = OBu), 79201-03-9; II (L = $As(C_6H_5)_3$, R = OBu), 79201-04-0; II (L = $Sb(C_6H_5)_3$, R = OBu), 79201-05-1; II (L = $P(p\text{-}C_6H_4Cl)_3$, R = OBu), 79215-36-4; II (L = $P(p\text{-}C_6H_4F)_3$, R = OBu), 79201-06-2; II (L = $P(p\text{-}C_6H_4Me)_3$, R = OBu), 79201-07-3; II (L = $P(p\text{-}C_6H_4OMe)_3$, R = OBu), 79201-08-4; II (L = $P(CH_2CH_2CN)_3$, R = OBu), 79215-37-5; II (L = CO, R = C_6H_5), 53062-44-5; II (L = $P(C_6H_5)_3$, R = C_6H_5), 79215-38-6; II (L = $P(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79215-39-7; II (L = $As(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79215-40-0; II (L = $Sb(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79201-09-5; II (L = $P(C_6H_5)_3$, R = Bu), 79215-41-1; II (L = $As(C_6H_5)_3$, R = Bu), 79215-42-2; II (L = $Sb(C_6H_5)_3$, R = Bu), 79215-43-3; II (L = $P(C_6H_5)_3$, PR_3 = diphos), 79215-44-4; II (L = $P(C_6H_5)_3$, R = $p\text{-}C_6H_4OMe$), 79215-45-5; II (L = CO, R = $p\text{-}C_6H_4Cl$), 67324-50-9; II (L = CO, R = CH_2CH_2CN), 79215-46-6.

---

[24] Kane-Maguire, L. A. P., personal communication.

Role of the Trichlorostannate Ligand in Homogeneous Catalysis. Mechanistic Studies of the Carbonylation of Phenylplatinum(II) Complexes

Gordon K. Anderson, Howard C. Clark,* and Julian A. Davies

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Received June 15, 1981

^{31}P NMR studies show that the complexes *trans*-$[Pt(SnCl_3)PhL_2]$ (L = PPh_3 or $PMePh_2$) react with carbon monoxide by an initial, rapid displacement of the trichlorostannate ligand to yield *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$. Further reaction to produce *trans*-$[Pt(SnCl_3)(COPh)L_2]$ occurs slowly in the absence of free CO (L = PPh_3 or $PMePh_2$) by initial nucleophilic attack of $SnCl_3^-$, but in the presence of excess CO an alternative route involving phosphine dissociation (L = PPh_3 only) operates. Comparative studies with other anions have led to a reinterpretation of the role of the trichlorostannate ligand in carbonylation and decarbonylation reactions of organoplatinum(II) complexes.

Introduction

The insertion of carbon monoxide into platinum–carbon bonds has been the subject of a number of studies,[1-6] and, in particular, the carbonylation of *trans*-$[PtXR^1(PR_3)_2]$ (X = halide; R^1 = alkyl or aryl) complexes has received considerable attention.[4-6] Kinetic studies have indicated that both associative and dissociative pathways are involved,[4] and the operation of the associative reaction path has been shown to be sensitive to the electronic character of the migrating organic group.[5] Several reaction intermediates have been identified, and the involvement of the $[PtXR^1(CO)(PR_3)]$ complexes, produced by phosphine dissociation, has been elucidated.[6]

Recently it has been shown[7] that decarbonylation of *trans*-$[PtCl(COR)(PPh_3)_2]$ (R = alkyl or aryl) complexes is promoted by tin(II) chloride, though the role of $SnCl_2$ was not well understood.

We have investigated the carbonylation of *trans*-$[Pt(SnCl_3)PhL_2]$ (L = PPh_3 or $PMePh_2$) and the reverse reaction with a view to discovering how the trichlorostannate ligand promotes the carbonyl insertion, or aryl migration, process.

Experimental Section

The complexes *trans*-$[PtClRL_2]$ (R = Ph or COPh; L = PPh_3 or $PMePh_2$) were prepared by displacement of 1,5-cyclooctadiene from the analogous platinum diolefin complexes.[8] The *trans*-

---

[1] Booth, G.; Chatt, J. *J. Chem. Soc. A* **1966**, 634.

[2] Glyde, R. W.; Mawby, R. J. *Inorg. Chem.* **1971**, *10*, 854. Wilson, C. J.; Green, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 421, 1293.

[3] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246; **1980**, 712.

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

[5] Sugita, N.; Minkiewicz, J. V.; Heck, R. F. *Inorg. Chem.* **1978**, *17*, 2809.

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

[7] Kubota, M.; Phillips, D. A.; Jacobsen, J. E. *J. Coord. Chem.* **1980**, *10*, 125.

0276-7333/82/2301-0064$01.25/0

Table I. NMR Data Obtained for $CDCl_3$ Solutions at 213 K (Unless Otherwise Stated)

complex	δP	${}^1J_{PtP}$/Hz	${}^2J_{SnP}$/Hz	other data
trans-$[PtClPh(PPh_3)_2]$[a]	24.2	3152		
trans-$[Pt(SnCl_3)Ph(PPh_3)_2]$	19.6	2837	234, 244	
trans-$[PtCl(COPh)(PPh_3)_2]$[a]	19.6	3384		
trans-$[Pt(SnCl_3)(COPh)(PPh_3)_2]$[b]	15.8	3037	278, 293	δC 218.8, ${}^1J_{PtC}$ = 883 Hz, ${}^2J_{PC}$ = 5 Hz
trans-$[PtPh(CO)(PPh_3)_2]^+$	15.4	2651		δC 177.8, ${}^1J_{PtC}$ = 958 Hz, ${}^2J_{PC}$ = 8 Hz; ν(CO) 2102 cm^{-1}
trans-$[PtClPh(PMePh_2)_2]$[a]	8.7	3010		
trans-$[Pt(SnCl_3)Ph(PMePh_2)_2]$	4.9	2642	239 (av)	
trans-$[PtCl(COPh)(PMePh_2)_2]$[a]	5.1	3215		
trans-$[Pt(SnCl_3)(COPh)(PMePh_2)_2]$	−0.2	2859	276, 286	
trans-$[PtPh(CO)(PMePh_2)_2]^+$	3.3	2554		ν(CO) 2103 cm^{-1}

[a] Spectrum recorded at ambient temperature. [b] A minor species with parameters δP 16.3, ${}^1J_{PtP}$ = 2837 Hz (no tin satellites), was also present and was probably an ion-paired complex.

$[PtR(SnCl_3)L_2]$ complexes were obtained by stirring chloroform solutions of the chloro species with excess tin(II) chloride and removing unreacted $SnCl_2 \cdot 2H_2O$ by filtration. Their NMR data are given in Table I.

