(2) W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).
(3) P. P. Gaspar and B. J. Herold, in "Carbene Chemistry", W. Kirmse, Ed., 2nd ed, Academic Press, New York, N.Y., 1971.
(4) J. C. Thompson and J. L. Margrave, *Science*, **155**, 669 (1967).
(5) J. L. Margrave and P. W. Wilson, *Acc. Chem. Res.*, **4**, 145 (1971).
(6) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).
(7) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).
(8) J. H. Purnell and R. Walsh, *Proc. R. Soc. London, Ser. A*, **293**, 543 (1966).
(9) I. DuBois, G. Herzberg, and R. D. Verma, *J. Chem. Phys.*, **47**, 4262 (1967).
(10) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring. *Inorg. Chem.*, **9**, 1068 (1970).
(11) M. Bowrey and J. H. Purnell, *J. Am. Chem. Soc.*, **92**, 2594 (1970).
(12) P. S. Skell and P. W. Owen, *J. Am. Chem. Soc.*, **94**, 5434 (1972).
(13) V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965).
(14) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).
(15) H. P. Hopkins, J. C. Thompson, and J. L. Margrave, *J. Am. Chem. Soc.*, **90**, 901 (1968).
(16) J. C. Thompson and J. L. Margrave, *Inorg. Chem.*, **11**, 913 (1972).
(17) P. P. Gaspar, B. D. Pate, and W. C. Eckelman, *J. Am. Chem. Soc.*, **88**, 3878 (1966).
(18) P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Am. Chem. Soc.*, **90**, 6914 (1968).
(19) P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968).
(20) P. P. Gaspar and P. Markusch, *Chem. Commun.*, 1331 (1970).
(21) P. P. Gaspar, P. Markusch, J. D. Holten III, and J. J. Frost, *J. Phys. Chem.*, **76**, 1352 (1972).
(22) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, *J. Am. Chem. Soc.*, **94**, 4355 (1972).
(23) G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 637 (1973).
(24) P. P. Gaspar, R.-J. Hwang, and W. C. Eckelman, *J. Chem. Soc., Chem. Commun.*, 242 (1974).
(25) O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y.-N. Tang, *J. Am. Chem. Soc.*, **96**, 5967 (1974).
(26) O. F. Zeck, Y. Y. Su, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 156 (1975).
(27) O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y.-N Tang, *J. Am. Chem. Soc.*, **98**, 3474 (1976).
(28) Preliminary information of this work has been reported in, R. A. Ferrieri, E. E. Siefert, M. J. Griffin, O. F. Zeck, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 6 (1977).
(29) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).
(30) T. H. Chao, S. L. Moore, and J. Laane, *J. Organomet. Chem.*, **33**, 157 (1971).
(31) For information concerning the copyrolysis of disilanes see, (a) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969); (b) P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970); (c) E. A. Chernyshev, N. G. Kamalenkov, and S. A. Bashkerova, *Zh. Obshch. Khim.*, **41**, 1175 (1971).
(32) J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, **5**, 729 (1966).
(33) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964); M. Jones, Jr., W. J. Baron, and Y. H. Shen, *ibid.*, **92**, 4745 (1970); U. Burger and R. Huisgen, *Tetrahedron Lett.*, **34**, 3057 (1970).
(34) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).
(35) For a review of methylene reactions and references see, "Carbene Chemistry", W. Kirmse, Ed., 2nd ed, Academic Press, New York, N.Y., 1971, Chapters 8 and 9.
(36) J. Graefe, M. Mühlstadt, and P. Kuhl, *Z. Chem.*, **10**, 192 (1970); **9**, 23 (1969); *Tetrahedron Lett.* 3431 (1969); H. Nozaki, M. Kawanisi, and R. Noyori, *J. Org. Chem.*, **30**, 2216 (1965).

Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711

Substituent Effects upon Dissociation and Migration Reactions of Five-Coordinate Platinum(II) Carbonyl Complexes

NOBUYUKI SUGITA,[†] JOSEPH V. MINKIEWICZ, and RICHARD F. HECK*

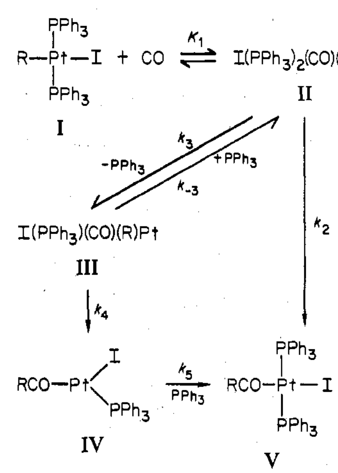
Received March 9, 1978

A series of five iodobis(triphenylphosphine)arylplatinum(II) complexes was prepared and rates of carbonylation in the presence and absence of excess triphenylphosphine were measured. Four related palladium(II) complexes were compared with the platinum complexes. The results are interpreted in terms of a five-coordinated carbonyl intermediate which forms the acylmetal product by two reaction paths—a migratory route and a dissociative route. The migratory reaction is much more sensitive to changes in the electronic character of the migrating group than the dissociative reaction is. The results show that carbon monoxide insertion is not rate limiting in the catalytic carbonylation of aryl halides.

The carbon monoxide insertion reaction is one of the basic reactions of organo-transition-metal compounds. Knowledge of the mechanism of this reaction would be useful in understanding how different ligands affect the reaction course. This information ultimately could lead to new catalysts with optimum activity for various carbonylation reactions.

We undertook a study of the reaction of halobis(triorganophosphine)organoplatinum, -palladium, and -nickel complexes with carbon monoxide with the above goal in mind.[1] With the platinum complexes the reaction was shown to involve a preequilibrium step forming a fluxional five-coordinate carbonyl complex, II, which then reacted by two paths to form the acylplatinum product V. One of the two paths involved a direct migration of the organic group from platinum to the carbon monoxide ligand and the other a dissociation of one of the triorganophosphine groups. In the second process fluxional intermediate III was believed to be formed which then underwent a migration to three-coordinate species IV. A final reassociation of a phosphine ligand gives the observed product. Numerous metal complexes were studied and

Scheme I



considerable knowledge of ligand effects in this reaction was acquired. We now report additional data bearing on how various aryl substituents influence the relative preference of the five-coordinated intermediate for the two reaction paths

† On leave from the Institute for Chemical Research, Kyoto University, Kyoto, Japan.

0020-1669/78/1317-2809$01.00/0

Table I. Kinetic Data for the Reaction of Various Metal Complexes with Carbon Monoxide at 760 mm Pressure

$RPt(PPh_3)_2I$												
R	concn × 10^2, M	$10^2[PPh_3]$, M	T, °C	$10^4 k_{obsd}$, s^{-1}	E_a (k_{obsd}),[a] kcal mol^{-1}	$\Delta S^{\ddagger}$ (k_{obsd}),[b] eu	$10^4 K_1k_2$, atm^{-1} s^{-1}	E_a (K_1k_2),[a] kcal mol^{-1}	$\Delta S^{\ddagger}$ (K_1k_2),[b] eu	$10^4 K_1k_3$, atm^{-1} s^{-1}	E_a (K_1k_3),[a] kcal mol^{-1}	$\Delta S^{\ddagger}$ (K_1k_3),[b] eu
4-$CH_3C_6H_4$–	0.965	0	24	5.00								
	0.731	0	30	5.79	6.2	−54.6						
	0.693	1.05	30	2.20								
	0.715	2.02	30	1.10			1.07	2.7	−70.0	4.72	7.7	−50.4
	0.714	2.90	30	1.04								
	0.725	0	45	9.94								
	0.540	1.51	45	4.77								
	0.688	4.47	45	1.37			1.32			8.62		
	0.652	6.00	45	1.27								
4-$CH_3OC_6H_4$–	0.803	0	20	2.83								
	0.820	3.37	20	1.07								
	0.805	5.93	20	0.420			0.416			2.414		
	0.835	11.2	20	0.413								
	0.753	0	30	5.50	11.7	−36.9						
	0.780	0	30	5.43[c]								
	1.01	3.66	30	0.933			0.925	14.1	−32.6	4.575	11.3	−38.6
	1.05	7.05	30	0.917								
C_6H_5–	0.705	0	20	2.40								
	0.677	0	20	2.40								
	1.17	2.46	20	0.130			0.13			2.27		
	0.691	0	30	4.91	12.6	−34.1						
	0.672	0	30	4.91								
	0.652	3.47	30	0.396			0.394	19.6	−16.1	4.52	12.2	−35.6
	0.683	5.23	30	0.392								
			30	1.72[d]	11.4	−40.1						
4-ClC_6H_4–	0.572	0	35.8	2.48								
	0.808	0	52	6.22								
	0.498	0	52	6.25								
	0.497	3.00	52	0.364			0.362			5.86		
	0.533	4.19	52	0.359								
		0	65.6	12.94[d]								
	0.527	4.74	65.6	1.23			1.22			11.72		
	0.520	6.69	65.6	1.21								
			30				0.045[d]	19.5[b]	−20.7[b]	1.67[d]	11.1[b]	−41.3[b]
4-$CH_3OCOC_6H_4$–	1.11	0	30	0.753	13.0	−36.6						
	1.09	0	44.5	2.20								
		0	52	3.42[d]								
	0.827	4.96	52	0.153			0.149			3.27		
	0.860	7.90	52	0.145								
	1.07	0	65	6.92								
	0.850	3.26	65	0.856								
	0.860	4.98	65	0.341			0.352			6.57		
	0.840	7.70	65	0.363								
			30				0.0267[d]	14.9[b]	−36.9[b]	0.850[d]	11.7[b]	−40.6[b]
			30	0.64[d]	15.5	−28.6						
4-$O_2NC_6H_4$–[e]	1.63	0	24	0.373								

