(6) M. A. Cohen and T. L. Brown, Abstracts of Papers, 170th National Meeting of the American Chemical Society, 1975.
(7) W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organomet. Chem.*, **66**, C11 (1974).
(8) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).
(9) (a) K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10**, 101 (1967); (b) K. Noack, *ibid.*, **12**, 181 (1968).
(10) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **97**, 1261 (1975).
(11) A complete analysis of the vibrational spectrum is currently in progress elsewhere. I. S. Butler and C. F. Shaw III, to be submitted for publication.
(12) B. D. Dombek and R. J. Angelici, submitted for publication.
(13) M. Poliakoff, private communication.
(14) (a) A. Berry and T. L. Brown, *Inorg. Chem.*, **11**, 1165 (1972); (b) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3380 (1975).
(15) R. J. Angelici, *Organomet. Chem. Rev.*, **3**, 173 (1968).
(16) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 6048 (1971).
(17) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).
(18) J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner and R. F. Turner, *J. Am. Chem. Soc.*, **97**, 4805 (1975), and references therein.
(19) J. M. Kelley, D. V. Bent, H. Hermann, D. Schulte-Frohlinde, and E. K. von Gustorf, *J. Organomet. Chem.*, **69**, 259 (1974).
(20) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972).
(21) (a) R. Hoffman, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972); (b) A. R. Rossi and R. Hoffman, *Inorg. Chem.*, **14**, 365 (1975).
(22) L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, **10**, 78 (1971).
(23) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).
(24) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **96**, 7568 (1974).
(25) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974).
(26) G. Michels and H. Svec, to be submitted for publication.
(27) (a) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 1068 (1970); (b) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3482 (1970); (c) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).
(28) R. K. Pomeroy and W. A. G. Graham, *J. Am. Chem. Soc.*, **94**, 274 (1972).
(29) (a) E. O. Fischer, H. Fischer, and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11**, 644 (1972); (b) H. Fischer, E. O. Fischer, and H. Werner, *J. Organomet. Chem.*, **73**, 331 (1974).
(30) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, p 192.
(31) (a) H. A. C. McKay, *Nature (London)*, **142**, 997 (1938); (b) *J. Chem. Soc.*, **65**, 702 (1943).
(32) H. Werner and R. Prinz, *Chem. Ber.*, **99**, 3582 (1966).
(33) The broadness of the absorptions of $W(CO)_4(CS)I^-$ dissolved in polar solvents prevented a reliable determination of its ^{13}CO content. Hence the compound was converted to $W(CO)_5(CS)$ and studied in a hydrocarbon solvent where the absorptions are very sharp.
(34) J. E. Pardue, M. N. Memering, and G. R. Dobson, *J. Organomet. Chem.*, **71**, 407 (1974).
(35) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
(36) H. D. Murdoch and R. Henzi, *J. Organomet. Chem.*, **5**, 166 (1966).
(37) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).
(38) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, p 157.
(39) A. D. Allen and P. F. Barrett, *Can. J. Chem.*, **46**, 1649 (1968).

The Mechanism of Carbonylation of Halo(bis ligand)organoplatinum(II), -palladium(II), and -nickel(II) Complexes