${}^{31}P$ and ${}^{13}C$ NMR spectra were recorded on a Brüker WP-60 spectrometer operating in the FT mode. Spectra were recorded for $CDCl_3$ solutions unless otherwise stated, and ${}^{31}P$ and ${}^{13}C$ chemical shifts were measured in ppm to high frequency of external H_3PO_4 and internal Me_4Si, respectively.

Solution infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer, using NaCl cells of 0.1-mm pathlength.

***trans*-$[PtPh(CO)L_2]^+SnCl_3^-$ (L = PPh_3 or $PMePh_2$).** *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ (ca. 30 mg) was dissolved in $CDCl_3$ (2 cm^3), and the yellow solution was cooled to 213 K. Carbon monoxide was passed through the solution for 1 h, and the ${}^{31}P$ NMR spectrum showed the presence of *trans*-$[PtPh(CO)(PPh_3)_2]^+$ only (δP 15.4, ${}^1J_{PtP}$ = 2651 Hz).

The methyldiphenylphosphine complex was prepared similarly. The complex *trans*-$[PtPh({}^{13}CO)(PPh_3)_2]^+SnCl_3^-$ was obtained by stirring a $CDCl_3$ solution of *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ under an atmosphere of ${}^{13}CO$ at 213 K for 4 h (δP 15.4, ${}^1J_{PtP}$ = 2651 Hz, ${}^2J_{PC}$ = 8 Hz).

Treatment of *trans*-$[PtPh({}^{13}CO)(PPh_3)_2]^+SnCl_3^-$ with ${}^{12}CO$ at 213 K caused no reaction, as monitored by ${}^{31}P$ NMR spectroscopy, but at ambient temperature almost complete isotopic exchange was achieved after 3 min.

When nitrogen gas was passed through a solution of *trans*-$[PtPh(CO)(PPh_3)_2]^+SnCl_3^-$ at ambient temperature, loss of CO to yield *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ was almost complete in 20 min.

Solutions of *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$ (L = PPh_3 or $PMePh_2$) were allowed to warm to ambient temperature and were monitored periodically, after being cooled to 213 K to prevent further reaction, by ${}^{31}P$ NMR spectroscopy. Slow conversion to *trans*-$[Pt(SnCl_3)(COPh)L_2]$ took place (Table I). For an investigation of the possible involvement of phosphine dissociation, the solutions were stirred with excess sulfur while being warmed to ambient temperature, and unreacted sulfur was filtered off before the NMR spectrum was recorded. With L = PPh_3, a strong singlet at δP 42.5 indicated the presence of Ph_3PS.

Reactions of *trans*-$[PtPh(CO)L_2]^+SO_3CF_3^-$ (L = PPh_3 or $PMePh_2$) with Sodium Salts. The complexes *trans*-$[PtPh(CO)L_2]^+SO_3CF_3^-$ were obtained by reacting *trans*-$[PtClPhL_2]$ with $AgSO_3CF_3$ in chloroform while carbon monoxide was passed through the solution. Silver chloride was removed by filtration, and the solutions were shaken for several days with a number of sodium salts. The extent of reaction was monitored peridically by ${}^{31}P$ NMR spectroscopy, and the nature of the products were determined from their ${}^{31}P$ NMR and solution infrared characteristics (Table II). In the cases where X = OCOMe, the reactions were performed by using *trans*-$[PtPh({}^{13}CO)L_2]^+SO_3CF_3^-$, and the loss of ${}^2J_{PC}$ indicated that *trans*-$[Pt(OCOMe)PhL_2]$ was formed.

Carbonylation and Decarbonylation Reactions. A stream of carbon monoxide was passed through chloroform solutions of *trans*-$[PtXPhL_2]$ (L = PPh_3, X = Cl, I, $SnCl_3$; L = $PMePh_2$, X = Cl, $SnCl_3$) at ambient temperature, and the solutions were cooled to 213 K before recording their ${}^{31}P$ NMR spectra. The extent of carbonylation after certain times was thus determined, and the NMR parameters are presented in Table II.

Table II. Spectroscopic Data for the Products of the Reaction of *trans*-$[PtPh(CO)L_2]^+SO_3CF_3^-$ (L = PPh_3 or $PMePh_2$) with Sodium Salts (at 298 K)

	NMR data		
complex	δP	${}^1J_{PtP}$/Hz	infrared data
trans-$[PtClPh(PPh_3)_2]$	24.1	3152	
trans-$[PtBrPh(PPh_3)_2]$	23.5	3132	
trans-$[PtIPh(PPh_3)_2]$	21.2	3081	
trans-$[Pt(N_3)Ph(PPh_3)_2]$	21.4	3120	
trans-$[PtBr(COPh)(PPh_3)_2]$	18.7	3364	ν(CO) 1620 cm^{-1}
trans-$[PtI(COPh)(PPh_3)_2]$	16.2	3320	ν(CO) 1623 cm^{-1}
trans-$[Pt(OCOMe)Ph(PPh_3)_2]$	22.0	3272	
trans-$[Pt(CN)Ph(PPh_3)_2]$	19.6	2922	
trans-$[PtClPh(PMePh_2)_2]$	8.4	3008	
trans-$[PtIPh(PMePh_2)_2]$	4.0	2935	
trans-$[Pt(N_3)Ph(PMePh_2)_2]$	6.6	2976	
trans-$[PtI(COPh)(PMePh_2)_2]$	−0.3	3154	ν(CO) 1620 cm^{-1}
trans-$[Pt(OCOMe)Ph(PMePh_2)_2]$	9.6	3135	

Decarbonylation of *trans*-$[Pt(SnCl_3)(COPh)(PPh_3)_2]$ in chloroform solution was slow at ambient temperature, as observed by ${}^{31}P$ NMR spectroscopy, and was incomplete even after 8 h at 55 °C. In the presence of a few drops of acetone, 75% reaction occurred after refluxing for 45 min. When *trans*-$[Pt(SnCl_3)(COPh)(PPh_3)_2]$ was dissolved in acetone, extrusion of $SnCl_2$ from the platinum–chlorine bond was quantitative without heating, and only *trans*-$[PtCl(COPh)(PPh_3)_2]$ (δP 19.4, ${}^1J_{PtP}$ = 3393 Hz) was observed in solution.