2.37	0	43.2	1.86						
1.66	5.97	43.2	0.615						
1.08	9.00	43.2	0.520	0.510			1.35		
1.14	12.2	43.2	0.500						
1.93	0	55.6	4.93						
1.70	5.17	55.6	2.12	2.16			2.77		
1.69	8.47	55.6	2.20						
		30		0.098^b	23.9^b	-4.6^b	0.542^d	12.7^b	-38.2^b

[a] Slope of ln K_{obsd} vs. $(1/T)K$ plot. [b] Calculated values at 30 °C. [c] P_{CO} 400 mm. [d] Extrapolated values. [e] Bromopalladium complex.

Table II. Rate Constants of the Reaction of Various Palladium Complexes with CO at 2.3 °C in Tetrachloroethane Solution at Atmospheric Pressure

$RPd(PPh_3)_2I$	rate constant $\times 10^4$, s^{-1}	relative rates
$4\text{-}O_2NC_6H_4\text{-}$	$0.28^{a,b}$	1
$4\text{-}CH_3OCOC_6H_4\text{-}$	6.9 ± 0.4	25
$C_6H_5\text{-}$	28 ± 2^a	100
$4\text{-}CH_3OC_6H_4\text{-}$	$>100^a$	>357

[a] Data taken from ref 1. [b] Value calculated by extrapolation assuming an activation energy of 15.4 kcal/mol, the value observed for the 4-trifluoromethylphenyl derivative.[1]

Table III. Rate Constants for the Palladium-Catalyzed Benzoxycarbonylation or Benzamidation of Various Aryl Iodides at 100.0 °C and 1 Atm Pressure[a]

aryl iodide	excess $[PR_3]$, M	nucleophile	rate constant	rel rates
$4\text{-}CH_3OC_6H_4I$	0	$C_6H_5CH_2OH$	$(0.93 \pm 0.18) \times 10^{-4}$	0.4
	0	$C_6H_5CH_2NH_2$	$(1.18 \pm 0.17) \times 10^{-4}$	
C_6H_5I	0	$C_6H_5CH_2OH$	$(2.49 \pm 0.44) \times 10^{-4}$	1.0
	0.36	$C_6H_5CH_2OH$	$(0.081 \pm 0.001) \times 10^{-4}$	
	0	$C_6H_5CH_2NH_2$	$(3.46 \pm 0.22) \times 10^{-4}$	
$4\text{-}CH_3OCOC_6H_4I$	0	$C_6H_5CH_2OH$	$(2.49 \pm 0.23) \times 10^{-4}$	1.0
$2\text{-}CH_3OCOC_6H_4I$	0	$C_6H_5CH_2OH$	$(0.45 \pm 0.05) \times 10^{-4}$	0.2

[a] Reaction conditions: 1 mol % $PdCl_2(PPh_3)_2$, based on halide; relative amounts of reactants, halide 10 mmol, nucleophile 12.5 mmol, base 12.5 mmol. No additional solvent was added.