Philip E. Garrou and Richard F. Heck*

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

Received September 8, 1975

Abstract: Rates of reaction of a variety of halo(bisphosphorus ligand)organoplatinum(II), -palladium(II), and -nickel(II) complexes with carbon monoxide to form acylmetal derivatives have been measured. Pseudo-first-order kinetics were observed in most instances from ca. 15 to 85% reaction. The effects of changing ligands and the metal upon the observed rate constants and $\Delta S^{\ddagger}$ are noted. In all cases the reaction rates decreased when excess ligand was present. The rate depressions reached a maximum value and thereafter remained constant with further increases in ligand concentration. Triarylphosphine ligands with electron donating substituents produced stepwise reactions and in the most favorable cases four separate steps were distinguishable. Rate constants and $\Delta S^{\ddagger}$ values were obtained where possible. These data are interpreted in terms of formation of an initial five-coordinate intermediate, $(XL_2R(CO)M)$, detectable in several cases and isolable in one, which reacts by two possible paths: (1) a dissociation route forming XL(CO)RM inhibited by excess ligand and (2) a migratory route forming XL(RCO)M which is not inhibited by excess ligand. The mechanism proposed is related to the ligand replacement reaction of square planar complexes. The kinetic analysis indicates the complicated nature of the observed (overall) rate constants and related $\Delta S^{\ddagger}$'s and why these data by themselves are very difficult to interpret.

Numerous carbonylation reactions are known which are catalyzed by platinum, palladium, and nickel complexes.[1] A typical example is the palladium catalyzed conversion of aryl halides into esters.[2] Although no previous, detailed studies have been reported, a possible mechanism for this reaction consists of the following four major steps: (A) Oxidative addition of ArX to a palladium(0) complex previously formed by in situ reduction of a palladium(II) complex initially added; (B) insertion of CO into the aryl–palladium bond forming an acyl–palladium complex; (C) alcoholysis of the latter product to ester and a hydridopalladium species; (D) regeneration of the catalyst by decomposition of the hydridopalladium complex back to the palladium(0) species and HX. The HX is then neutralized by the tertiary amine also present. The scheme below is the suggested reaction course.[2]

$$[(X)_2(PPh_3)_2Pd + CO + 2n\text{-BuOH} \rightarrow (n\text{-BuO})_2CO + 2HX + (CO)(PPh_3)_2Pd]$$

$$(CO)(PPh_3)_2Pd + RX \rightarrow (X)(PPh_3)_2(R)Pd + CO \quad (A)$$

$$(X)(PPh_3)_2(R)Pd + CO \rightarrow (X)(PPh_3)_2(RCO)Pd \quad (B)$$

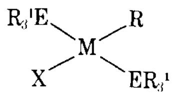
$$(X)(PPh_3)_2(RCO)Pd + n\text{-BuOH} \rightarrow RCOOBu\text{-}n + (H)(X)(PPh_3)_2Pd \quad (C)$$