Results and Discussion

When a stream of carbon monoxide was passed through a chloroform solution of *trans*-$[PtClPh(PPh_3)_2]$, the corresponding aroyl complex was produced.[9] The reaction was found to have proceeded to the extent of 15% after 1 h. When a similar solution of *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ was treated with CO at ambient temperature, however, the ${}^{31}P$ NMR spectrum indicated that no starting complex remained after only 1 min. The single phosphorus-containing species present in solution at this stage was identified as the *trans*-$[PtPh(CO)(PPh_3)_2]^+$ cation (Table I). Further treatment of this solution with CO for 1 h produced a 50:50 mixture of *trans*-$[PtPh(CO)(PPh_3)_2]^+$ and *trans*-$[Pt(SnCl_3)(COPh)(PPh_3)_2]$. (It is worth noting,

---

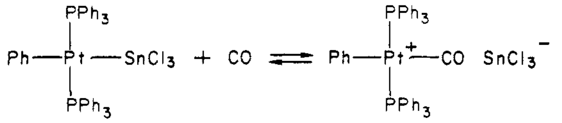
(8) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 944.

(9) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.*, in press.

however, that when 10% acetone was added to the solvent, the conversion to the aroylplatinum complex was virtually quantitative after 50 min.)

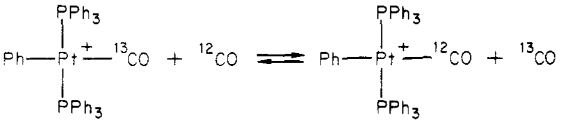
Reaction of *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ in chloroform with carbon monoxide at 213 K for 20 min produced *trans*-$[PtPh(CO)(PPh_3)_2]^+$ as the only phosphorus-containing species in solution. It has previously been shown[6] that addition of excess chloride ion to the *trans*-$[PtPh(CO)(PPh_3)_2]^+$ cation rapidly results in regeneration of *trans*-$[PtClPh(PPh_3)_2]$. If dissociation of the trichlorostannate anion to $SnCl_2$ and Cl^- occurred under these conditions, attack of chloride ion to yield *trans*-$[PtClPh(PPh_3)_2]$ would result.[10] Hence, dissociation does not take place, and the $SnCl_3^-$ anion must be present in solution. As the ^{31}P NMR parameters obtained are identical with those for the complex *trans*-$[PtPh(CO)(PPh_3)_2]^+SO_3CF_3^-$, the same free cation must be present in both cases and ion pairing cannot occur to any significant degree.

That a dynamic equilibrium exists between *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ and the ionic species was shown by passing nitrogen through a solution of *trans*-$[PtPh(CO)(PPh_3)_2]^+SnCl_3^-$ at ambient temperature. Within 20 min almost complete loss of carbon monoxide and formation of *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ had taken place, and, since a nitrogen stream would only remove free CO, an equilibrium (eq 1) must be involved, which lies far to the right at low temperatures.



$$\mathrm{Ph{-}\overset{PPh_3}{\underset{PPh_3}{Pt}}{-}SnCl_3 + CO \rightleftharpoons Ph{-}\overset{PPh_3}{\underset{PPh_3}{Pt^{+}}}{-}CO\ \ SnCl_3^-} \quad (1)$$

When *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ was reacted with ^{13}CO in chloroform solution at 213 K, the ^{31}P NMR spectrum contained a doublet ($^2J_{PC}$ = 8 Hz) with ^{195}Pt satellites, due to the *trans*-$[PtPh(^{13}CO)(PPh_3)_2]^+$ cation. Passing ^{12}CO through this solution at 213 K caused no change in the ^{31}P NMR spectrum, while a strong singlet resonance, flanked by a very weak doublet, was observed after reaction for 3 min at ambient temperature. Thus exchange of carbon monoxide, which is likely to proceed via an associative mechanism in the presence of free CO, is rapid at ambient temperature (eq 2). Nitrogen was passed through such a solution for 3 min, and considerable loss of CO took place, *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ and *trans*-$[PtPh(CO)(PPh_3)_2]^+$ then being present in a 50:50 ratio.



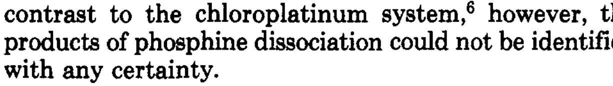
$$\mathrm{Ph{-}\overset{PPh_3}{\underset{PPh_3}{Pt^{+}}}{-}{}^{13}CO + {}^{12}CO \rightleftharpoons Ph{-}\overset{PPh_3}{\underset{PPh_3}{Pt^{+}}}{-}{}^{12}CO + {}^{13}CO} \quad (2)$$

When a solution of *trans*-$[PtPh(CO)(PPh_3)_2]^+SnCl_3^-$, prepared at 213 K, was allowed to warm to ambient temperature in the absence of excess carbon monoxide, conversion to *trans*-$[Pt(SnCl_3)(COPh)(PPh_3)_2]$ took place, the reaction being 60% complete after 4 h.

It has previously been shown[6] that dissociation of PPh_3 is involved in the carbonylation of *trans*-$[PtClPh(PPh_3)_2]$, and the addition of sulfur was used to trap the free phosphine as its sulfide. When *trans*-$[PtPh(CO)(PPh_3)_2]^+SnCl_3^-$ in dichloromethane was stirred with sulfur in the presence of free CO at room temperature for 1 h, the ^{31}P NMR spectrum indicated that the major phosphorus-containing platinum species was still the *trans*-$[PtPh(CO)(PPh_3)_2]^+$ cation. An intense signal was also prresent at δP 42.5, due to triphenylphosphine sulfide, indicating that phosphine dissociation takes place. In contrast to the chloroplatinum system,[6] however, the products of phosphine dissociation could not be identified with any certainty.

Carbonylation of a chloroform solution of *trans*-$[Pt(SnCl_3)Ph(PPh_3)_2]$ in the presence of excess sulfur also produced Ph_3PS and *trans*-$[PtPh(CO)(PPh_3)_2]^+$, the latter being the major phosphine-containing metal complex, according to the ^{31}P NMR spectrum.

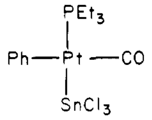
In an attempt to identify the species obtained on dissociation of PPh_3, the dimeric complex, $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$, was cleaved by carbon monoxide (eq 3) to yield two isomers, A and B, of $[PtClPh(CO)(PPh_3)]$,[6] which were then treated with $SnCl_2{\cdot}2H_2O$. The ^{31}P NMR spectrum at 213 K indicated the presence of a small amount of the cation, *trans*-$[PtPh(CO)(PPh_3)_2]^+$, but the major species (δP 17.6, $^1J_{PtP}$ = 3181 Hz), which showed no tin satellites (due to coupling to ^{117}Sn or ^{119}Sn), was of uncertain identity. Addition of a few drops of acetone caused considerable conversion to *trans*-$[PtPh(CO)(PPh_3)_2]^+$.



$$[\mathrm{Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2}] + \mathrm{CO} \longrightarrow \mathrm{Ph{-}\overset{PPh_3}{\underset{Cl}{Pt}}{-}CO + Ph{-}\overset{PPh_3}{\underset{CO}{Pt}}{-}Cl} \quad (3)$$