Table IV. Relative Rates of Reaction of Platinum Complexes with CO at 30.0 °C in Tetrachloroethane Solution at Atmospheric Pressure

R in $RPt(PPh_3)_2I$	K_1k_3,[c] $atm^{-1}\ s^{-1}$	K_1k_2,[d] $atm^{-1}\ s^{-1}$	dissociation/migration
$4\text{-}CH_3OC\text{-}OC_6H_4\text{-}$	1.0^a	1.0^a	32
$4\text{-}ClC_6H_4\text{-}$	1.9^a	1.9^a	32
$C_6H_5\text{-}$	5.3	15	12
$4\text{-}CH_3OC_6H_4\text{-}$	5.4	35	5
$4\text{-}CH_3C_6H_4\text{-}$	5.6	40	5
$2\text{-}CH_3OC\text{-}OC_6H_4\text{-}$	0.1^b	4.4^b	0.7^b

[a] Data calculated from extrapolated rate constants. [b] Calculated at 40.0 °C. [c] Relative rate of dissociation of PPh_3. [d] Relative rate of migration of R to CO.

and some additional information on the reactions of the related palladium(II) complexes.

Results

Platinum Complexes. Five iodobis(triphenylphosphine)arylplatinum(II) complexes were reacted with carbon monoxide, and the reaction rates were measured by gas volume changes in tetrachloroethane solution in the presence of and in the absence of (excess) triphenylphosphine. The data obtained are given in Table I. Good first-order kinetics were observed in all cases between about 5 and 85% reaction. Attempts to use a 4-nitrophenyl derivative were abandoned since the reaction was too slow to observe. In all instances the reaction products were shown to be the corresponding acylplatinum complexes both by the ν_{CO} at 1600–1630 cm^{-1} and by the fact that very close to 1 equiv of CO was absorbed/mol of platinum complex reacted. In these examples with triphenylphosphine ligands there was no clearly detectable accumulation of the five-coordinate intermediate. All reactions were carried out with a series of concentrations of triphenylphosphine to determine the maximum depression of the reaction rate achievable.

Palladium Complexes. The much higher rates of carbonylation of arylpalladium complexes prevented us from obtaining as much data as we did with the platinum compounds. However, substituent effects appeared to be similar. The results are summarized in Table II with some pertinent results obtained previously. Only two values of the ratio of rates of the dissociation to migration paths are known. They are the value of 32 obtained at 2.3 °C for bromobis(triphenylphosphine)phenylpalladium(II)[1] and a value of 4.6 at 43.2 °C obtained for the bromobis(triphenylphosphine)(4-(trifluoromethyl)phenyl)palladium(II) complex.[1] The corresponding iodophenylplatinum complex had a value of 12 at 30 °C.[1]

It has been suggested that the carbon monoxide insertion reaction of arylpalladium complexes is involved in the palladium-catalyzed alkoxycarbonylation[2] and amidation reactions.[3] Therefore it was of interest to see if substituent effects in the catalytic reaction paralleled those of the stoichiometric carbonylation. Catalytic reactions of 4-iodoanisole, iodobenzene, and methyl 4-iodobenzoate were carried out with carbon monoxide, tri-*n*-butylamine, and benzyl alcohol in dimethylacetamide as solvent. Amidations with benzylamine were also carried out with the first two halides. The results are summarized in Table III. The first-order rate constants showed rather large average errors; however, the trends are clear. The substituent effects in the catalytic reaction are remarkably small; all reactions occurred at rates within a factor of 5 of each other and no correlation with the stoichiometric reaction was apparent.