$$(H)(X)(PPh_3)_2Pd + CO \rightarrow (CO)(PPh_3)_2Pd + HX \quad (D)$$

$$[HX + n\text{-Bu}_3N \rightarrow n\text{-Bu}_3NH^+X^-]$$

$$X = \text{halide}$$

Table I. Analyses and Spectral Data of the Metal Complexes Prepared

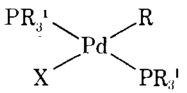


No.	E	R'	M	X	R	Mp, °C dec (reported)	% C (theor)	% H (theor)	% other (theor)	^{1}H NMR^a τ, J_{P-H}, J_{Pt-H} (Hz)	^{31}P[H^1]NMR^b δP, J_{Pt-P} (Hz)	ν_{CO} (cm^{-1})	Method of prep^c
1	P	C_6H_5	Pd	Cl	C_6H_5	240–243 (240)^d	67.74 (68.25)	4.84 (4.74)			−23.7		I
2	P	C_6H_5	Pd	Cl	4-CNC_6H_4	225–228 (224–226)^e			Cl 4.55 (4.63)				I
3	P	C_6H_5	Pd	Cl	4-$NO_2C_6H_4$	189–190 (193–196)^e			Cl 4.52 (4.34) N 1.94 (1.72)				I
4	P	C_6H_5	Pd	Br	C_6H_5	178–180 (216–220)^e	63.89 (64.00)	4.46 (4.47)	Br 10.09 (10.20)		−23.5		I
5	P	C_6H_5	Pd	Br	4-MeC_6H_4	152–156	64.47 (64.72)	4.74 (4.63)		8.5 (CH_3)			I
6	P	C_6H_5	Pd	Br	4-CNC_6H_4	204–208	62.56 (63.78)	4.17 (4.20)					I
7	P	C_6H_5	Pd	Br	4-$CF_3C_6H_4$	175–177	56.91 (57.75)	3.64 (3.99)					I
8	P	C_6H_5	Pd	Br	4-$NO_2C_6H_4$	150–154	60.28 (60.87)	4.19 (4.23)					I
9	P	C_6H_5	Pd	I	C_6H_5	180–182 (171–186)^f	60.27 (60.64)	4.01 (4.21)			−22.8		I
10	P	C_6H_5	Pd	I	4-$MeOC_6H_4$		50.68 (49.94)	4.52 (4.30)		6.7 (OCH_3)			I
11	P	C_6H_5	Pd	I	4-$NO_2C_6H_4$	191–194 (192–196)^e	57.14 (57.53)	3.94 (3.88)					I
12	P	C_6H_5	Pd	I	Me	150–155 (151–154)^d	57.62 (57.74)	4.24 (4.29)		9.7 (CH_3); J_{P-H}, 6.0			I
13	P	C_6H_5	Pd	Br	$C_6H_5CH_2$	124–130^f	64.15 (64.74)	4.37 (4.64)		7.2 (CH_2)			I
14	P	C_6H_5	Pd	Br	4-$NO_2C_6H_4CH_2$	131–133	60.70 (61.21)	4.14 (4.27)					I
15	P	CH_3CH_2	Pd	Br	C_6H_5	88–91	57.94 (58.06)	9.62 (9.48)			−12.4		I
16	P	4-$CH_3C_6H_4$	Pd	I	C_6H_5	147–151	63.29 (62.54)	5.03 (5.13)					I
17	P	C_6H_5	Pd	Br	C_6H_5CO	*g*	63.30 (63.55)	4.25 (4.31)				1650	III
18	P	C_6H_5	Pd	I	C_6H_5CO	*g*	56.80 (57.08)	3.92 (3.87)			−19.0		III
19	P	C_6H_5	Pd	Br	4-CNC_6H_4CO	*g*	62.75 (63.01)	4.00 (4.06)				1653	III
20	P	C_6H_5	Pd	Br	4-$NO_2C_6H_4CO$	*g*	58.93 (59.86)	3.85 (3.94)				1649	III
21	P	C_6H_5	Pd	Br	4-$CF_3C_6H_4CO$	*g*	59.40 (59.93)	3.71 (3.86)				1654	III
22	P	C_6H_5	Pd	Br	$C_6H_5CH_2CO$	*g*	63.40 (63.92)	4.25 (4.47)				1696	III
23	P	CH_3CH_2	Pd	Br	C_6H_5CO	*g*	42.89 (43.59)	6.56 (6.69)					III
24	P	C_6H_5	Pd	I	CH_3CO	*g*	56.84 (57.21)	3.99 (4.14)		8.45 (CH_3)			III
25	P	C_6H_5	Pt	I	C_6H_5	>250	53.90 (54.60)	3.80 (3.79)			−21.8		I, II
26	P	C_6H_5	Pt	Br	C_6H_5	>225	57.12 (57.53)	3.92 (3.99)			J_{Pt-P}, 3088.4		II
27	P	C_6H_5	Pt	I	4-$MeOC_6H_4$	>250	53.87 (54.14)	3.79 (3.88)					I, II
28	P	C_6H_5	Pt	I	4-ClC_6H_4	>250	43.42 (43.89)	3.47 (3.55)					II
29	P	C_6H_5	Pt	I	4-$NO_2C_6H_4$	>250	52.14 (52.07)	3.59 (3.51)					II
30	P	C_6H_5	Pt	Br	$C_6H_5CH_2$	202–205	57.75 (58.04)	4.19 (4.16)			−26.2; J_{Pt-P}, 3253.2		I
31	P	C_6H_5	Pt	Cl	Me	>250	57.66 (57.74)	4.34 (4.29)			−29.3; J_{Pt-P}, 3147.5		II
32	P	C_6H_{11}	Pt	Cl	C_6H_5	>250	57.76 (57.73)	7.74 (7.44)					II
33^h	P	OC_6H_5	Pt	Cl	C_6H_5	152–156	54.25 (54.37)	3.75 (3.78)			−89.2 ABX		II
34	P	4-$CF_3C_6H_4$	Pt	I	C_6H_5	254–257	42.86 (43.28)	2.25 (2.18)					II
35	P	4-$CF_3C_6H_4$	Pt	Cl	CH_3	>250	44.45 (43.84)	2.24 (2.29)		(CH_3), J_{P-H} 6.2			II
36	P	4-$CF_3C_6H_4$	Pt	I	CH_3	>225				J_{Pt-H}, 75.6			II
37	P	4-$Me_2NC_6H_4$	Pt	I	C_6H_5	>225	53.91 (54.87)	5.36 (5.50)		7.1 (CH_3)	−17.49; J_{Pt-P}, 2966.3		II
38	P	4-$MeOC_6H_4$	Pt	I	C_6H_5	247–250	53.25 (52.80)	4.47 (4.31)		6.45 (OMe)	−18.29; J_{Pt-P}, 3036.9		II
39	P	4-MeC_6H_4	Pt	I	CH_3	215–220	54.33 (54.37)	4.72 (4.74)			−25.9; J_{Pt-P}, 3017		II
40	P	4-MeC_6H_4	Pt	I	C_6H_5	>225	56.68 (56.86)	4.67 (4.63)		7.7 (CH_3)	−20.71; J_{Pt-P}, 3056.6		II