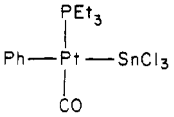
A B

Since the triphenylphosphine ligands were found to be of considerable lability in the above system, analogous reactions of the triethylphosphine system, where phosphine dissociation was not expected to occur, were carried out. Treatment of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$ with CO gave the corresponding two isomers of $[PtClPh(CO)(PEt_3)]$,[6] and addition of $SnCl_2{\cdot}2H_2O$ at 213 K yielded two species, C and D. The large two-bond couplings in C indicate that mutually trans arrangement of the phosphine and $SnCl_3$ ligands, while the minor nature of D prevented the observation of the cis couplings. On standing, the latter species diminished in intensity.



$$\mathrm{Ph{-}\overset{PEt_3}{\underset{SnCl_3}{Pt}}{-}CO}$$

C, δP 20.4, $^1J_{PtP}$ = 2979 Hz, $^2J_{^{119}Sn\text{-}^{31}P}$ = 3335 Hz, $^2J_{^{117}Sn\text{-}^{31}P}$ = 3186 Hz



$$\mathrm{Ph{-}\overset{PEt_3}{\underset{CO}{Pt}}{-}SnCl_3}$$

D, δP 8.5, $^1J_{PtP}$ = 3027 Hz

Thus, while the triethylphosphine complexes undergo insertion of $SnCl_2$ into the platinum–chlorine bond to give the expected products, the PPh_3-containing complexes undergo a rearrangement in the presence of tin(II) chloride to give a bis(phosphine)platinum complex and, necessarily, a species containing no phosphine ligands. (Interestingly, this ligand migration is promoted by acetone, and such rearrangements in this solvent have recently been observed in other systems.[11,12]) The tendency is, therefore, for the $[Pt(SnCl_3)Ph(CO)(PPh_3)]$ complexes to undergo rearrangement to give the *trans*-$[PtPh(CO)(PPh_3)_2]^+$ cation, rather than vice versa, even in the absence of excess phosphine. While phosphine dissociation from *trans*-$[PtPh(CO)(PPh_3)_2]^+$ does occur, as evidenced by the for-

---

(10) Even with very low chloride concentrations the reaction to produce *trans*-$[PtClPh(PPh_3)_2]$ takes place, as evidenced by the slow formation of the complex when a chloroform solution of *trans*-$[PtPh(CO)(PPh_3)_2]^+SO_3CF_3^-$ was treated with sparingly soluble sodium chloride.

(11) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.*, in press.

(12) Anderson, G. K.; Clark, H. C.; Davies, J. A., unpublished results.

mation of $\mathrm{Ph_3PS}$ on addition of sulfur, regeneration of the cation seems particularly likely in the presence of the free triphenylphosphine thus produced.

When *trans*-$[\mathrm{Pt(SnCl_3)Ph(PMePh_2)_2}]$ in chloroform solution was treated with CO at ambient temperature, the corresponding aroyl complex was rapidly produced. It has previously been shown that the reaction of *trans*-$[\mathrm{PtClPh(PMePh_2)_2}]$ with carbon monoxide proceeds too slowly to be measured kinetically[4] and that phosphine dissociation does not take place.[6]

The ionic complex, *trans*-$[\mathrm{PtPh(CO)(PMePh_2)_2}]^+\mathrm{SnCl_3}^-$, was produced quantitatively when CO was passed through a chloroform solution of *trans*-$[\mathrm{Pt(SnCl_3)Ph(PMePh_2)_2}]$ at 213 K for 1 h. When such a solution was allowed to warm to ambient temperature in the presence of sulfur, no phosphine sulfide was evident from the ^{31}P NMR spectrum, indicating that in this case dissociation of $\mathrm{PMePh_2}$ does not occur. At 298 K, however, rearrangement of the ionic species to yield *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PMePh_2)_2}]$ does proceed, and the reaction was 60% complete after 3 h.

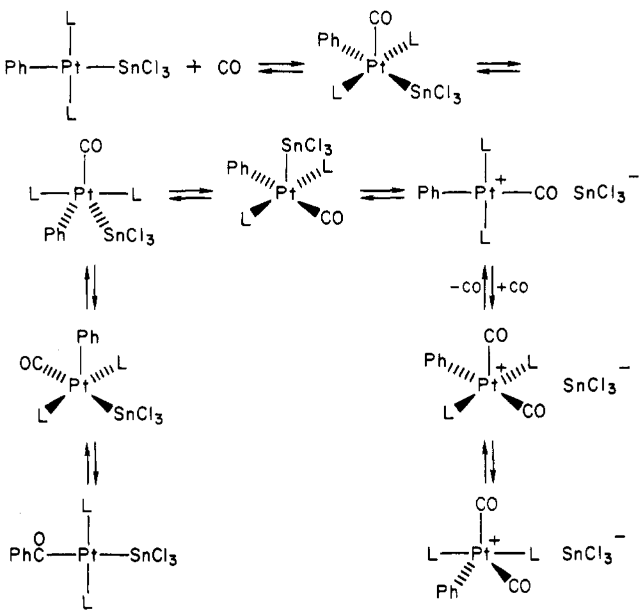
Thus, rearrangement of *trans*-$[\mathrm{PtPh(CO)(PMePh_2)_2}]^+\mathrm{SnCl_3}^-$ to give the neutral aroyl product, which proceeds without dissociation of tertiary phosphine, occurs at a rate which is comparable with that for the triphenylphosphine complex, in which phosphine dissociation is involved. Where phosphine dissociation does not occur, it is believed[4,6] that aryl migration occurs from a five-coordinate species, and it is unlikely that the rates of formation of, and aryl migration from, the complexes $[\mathrm{Pt(SnCl_3)Ph(CO)L_2}]$ (L = $\mathrm{PPh_3}$ or $\mathrm{PMePh_2}$) will be significantly different. In light of these observations and the tendency of the $[\mathrm{Pt(SnCl_3)Ph(CO)(PPh_3)}]$ complexes to rearrange to *trans*-$[\mathrm{PtPh(CO)(PPh_3)_2}]^+\mathrm{SnCl_3}^-$, it appears that phosphine dissociation does not result in any significant contribution to the overall rate of production of *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PPh_3)_2}]$ from *trans*-$[\mathrm{PtPh(CO)(PPh_3)_2}]^+\mathrm{SnCl_3}^-$. In contrast to the chloroplatinum systems, where the trichlorostannate ligand is involved, the nondissociative route to *trans*-$[\mathrm{Pt(SnCl_3)(COPh)L_2}]$ is favored, regardless of the electronic nature of the tertiary phosphine.