The carbonylation of one platinum complex, iodobis(tri-

Table V. Properties of Platinum Complexes Prepared

R in $R(I)Pt(PPh_3)_2$	mp, °C	% yield	anal. % C calcd	anal. % C found	anal. % H calcd	anal. % H found	anal. % I calcd	anal. % I found	ν_{CO} of carbonylated product, cm^{-1}
$4\text{-}CH_3OCOC_6H_4$-	>250	93	53.83	53.84	3.79	3.90	12.93	12.90	1600
$4\text{-}ClC_6H_4$-	>250	41	52.65	52.89	3.58	3.68	13.24	12.73	1610
C_6H_5-	>250	80	54.61	54.64	3.82	3.83	13.74	13.90	1620
$4\text{-}CH_3OC_6H_4$-	>250	68	54.15	54.29	3.91	4.06	13.31	13.12	1625
$4\text{-}CH_3C_6H_4$-	>230	60	55.08	55.16	3.98	4.06	13.53	13.12	1630

phenylphosphine)-4-anisylplatinum(II), was shown to be first order in carbon monoxide as expected but not established previously.

Discussion of Results

The results of the stoichiometric platinum carbonylations are best discussed in terms of the mechanism proposed previously[1] (Scheme I).

The observed reaction rates can be expressed in terms of the individual steps

$$K_1' = K_1[CO] = [II]/[I] \tag{1}$$

$$d[III]/dt = k_3[II] - k_{-3}[III][PPh_3] - k_4[III] \tag{2}$$

$$d[IV]/dt = k_4[III] - k_5[IV][PPh_3] \tag{3}$$

$$\frac{d[CO]}{dt} = -\frac{d[I]}{dt} \tag{4}$$

$$[I]_0 = [I] + [II] + [III] + [IV] + [V] \tag{5}$$

$$[PPh_3] = [III] + [IV] + [PPh_3]_0 \tag{6}$$

where suffix 0 denotes the initial concentration. If it is assumed that $k_5 >> k_4$ and the steady-state approximation is made for [II], [III], and [IV], then [IV] must be negligible compared with $[III] + [PPh_3]_0$ and eq 6 reduces to $[PPh_3] \approx [III] + [PPh_3]_0$. If the steady-state approximation holds, then [II] + [III] + [IV] must be small compared with [I] + [V] and $[I]_0 \approx [I] + [V]$. It follows that

$$\frac{d[CO]}{dt} = -\frac{d[I]}{dt} \approx \frac{d[V]}{dt} \approx k_4[III] + k_2[II]$$

Substituting $[II] = K_1'[I]$ and letting $d[III]/dt = 0$

$$[III] = \frac{1}{2k_{-3}}\{-(k_{-3}[PPh_3]_0 + k_4) + ((k_{-3}[PPh_3]_0 + k_4)^2 + 4K_1'k_3k_{-3}[I])^{1/2}\}$$

From the fact that $4K_1'k_3k_{-3}[I]/(k_{-3}[PPh_3]_0 + k_4) \approx 10^{-3}$ it follows that $(k_{-3}[PPh_3]_0 + k_4)^2 >> 4K_4'k_3k_{-3}[I]$ and $[III] \approx K_1'k_3[I]/(k_{-3}[PPh_3]_0 + k_4)$; therefore

$$\frac{d[CO]}{dt} = -\frac{d[I]}{dt} \approx \left[\frac{K_1k_3k_4}{dk_{-3}[PPh_3]_0 + k_4} + K_1k_2\right][CO][I]$$

or

$$\ln\frac{[I]_0}{[I]} \approx \left[\frac{K_1k_3k_4}{k_{-3}[PPh_3]_0 + k_4} + K_1k_2\right][CO]t$$

where $[I] = [I]_0 - [CO]_{absorbed}$ and [CO] remains constant. Thus

$$k_{obsd} \approx \left[\frac{K_1k_3k_4}{k_{-3}[PPh_3]_0 + k_4} + K_1k_2\right]$$

The rate constants for the triphenylphosphine suppressed rates then are K_1k_2. The relative values are listed in Table IV. They represent rates of migration of the aryl group from platinum to carbon monoxide. The difference between these values and the unsuppressed rate constants is the rate constant for the triphenylphosphine dissociation path leading to product, essentially K_1k_3. The ratios of the dissociative rate constants to the migratory rates are k_3/k_2. These values are listed in Table IV along with relative rate constants for both reaction paths. It is clear that rates of dissociation are considerably less sensitive to changes in the electronic character of the σ-bonded aryl group than the migratory rates are. The selectivity of dissociation relative to migration decreases from 32 to 5 as the para substituent becomes more electron donating going from 4-carbomethoxy or 4-chloro to 4-methoxyl or 4-methyl. A plot of log (K_1k_2) against the σ value gives a ρ for the aryl migration reaction of −3.6 at 30 °C.