41	P	4-MeC_6H_4	Pt	I	4-MeOC_6H_4	>225	55.81 (56.31)	4.63 (4.70)				II
42	P	4-MeC_6H_4	Pt	I	4-MeC_6H_4	>225	56.92 (57.20)	4.81 (4.77)				II
43	P	4-MeC_6H_4	Pt	I	4-ClC_6H_4	>225	54.75 (54.96)	4.27 (4.39)				II
44	As	C_6H_5	Pt	I	C_6H_5		49.76 (50.05)	3.39 (3.48)				II
45	Sb	C_6H_5	Pt	I	C_6H_5	190–197	44.21 (45.70)	2.96 (3.17)				II
46	P	C_6H_5	Pt	I	C_6H_5CO	*g*	54.45 (54.30)	3.88 (3.68)		−16.9; J_{Pt-P}, 3325.5	1612	III
47	P	C_6H_5	Pt	I	4-MeOC_6H_4CO	*g*	53.99 (53.82)	3.82 (3.77)	6.32 (OCH_3)			III
48	P	C_6H_5	Pt	I	4-ClC_6H_4CO	*g*	53.01 (52.39)	3.69 (3.45)				III
49	P	C_6H_5	Pt	I	4-$NO_2C_6H_4$CO	*g*	53.81 (54.21)	3.29 (3.41)				III
50	P	C_6H_5	Pt	Br	$C_6H_5CH_2CO$	*g*	57.33 (57.64)	3.94 (4.03)	7.0 (CH_2) J_{P-H} <3			III
51[h]	P	OC_6H_5	Pt	Cl	C_6H_5CO	*g*				−91.2 (AB)	1643	III
52	P	C_6H_5	Pt	I	CH_3CO	*g*	50.98 (51.34)	3.86 (3.71)				III
53	P	4-MeOC_6H_4	Pt	I	C_6H_5CO	*g*	52.68 (51.72)	4.42 (4.13)		−13.34; J_{Pt-P}, 3231	1625	III
54	P	4-MeOC_6H_4	Pt	Cl	CH_3CO	*g*	64.81 (63.95)	5.97 (5.71)	6.2 (OMe) J_{Pt-H} 81 10.1 (Me) J_{P-H} 6.3	−17.0; J_{Pt-P}, 3413	1633	III
55	P	4-$CF_3C_6H_4$	Pt	Cl	CH_3CO	*g*	43.87 (43.18)	2.45 (2.24)				III
56	P	C_6H_5	Pt	Br	$C_6H_5CH_2CO$	*g*	54.18 (54.83)	3.29 (3.74)		−19.4; J_{Pt-P}, 3451.7	1662	III
57	P	4-MeC_6H_4	Pt	I	C_6H_5CO	*g*	56.28 (56.48)	4.50 (4.51)				III
58	P	C_6H_5	Ni	Cl	C_6H_5	121–123 (122–123)[i]						I
59	P	C_6H_5	Ni	Br	C_6H_5	119–121 (124–125)[i]				−28.9		I
60	P	C_6H_5	Ni	I	C_6H_5	115–118						I
61	$Cl(PPh_2Me)_2(C_6H_5)Pt$					182–183	54.43 (54.31)	4.32 (4.38)	8.38 (CH_3) J_{P-H} 4 J_{Pt-H} 33	−8.9; J_{Pt-P}, 3010		II
62	$Cl(PPh_2Me)_2(C_6H_5CO)Pt$					168–171	53.81 (53.92)	3.76 (4.22)	8.18 (CH_3) J_{P-H} 4, J_{Pt-H} 35	−5.52; J_{Pt-P}, 3218.2	1625	III