It has already been noted that *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PPh_3)_2}]$ readily undergoes decarbonylation in refluxing benzene,[7] though the intermediates in the reaction were not conclusively identified. When a chloroform solution of the aroyl complex was heated to 328 K, decarbonylation resulted, the reaction being 50% complete after 1 h. The decarbonylation was essentially complete after 8 h, but, in addition to *trans*-$[\mathrm{Pt(SnCl_3)Ph(PPh_3)_2}]$, extrusion of $\mathrm{SnCl_2}$ resulted in minor amounts of *trans*-$[\mathrm{PtClPh(PPh_3)_2}]$ and *trans*-$[\mathrm{PtCl(COPh)(PPh_3)_2}]$ also being produced.

When a dichloromethane solution of *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PPh_3)_2}]$ to which a few drops of acetone had been added was allowed to stand at ambient temperature for 5 h, the ^{31}P NMR spectrum indicated that significant amounts of *trans*-$[\mathrm{PtPh(CO)(PPh_3)_2}]^+\mathrm{SnCl_3}^-$ and *trans*-$[\mathrm{Pt(SnCl_3)Ph(PPh_3)_2}]$ (up to 20% each) had been formed. After the solution was refluxed for 45 min, the major species in solution was *trans*-$[\mathrm{Pt(SnCl_3)Ph(PPh_3)_2}]$, with signals due to the aroyl and ionic complexes still being present in the ^{31}P NMR spectrum.

Thus, significant amounts of the ionic complex, *trans*-$[\mathrm{PtPh(CO)(PPh_3)_2}]^+\mathrm{SnCl_3}^-$, are built up during the decarbonylation process. The solution infrared spectrum of the ionic species has ν(CO) at 2102 cm^{-1}, and the intermediate which was previously assigned[7] as $[\mathrm{Pt(SnCl_3)Ph(CO)(PPh_3)}]$ should undoubtedly have the above ionic structure. This ionic species did not react with free $\mathrm{PPh_3}$ at ambient temperature, but after the solution was heated to 50 °C a complex mixture of products was obtained, and the likelihood of CO displacement being involved might account for the enhanced rate of CO evolution observed by Kubota[7] when $\mathrm{PPh_3}$ was added to a solution of *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PPh_3)_2}]$ 500 s after refluxing was commenced. Conversely, initial addition of $\mathrm{PPh_3}$ resulted in a reduction in the rate of CO loss,[7] and *trans*-$[\mathrm{Pt(SnCl_3)(COPh)(PPh_3)_2}]$ was found to react with $\mathrm{PPh_3}$ to give a number of unidentified products, from which CO elimination may not readily occur.

Scheme I[a]



[a] L = $\mathrm{PPh_3}$ or $\mathrm{PMePh_2}$.

These observations show that the addition of quantities of free ligand, in this case tertiary phosphine, which results in a decreased or increased reaction rate, as measured by CO evolution,[7] does not necessarily imply a dissociative mechanism. Where an alternative pathway is possible or a significant buildup of an intermediate species occurs, the conclusions drawn from such studies may well be erroneous. In the kinetic study by Garrou and Heck of the carbonylation of *trans*-$[\mathrm{PtXR^1(PR_3)_2}]$ complexes,[4] the buildup of the ionic intermediates was minimal, but displacement of CO from such species by deliberately added tertiary phosphine would result in a nonlinear uptake of gas with time and hence inaccuracies in the calculated rate constants.

Thus it must be borne in mind that in "proving" a dissociative mechanism by the use of added ligands, while the reactants and products may be inert toward the ligand under study, alternative reaction pathways involving intermediate species may become important. To ignore such possibilities may lead to questionable conclusions.

The results for the carbonylation of *trans*-$[\mathrm{Pt(SnCl_3)PhL_2}]$ (L = $\mathrm{PPh_3}$ or $\mathrm{PMePh_2}$), and the corresponding decarbonylations, are summarized in Scheme I. The low-temperature reaction of *trans*-$[\mathrm{Pt(SnCl_3)PhL_2}]$ with CO involves ligand displacement to yield the ionic species, and this is depicted as involving initial coordination of the incoming nucleophile in an axial fashion and rearrangement through a trigonal-bipyramidal species to one with the leaving trichlorostannate ligand in an axial position prior to its elimination. Any alternative mechanism to the stereospecific ligand displacement shown in Scheme I would involve a complex series of rearrangements, and no