The aryl group may be migrating as an anion as in the 1,2 shifts in carbon compounds but with much smaller rate effects from the substituent. This cannot yet be concluded, however, since we do not know how changing the electronic character of the aryl group influences the composition of the equilibrium mixture of five-coordinate intermediate complexes. Undoubtedly, different isomers will show different preferences for the two reaction paths. If the transition state most resembles a square pyramid,[4] 11 isomeric forms of the intermediate are possible. Of these it would seem reasonable to assume that only complexes with apical triphenylphosphine groups will dissociate and only isomers with cis aryl and carbonyl groups can undergo the migration reaction.

Activation energies and entropies for the carbonylation reactions are shown in Table I. The values vary widely from compound to compound as might be anticipated from the complex nature of the reactions.

Stoichiometric carbonylation data for one palladium complex, bromobis(triphenylphosphine)(4-nitrophenyl)palladium(II), is also given in Table I. The $k_3{:}k_2$ value is 6.3 at 30 °C, about a fifth of the value 32 found for the platinum complexes with electron-withdrawing para substituents in the aryl group at the same temperature. Other palladium complexes with less electron-withdrawing substituents were too reactive to be measured in our apparatus at temperatures where they had sufficient solubility.

The absence of a correlation for different substituents between the stoichiometric CO insertion and the catalytic carbonylation of aryl halides demonstrates that the insertion of CO is not rate determining in the catalytic reaction if it is involved.

Experimental Section

Materials. Tetrachloroethane (Aldrich) was washed with aqueous potassium carbonate and with water until the washings were neutral and dried over molecular sieves. The preparation of iodobis(triphenylphosphine)(4-nitrophenyl)palladium was described previously.[1] Platinum complexes were prepared as described below. Triphenylphosphine was a product of the Ventron Corp. and it was used without further purification.

Tetrakis(triphenylphosphine)platinum(0). To a solution of 6.55 g (0.025 mol) of triphenylphosphine in 50 mL of warm absolute ethanol was added under argon a solution of 2.59 g (0.005 mol) of chloroplatinic acid hexahydrate dissolved in 7 mL of absolute ethanol. After about 5 min of stirring, 15 mL of 85% hydrazine hydrate was added. The milky solution immediately turned yellow and the product crystallized. After the mixture was cooled to room temperature, the product was filtered and washed with warm ethanol, with cold water, and finally with cold ethanol. After drying was done under reduced pressure, 5.88 g (92%) of the product was obtained.

General Procedure for Preparation of Platinum Complexes. A two- to threefold excess of aryl halide was stirred with a solution of the tetrakis(triphenylphosphine)platinum(0) complex in benzene (2.4 g in 35 mL was generally used). The clear solutions were stirred at room temperature for about 3 h and heated at reflux temperature for about 2 h more. On cooling of the mixtures, the yellow-orange crystalline products were separated by filtration, washed with ether, and dried under reduced pressure. Yields were 40–90% of theory. Analyses and melting points are given in Table V. The ν_{CO} observed in the carbonylation product is also listed (Table V).

Acknowledgment. This research was supported by a grant from the National Science Foundation. We thank Dr. N. Cortese for preparing most of the complexes and Matthey Bishop, Inc., for the loan of the chloroplatinic acid used in this study.

Registry No. 4-$CH_3OCOC_6H_4(I)Pt(PPh_3)_2$, 67226-47-5; 4-$ClC_6H_4(I)Pt(PPh_3)_2$, 67254-03-9; $C_6H_5(I)Pt(PPh_3)_2$, 67254-04-0; 4-$CH_3OC_6H_4(I)Pt(PPh_3)_2$, 67254-05-1; 4-$CH_3C_6H_4(I)Pt(PPh_3)_2$, 67254-06-2; 2-$CH_3OCOC_6H_4Pt(PPh_3)_2I$, 67226-48-6; 4-$O_2NC_6H_4Pd(PPh_3)_2Br$, 67254-07-3; 4-$O_2NC_6H_4Pd(PPh_3)_2I$, 67254-08-4; 4-$CH_3OCOC_6H_4Pd(PPh_3)_2I$, 67226-49-7; 4-$CH_3OC_6H_4I$, 696-62-8; C_6H_5I, 591-50-4; 4-$CH_3OCOC_6H_4I$, 619-44-3; 2-$CH_3OCOC_6H_4I$, 610-97-9; $C_6H_5CH_2OH$, 100-51-6; $C_6H_5CH_2NH_2$, 100-46-9; $PdCl_2(PPh_3)_2$, 13965-03-2; CO, 630-08-0.