[a] In $CDCl_3$ vs. $Me_4Si = 10\tau$. [b] δP vs. 85% H_3PO_4, downfield shifts being negative. [c] Methods of preparation: (I) $(PR'_3)_4M + RX$, (II) $X(COD)(R)Pt + 2PR'_3$, (III) $X(PR'_3)_2(R)M + CO$. [d] Reference 18. [e] Reference 15. [f] Reference 19. [g] Decarbonylates and decomposes at temperature of corresponding alkyl or aryl. [h] Cis isomer.

Table II. The Effect of Ligands on k_{obsd} with Pd Complexes[a]



X	Cl	Cl	Br	Br	Br	Br	Br	Br	Br	I	I	I	I
R	*p*-NCC_6H_4-	*p*-$NO_2C_6H_4$–	Ph–	*p*-tol–	*p*-NCC_6H_4–	*p*-$CF_3C_6H_4$	4-$NO_2C_6H_4$–	$C_6H_5CH_2$–	Ph–	Ph–	*p*-An–	*p*-$NO_2C_6H_4$–	Me–
PR'_3	PPh_3	PPh_3	PPh_3	PPh_3	PPh_3	PPh_3	PPh_3	PPh_3	PEt_3	PPh_3	PPh_3	PPh_3	PPh_3
No. of Complex	**2**	3	4	**5**	6	7	8	13	**15**	9	**10**	11	12
10^4k_{obsd} at 43.2 °C, s^{-1}	2.10	1.15	—	—	4.10	9.65	1.86	—	—	—	—	10.7	—
10^4k_{obsd} at 2.3 °C, s^{-1}	—	—	35	>100	—	—	—	>100	0.25	28.3	>100	—	>100
Rel k_{obsd} at 43.2 °C													
$\Delta S^{\ddagger}$	—	—	—	—	−22.8	−29.7	—	—	2.4	—	-	—	—

[a] Measured under 1 atm of CO in tetrachloroethane solution.