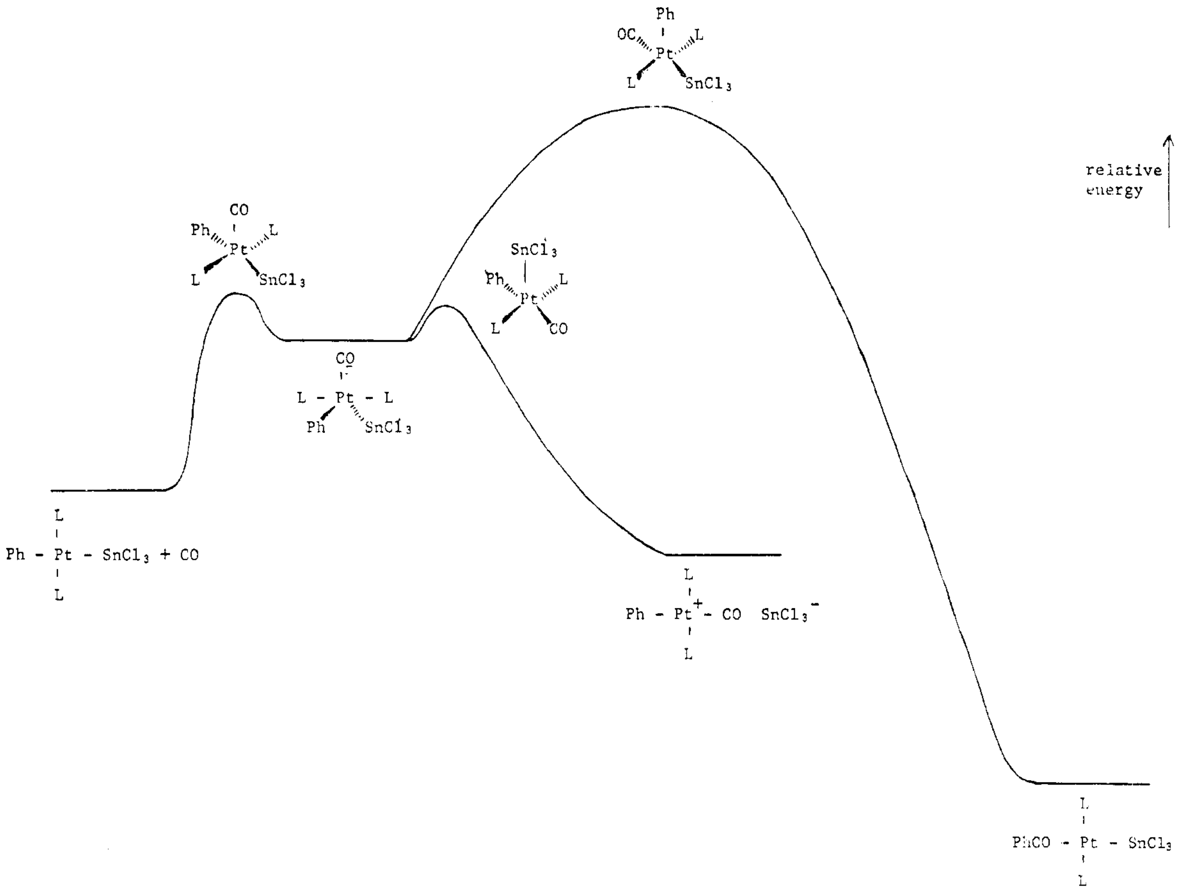


Figure 1. Reaction profile for the carbonylation of *trans*-$[Pt(SnCl_3)PhL_2]$ (L = PPh_3 or $PMePh_2$).

spectroscopic evidence for such processes was found, even at low temperature. Attack of CO on the *trans*-$[PtPh(CO)L_2]^+$ cation to give a five-coordinate species ultimately leads to carbonyl group exchange. When L = PPh_3, attack of $SnCl_3^-$ on *trans*-$[PtPh(CO)(PPh_3)_2]^+$ leading to phosphine dissociation also occurs, but this is apparently not a significant step in the carbonyl insertion sequence. Distortion of the five-coordinate complexes, $[Pt(SnCl_3)Ph(CO)L_2]$, such that the phenyl and carbonyl groups come into close proximity (making an angle at platinum approaching 90°) would allow phenyl migration and generation of an aroyl moiety from a five-coordinate species. Such distortions have been predicted by a molecular orbital study.[13]

A reaction profile for the carbonylation reaction is shown in Figure 1. The most symmetrical five-coordinate species is likely to be of lower energy than the others, and a relatively low energy pathway exists between *trans*-$[Pt(SnCl_3)PhL_2]$ + CO and the ionic complex, since this reaction proceeds at low temperature. The reverse process occurs readily at ambient temperature, particularly when free CO is removed from the system. The aroyl complex is of lowest energy, since it is essentially irreversibly formed at ambient temperature. The transition state in which the platinum–carbon bond is weakened prior to aryl migration represents an energy maximum, and thus, although the aroyl complex is thermodynamically favored, *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$ is the kinetic product due to the lower energy of activation involved in its production.

Conversely, a high activation energy is involved in the migration of the phenyl group from CO to the metal, and this is consistent with the observations regarding the decarbonylation reaction; that is, the reaction is very slow at ambient temperature but is quite rapid in refluxing benzene. Both the decarbonylated product and the ionic complex are produced, since they are formed from a common five-coordinate intermediate and are not too dissimilar in energy, and the ultimate quantitative formation of *trans*-$[Pt(SnCl_3)PhL_2]$ simply reflects the driving of the equilibrium in this direction by loss of CO from the system at these temperatures.

When the complexes *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$ (L = PPh_3 or $PMePh_2$) were allowed to warm to ambient temperature in the absence of excess carbon monoxide, conversion to the aroylplatinum compounds took place, as has already been noted, at a rate which was approximately independent of the nature of the tertiary phosphine. It has also been suggested that aryl migration occurs from a five-coordinate species, formed by nucleophilic attack of the $SnCl_3^-$ anion. In the presence of excess CO, on the other hand, *trans*-$[PtPh(CO)(PMePh_2)_2]^+SnCl_3^-$ undergoes very little reaction, only a trace of the aroyl complex being detected after 1 h. In the analogous triphenylphosphine case the ionic and aroyl complexes were present in 50:50 ratio after 1 h in the presence of free CO, and it has already been pointed out that PPh_3 dissociation occurs under these conditions.

These results may be explained in terms of eq 1, where excess carbon monoxide maintains an equilibrium position far to the right, which prevents significant buildup of a five-coordinate species from which aryl migration might occur. Thus *trans*-$[PtPh(CO)(PMePh_2)_2]^+SnCl_3^-$ undergoes little reaction under these conditions, while in the absence of free CO the equilibrium (eq 1) is displaced to the left and formation of the aroyl product from the five-coordinate intermediate becomes a viable process. A similar situation prevails for the triphenylphosphine system under these circumstances, but when excess CO is

---

[13] Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

present an additional, dissociative, pathway, involving displacement of PPh$_3$ by CO, would permit formation of *trans*-[Pt(SnCl$_3$)(COPh)(PPh$_3$)$_2$] even when eq 1 is displaced far to the right.

The role of the SnCl$_3^-$ ligand is clearly not a simple one, and in order to gain further insight into how this ligand affects the energetics of the system, *trans*-[PtPh(CO)L$_2$]$^+$SO$_3$CF$_3^-$ (L = PPh$_3$ or PMePh$_2$) was treated with a variety of anions in chloroform solution. The sparingly soluble sodium salts were employed in order to achieve a slow rate of reaction such that the thermodynamic rather than the kinetic product should be favored. The course of the reaction was determined for each anion, and, while the results are affected by the slightly differing solubilities of the sodium salts, some measure of the reaction rate was obtained by monitoring the ^{31}P NMR spectrum. The ^{31}P NMR data, and infrared data if applicable, for the reaction products are presented in Table II.

With *trans*-[PtPh(CO)(PPh$_3$)$_2$]$^+$SO$_3$CF$_3^-$ no reaction took place in the presence of fluoride, nitrate, or nitrite, and a similar observation was made for the addition of sodium nitrate to *trans*-[PtPh(CO)(PMePh$_2$)$_2$]$^+$SO$_3$CF$_3^-$. The triphenylphosphine complex underwent CO loss rapidly in the presence of cyanide, and displacement of PPh$_3$ had begun after 24 h and was complete after 6 days.

The *trans*-[PtPh(CO)(PPh$_3$)$_2$]$^+$SO$_3$CF$_3^-$ complex reacted with chloride and azide ions by displacement of carbon monoxide, the reaction being 30% complete after 1 day and 60% after 6 days in each case. With sodium acetate displacement of CO also occurred, the reaction being 30% and 90% complete after 1 and 6 days, respectively. (The presence of acetate precluded meaningful infrared studies of the reaction mixture, so *trans*-[PtPh(^{13}CO)(PPh$_3$)$_2$]$^+$SO$_3$CF$_3^-$ was treated with NaOCOMe, and the loss of coupling to carbon in the ^{31}P NMR spectrum indicated that displacement of ^{13}CO had taken place.) In the reaction with NaBr the only new species observable after 24 h was *trans*-[PtBrPh(PPh$_3$)$_2$], but after 6 days the phenyl and benzoyl complexes were present in a 2:1 ratio and the reaction was 90% complete. The reaction with iodide was complete with 24 h, and the products of CO insertion and displacement were present in a 3:1 ratio.