References and Notes

(1) P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc.*, **98**, 4115 (1976).
(2) A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).
(3) A. Schoenberg and R. F. Heck, *J. Org. Chem.*, **39**, 3327 (1974).
(4) A. D. English, P. Meakin, and J. P. Jesson, *J. Am. Chem. Soc.*, **98**, 7590 (1976).

Contribution from the Istituto di Chimica Fisica, the University, Messina, Italy, and Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione del C. N. R., Istituto di Chimica Industriale, the University, Padova, Italy

Mechanism of Electrophilic Cleavage of the Platinum–Carbon Bond in Platinum(II)–Diaryl Complexes

R. ROMEO,* D. MINNITI, S. LANZA, P. UGUAGLIATI,* and U. BELLUCO

Received October 16, 1977

A kinetic study is described of the electrophilic cleavage by the proton of one Pt–C σ bond in complexes of type *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ (Y = *p*-NMe_2, *p*-Me, *p*-OMe, H, *m*-OMe, *p*-F, *p*-Cl, *m*-F, *o*-Me, *o*-Et, *m*-CF_3) yielding *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ and YC_6H_5 in methanol and aqueous methanol. Electron-releasing substituents in the platinum-bonded aromatic rings increase the rates of electrophilic attack and a fairly good LFER is observed on plotting log k_{rel} vs. the Hammett σ parameter of the substituent Y in both solvents. Steric retardation occurs when the Pt–C bond is crowded by a neighboring ortho group. A large (ca. 6) kinetic isotope effect is observed on carrying out the Pt–C bond cleavage with DCl in $MeOD/D_2O$ (90/10% v/v). The rates decrease with increasing water content of the solvent mixture. A mechanism is proposed which involves rate-determining direct attack of the proton on the Pt–C bond with release of YC_6H_5 in a three-center transition state. The resulting transient intermediate may be either converted to *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ by scavenging chloride ion (if present) or isomerized to *trans*-$[Pt(PEt_3)_2(YC_6H_4)S]^+$ in the absence of good nucleophiles (S = solvent). The mechanism is discussed within the framework of general acidolysis of metal–carbon bonds in organometallic compounds.

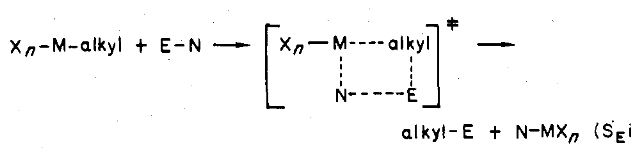
Introduction

The cleavage of non-transition-metal–carbon bonds (*demetalation*) has been extensively investigated and its mechanism elucidated in detail.[1] When alkyl groups are being cleaved in a bimolecular process, electrophilic substitution at the saturated carbon may take place via an open transition state (S_E2). A cyclic mechanism (S_Ei) may also occur through

$$X_n\text{–M–alkyl} + \text{E–N} \rightarrow [X_n\text{–}\overset{\delta+}{\text{M}}\cdots\overset{\delta-}{\text{alkyl}}\cdots\text{E}\cdots\text{N}]^{\ddagger} \rightarrow \text{alkyl–E} + \text{N}^- + \text{MX}_n^+ \quad (S_E2)$$

E = electrophilic end } of the reagent
N = nucleophilic end }

a cyclic transition state by concurrent attack of the two ends of the reagent on the polarized metal–carbon bond. This



mechanistic view applies particularly to the cleavage of the metal–carbon bond in group 2B and 4B organometallics. In particular, for protonolysis reactions the driving force of the electrophilic attack is in any case the rate-determining proton transfer to the substrate. The extent of interaction of the proton with the alkyl group and of the nucleophile with the metal will depend on the charge separation being developed on both the cleaved group and the metal moiety, as well as

*To whom correspondence should be addressed: R.R., Messina; P.U., Padova.