We have chosen to investigate in detail the process by which halo(bis ligand)organoplatinum, -palladium, and -nickel complexes react with CO. An early study on (X)$(PEt_3)_2(Me)Pd$ revealed that carbonylation occurred to form acyl derivatives at 25° with 1 atm of CO in 24 h, whereas for $(X)(PEt_3)_2(Me)Pt$, 90° and 80 atm of CO were needed.[3] Although no reaction mechansim was then proposed, others[4,5] have noted that $(X)(CO)(PR_3)_2(R)M$ (M = Pd or Pt) is a likely intermediate. A survey of the literature reveals a general lack of information on how the nature of R and the nature of ancilliary ligands affect the rate of CO insertion.[4] To our knowledge, no comparative studies of this reaction have been carried out for complexes with the same ligands for even two members of a given triad. Only one related quantitative study appears to have been published. This was a kinetic study of the conversion of $Cl(CO)(PPh_3)(CH_3)Pt$ into acyl derivatives.[6]

After initiating this work, it became clear why such a fundamental reaction probably had not been reported upon previously. The reaction has turned out to involve multiple reaction paths and various intermediates. Without the fortuitous discovery that certain substituted phosphine complexes would allow accumulation of identifiable intermediates, substantial progress in determining the reaction course would not have been made.

Results

Preparation of Complexes. The complexes prepared for this study are listed in Table I along with analytical results, melting points, infrared and NMR spectral data, and the methods of preparation. The preparations were generally either by the reaction of halo(1,5-cyclooctadiene)arylplatinum with phosphines or by the oxidative addition reaction from zero valent organophosphine compounds.

$$X(COD)(R)Pt + 2PR^1_3 \rightarrow X(PR^1_3)_2(R)Pt + COD$$

$$COD = 1,5\text{-cyclooctadiene}$$

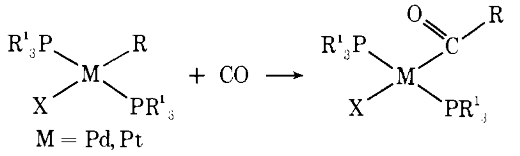
$$(PR^1_3)_4M + RX \rightarrow (X)(PR^1_3)_2(R)M + 2PR^1_3$$

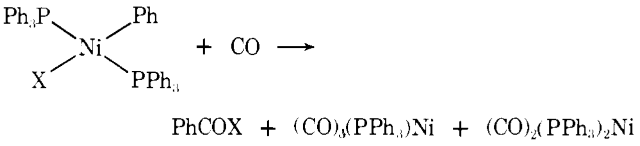
Previous reports of oxidative addition reactions of Ni,[7] Pd,[8] and Pt[9] have been made but in only one instance have qualitative data regarding substituent effects in the aryl halide additions been reported.[8] In this work we have examined a wider range of reactants and qualitatively observed the following orders of decreasing ease of oxidative addition of aryl halides: Ni > Pd > Pt; PhI > PhBr > PhCl; p-NO_2 > p-CN > p-CF_3 > H > p-Me > p-OCH_3.

Carbonylations. Initial investigations of the rates of carbonylation of *trans*-$Br(PPh_3)_2(Ph)Pd^{II}$, complex **4**, and *trans*-$I(PPh_3)_2(Ph)Pt^{II}$, complex **25**, in tetrachloroethane solution at 1 atm of CO revealed that pseudo-first-order kinetics were followed between ca. 15 and 85% reaction, measuring the rates of gas absorption. Below ca. 15% reaction the "first-order constants" increased rapidly. A variety of related complexes with different halo, organophosphine, and aryl (or benzyl or methyl) groups were investigated. Most of these behaved similarly to the above compounds in the carbonylation reaction. With only three exceptions, all of the palladium and platinum complexes absorbed 1 equiv of CO and gave only the corresponding acylmetal derivatives as final, isolable products. One exception to the general result was found with *trans*-chloro[bis(tricyclohexylphosphine)]phenylplatinum(II), complex **32,** which on carbonylation in a very slow reaction produced only the ligand replacement product, chlorocarbonyltricyclohexylphosphinephenylplatinum(II), complex **63,** even at elevated temperatures.

$$\underset{\mathbf{32}}{Cl[P(C_6H_{11})_3]_2(Ph)Pt} + CO \rightarrow \underset{\mathbf{63}}{Cl(CO)[P(C_6H_{11})_3](Ph)Pt} + P(C_6H_{11})_3$$