Similar results were obtained for the reactions of *trans*-[PtPh(CO)(PMePh$_2$)$_2$]$^+$SO$_3$CF$_3^-$. The reaction with Cl$^-$ proceeded to 70% completion after 6 days, while quantitative formation of *trans*-[Pt(N$_3$)Ph(PMePh$_2$)$_2$] occurred in the same time, and the reaction with sodium acetate was slower than in the triphenylphosphine case (45% after 6 days). A 4:1 ratio of *trans*-[PtI(COPh)(PMePh$_2$)$_2$] to its phenyl analogue was obtained with NaI after 2 days.

Thus only iodide, and to a lesser extent bromide, reacts with the *trans*-[PtPh(CO)L$_2$]$^+$ (L = PPh$_3$ or PMePh$_2$) cation to give the corresponding aroylplatinum complex, the reaction which occurs with the SnCl$_3^-$ anion. Possibly some comparisons can be drawn, therefore, between the trichlorostannate and iodide ions in this context.

Carbon monoxide was passed through solutions of *trans*-[PtXPhL$_2$] (L = PPh$_3$, X = Cl, I, SnCl$_3$; L = PMePh$_2$, X = Cl, SnCl$_3$) in chloroform for 1 h, the extent of reaction being monitored after certain intervals by cooling the solution to 213 K, in order to quench the reaction, and recording the ^{31}P NMR spectrum at this temperature. No observable reaction occurred with *trans*-[PtClPh(PMePh$_2$)$_2$] within 1 h, while 15% reaction took place with its triphenylphosphine analogue, the phenyl and benzoyl complexes being the only species detected in solution.

With *trans*-[PtIPh(PPh$_3$)$_2$], after 3 min the major species was the starting complex, but 25% reaction had occurred to give an ion-paired species,[6] *trans*-[PtPh(CO)(PPh$_3$)$_2$]$^+$···I$^-$ (δP 7.6, $^1J_{\mathrm{PtP}}$ = 2925 Hz). After 15 min, 30% reaction had occurred to give a 1:1 mixture of the ion-paired species and the aroyl complex, and after 1 h 60% reaction to *trans*-[PtI(COPh)(PPh$_3$)$_2$] had taken place, but a small amount (10%) of the ion-paired intermediate remained. The treatment with CO of *trans*-[Pt(SnCl$_3$)PhL$_2$] (L = PPh$_3$ or PMePh$_2$) produced *trans*-[PtPh(CO)L$_2$]$^+$SnCl$_3^-$ exclusively within 1 min, and a 1:1 mixture of *trans*-[PtPh(CO)(PPh$_3$)$_2$]$^+$ and *trans*-[Pt(SnCl$_3$)(COPh)(PPh$_3$)$_2$] was formed after 1 h, while less than 10% reaction of the *trans*-[PtPh(CO)(PMePh$_2$)$_2$]$^+$ cation had occurred in this time. (The faster reaction of the triphenylphosphine complex in the presence of free CO, probably due to phosphine dissociation, has been discussed above.)

It is clear that the trichlorostannate ligand is superior to iodide in promoting formation of the ionic species; that is, the SnCl$_3^-$ anion is readily displaced. In fact, in chlorinated solvents only ion-paired species are obtained with iodide, and, unlike the trichlorostannate case, such species cannot be formed quantitatively. In the absence of free CO, the ionic complexes *trans*-[PtPh(CO)L$_2$]$^+$SnCl$_3^-$ (L = PPh$_3$ or PMePh$_2$) underwent reaction over several hours at ambient temperature to yield the aroyl complexes, while addition of iodide to *trans*-[PtPh(CO)L$_2$]$^+$SO$_3$CF$_3^-$ caused complete reaction to occur in less than 24 h, *trans*-[PtI(COPh)L$_2$] being the major product. When excess CO was present, the reactions of *trans*-[PtPh(CO)L$_2$]$^+$SnCl$_3^-$ (L = PPh$_3$ or PMePh$_2$) were relatively slow, and production of the aroyl complex was faster in the reaction of *trans*-[PtIPh(PPh$_3$)$_2$]. Thus, the carbonylation of the complexes *trans*-[PtXPhL$_2$] is fastest where X = I under the normal carbonylation conditions, that is, reaction of the phenylplatinum complex with excess CO for several hours.

The role of tin(II) chloride in promoting reactions at metal centers has been the subject of much comment,[14-20] and its ability in this respect has variously been attributed to the trans influence[16] and trans effect[17-19] of the SnCl$_3^-$ ligand and to its supposed stabilization of five-coordinate species.[15,17,18] In the decarbonylation of *trans*-[Pt(SnCl$_3$)(COR)(PPh$_3$)$_2$] the unique properties of the SnCl$_3^-$ ligand were suggested[7] to be its ability to labilize tertiary phosphine, its stabilization of five-coordinate intermediates, and its low tendency to form SnCl$_3$-bridged species. In fact, the most striking feature of the trichlorostannate ligand appears to be its ready displacement, a consequence normally associated with a ligand of low trans effect[21] and nucleophilicity. With excess CO, nucleophilic attack of SnCl$_3^-$ on the cationic species is prevented, indicating that CO is a better ligand for platinum than trichlorostannate. No dissociation of PMePh$_2$ occurs, as in the case where X = Cl, which suggests that labilization of tertiary phosphine is not a feature of this particular system.

---

(14) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. II.

(15) Young, J. F. *Adv. Inorg. Chem. Radiochem.* **1968**, *11*, 91.

(16) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1978**, *61*, 1848.

(17) Lindsey, R. V.; Parshall, G. W.; Stolberg, U. G. *J. Am. Chem. Soc.* **1965**, *87*, 658.

(18) Clark, H. C.; Billard, C.; Wong, C. S. *J. Organomet. Chem.* **1980**, *190*, C105.

(19) Cramer, R. D.; Lindsey, R. V.; Prewitt, C. T.; Stolberg, U. G. *J. Am. Chem. Soc.* **1965**, *87*, 658.

(20) Clark, H. C.; Jablonski, C. R.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1541.

(21) A low trans effect relative to that of the trans ligand, in this case a phenyl group.

It appears that the role of the $SnCl_3^-$ ligand is to provide a good leaving group which, in the absence of added ligands including CO, slowly reattacks the platinum center to form a five-coordinate species from which aryl migration to yield the product can occur. This differs from the case wher X = I, which constitutes the only other system studied in which CO insertion readily occurs, to the extent that iodide is a better nucleophile which is less readily displaced but competes effectively with carbon monoxide to form a five-coordinate species from which aryl migration (and probably also phosphine dissociation) can occur. Thus, while tin(II) chloride can be used to catalyze the above carbonylation and decarbonylation reactions, its properties in this situation, at least, are not nearly so unique as has previously been claimed. Consequently, a reexamination of the role of the trichlorostannate ligand in other catalytic systems would appear to be warranted.

Acknowledgment. The continued financial support of the Natural Sciences and Engineering Research Council (to H.C.C.) is gratefully acknowledged. Thanks are expressed to Johnson Matthey Ltd. for a generous loan of platinum salts and to Dr. A. Woon-Fat for certain of the NMR spectra.

Registry No. *trans*-[$PtClPh(PPh_3)_2$], 18421-49-3; *trans*-[$PtClPh(PMePh_2)_2$], 60772-01-2; *trans*-[$Pt(SnCl_3)Ph(PPh_3)_2$], 72638-21-2; *trans*-[$PtCl(COPh)(PPh_3)_2$], 18421-48-2; *trans*-[$Pt(SnCl_3)(COPh)(PPh_3)_2$], 74304-53-3; *trans*-[$PtPh(CO)(PPh_3)_2]^+$-$SnCl_3^-$, 78804-26-9; *trans*-[$Pt(SnCl_3)Ph(PMePh_2)_2$], 78804-27-0; *trans*-[$PtCl(COPh)(PMePh_2)_2$], 60742-07-6; *trans*-[$Pt(SnCl_3)(COPh)(PMePh_2)_2$], 78804-28-1; *trans*-[$PtPh(CO)(PMePh_2)_2]^+$-$SnCl_3^-$, 78804-29-2; *trans*-[$PtBrPh(PPh_3)_2$], 41620-24-0; *trans*-[$PtIPh(PPh_3)_2$], 53424-01-4; *trans*-[$Pt(N_3)Ph(PPh_3)_2$], 78804-30-5; *trans*-[$PtBr(COPh)(PPh_3)_2$], 57665-38-0; *trans*-[$PtI(COPh)(PPh_3)_2$], 60751-00-0; *trans*-[$Pt(OCOMe)Ph(PPh_3)_2$], 78804-31-6; *trans*-[$Pt(CN)Ph(PPh_3)_2$], 78804-32-7; *trans*-[$PtIPh(PMePh_2)_2$], 78804-33-8; *trans*-[$Pt(N_3)Ph(PMePh_2)_2$], 78804-34-9; *trans*-[$PtI(COPh)(PMePh_2)_2$], 78804-35-0; *trans*-[$Pt(OCOMe)Ph(PMePh_2)_2$], 78804-36-1.

Catalytic Homogeneous Carbonylation of Azirines by Palladium(0). Important Influence of Catalyst Ligands on the Reaction Pathway

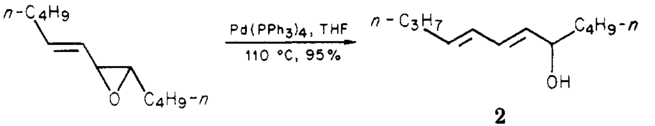
Howard Alper*[1] and Chulangani Perera Mahatantila

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Received June 25, 1981

The use of soluble palladium(0) catalysts for the carbonylation of azirines results in the novel syntheses of two important classes of compounds. The reaction course is dependent on the nature of the ligands attached to the metal. Tetrakis(triphenylphosphine)palladium(0) catalyzes the conversion of azirines to β-lactams, while vinyl isocyanates are formed in a regiospecific reaction using bis(dibenzylideneacetone)palladium(0) as the catalyst. A mechanism is proposed for these reactions.

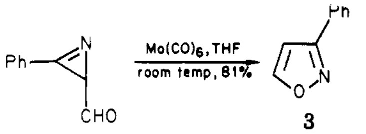
The cleavage of strained ring systems by transition-metal complexes is a topic of considerable recent interest.[2,3] For example, tetrakis(triphenylphosphine)palladium(0) can catalyze the conversion of vinyl epoxides to either allylic alcohols (e.g., 1 → 2) or β,γ-unsaturated ketones, depending on the nature of the organic reactant.[4]



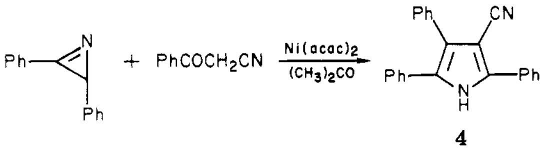
1

2

Azirines are another class of three-membered ring compounds which undergo some interesting and useful ring-opening reactions in the presence of organometallic and inorganic compounds.[5-19] For instance, group 6 metal carbonyls can effect intramolecular cycloaddition of appropriately substituted azirines to give five-membered ring heterocycles (e.g., 3) in high yields.[12] Molybdenum hexacarbonyl induced intermolecular cycloaddition reactions of azirines with alkynes affords 2*H*- or 1*H*-pyrroles, but in low yields.[18] Better product yields can be obtained by the nickel(II)-catalyzed reaction of azirines with activated ketones, leading to pyrroles (e.g., 4).[11] The synthesis of styryl indoles, important intermediates in alkaloid synthesis, can be achieved in fine yields by the cleavage of



3



4

---

(1) E. W. R. Steacie Fellow, 1980–82.

(2) Bishop III, K. C. *Chem. Rev.* **1976**, *76*, 461.

(3) Alper, H. *Isr. J. Chem.*, in press.

(4) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623.

(5) Hayashi, K.; Isomura, K.; Taniguchi, H. *Chem. Lett.* **1975**, 1011.

(6) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 483.

(7) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 983.

(8) Alper, H.; Prickett, J. E. *Tetrahedron Lett.* **1976**, 2589.

(9) Alper, H.; Prickett, J. E. *Inorg. Chem.* **1977**, *16*, 67.

(10) Komendantov, M. I.; Bekmuchametov, R. R. *Khim. Geterotsikl. Soedin.* **1977**, 1570.

(11) Schuchardt, U.; Faria dos Santos Filho, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 647.

(12) Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.

(13) Isomura, K.; Uto, K.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 664.

(14) Nakamura, Y.; Bachmann, K.; Heimgartner, H.; Schmid, H.; Daly, J. J. *Helv. Chim. Acta* **1978**, *61*, 589.

(15) Bellamy, F. *J. Chem. Soc., Chem. Commun.* **1978**, 998.

(16) Bellamy, F. *Tetrahedron Lett.* **1978**, 4577.

(17) Alper, H.; Sakakibara, T. *Can. J. Chem.* **1979**, *57*, 1541.

(18) Inada, A.; Heimgartner, H.; Schmid, H. *Tetrahedron Lett.* **1979**, 2983.

(19) Sakakibara, T.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1979**, 458.