The second exception to forming an acylmetal product was with complex **37** which will be discussed later. A third exception was with chlorobis(triphenylphosphine)phenylpalladium(II), complex **1,** which only absorbed 56% of 1 mol of CO at 20° and 1 atm apparently giving an equilibrium mixture of **1** and the benzoyl palladium derivative. This complex was not investigated further. In contrast, the three related nickel complexes, subsequently prepared and carbonylated, complexes **58, 59,** and **60,** absorbed between 3.5 and 3.7 equiv of CO per mole of complex in pseudo-first-order reactions producing acyl halides and mixtures of tricarbonylmonophosphine- and dicarbonyldiphosphinenickel complexes. No evidence for intermediate acylnickel complexes could be obtained by ir. A similar result has just been reported by Corain and Favevo.[10]

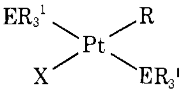




A selection of the rate constants obtained in the carbonylation of a variety of substituted palladium complexes of the type $X(PR^1_3)_2(R)Pd$ is shown in Table II. While we do not have sufficient data to compare all of the complexes quantitatively, several qualitative observations can be made. Electron withdrawing, para substituents in the phenyl attached directly to the palladium decrease the reaction rate and electron supplying groups increase it compared with the unsubstituted phenyl compounds, **4** or **9.** In two cases (more will be discussed below) changing halide groups on the palladium had little effect upon the rate (less than a factor of two). The methyl- and benzylpalladium derivatives are considerably more reactive than the phenyl complexes, **4** or **9.** The triethylphosphine ligand in complex **15** reduces the rate of carbonylation compared with the related triphenylphosphine derivative by a factor of 140 at 2.3 °C. The $\Delta S^{\ddagger}$ for three of the reactions are −22.8, −29.7, and +2.4 eu; a wide range for presumably similar reactions.

A related series of carbonylation rates of platinum complexes is given in Table III. Data are sufficient to quantitatively compare these complexes. Again electron withdrawing para-substituents in the phenyl σ bonded to the metal decrease the rates of carbonylation and electron supplying groups increase them: 4-nitro:H:4-CH_3O = 0.005:1.0:4.0. The iodo and chloro complexes **36** and **35** again show the minor effect of changing the halogen group. The cis triphenyl phosphite complex **33** is similar in reactivity to the related trans PPh_3 derivative **25** if halide differences are assumed minor. The methyldiphenylphosphine ligand in **61** substantially deactivates compared with PPh_3 in **25,** again assuming the halide difference will be minor. The complexes with triphenylarsine (**44**) and triphenylstibine (**45**) reacted too rapidly to measure. They were at least 30 times more reactive than the corresponding PPh_3 complex, **25.** In many instances the low solubilities of the complexes prevented measuring the rates at low temperatures.

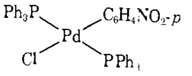
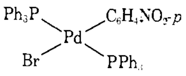
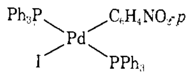
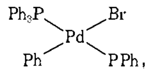
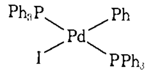
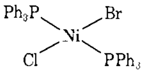
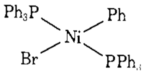
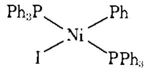
Table III. The Effect of Ligands on k_{obsd} with Pt Complexes[a]



X	I	I	I	I	I	I	Cl	Cl	Cl
R	Ph	Ph	Ph	Me	p-An	p-$NO_2C_6H_4$	Me	Ph	Ph
ER^1_3	PPh_3	$AsPh_3$	$SbPh_3$	$P(p\text{-}CF_3C_6H_4)_3$	PPh_3	PPh_3	$P(p\text{-}CF_3C_6H_4)_3$	$P(OPh)_3$[b]	PPh_2Me
No. of Complex	25	44	45	36	27	29	35	33	61
10^4k_{obsd} at 20 °C, s^{-1}	3.72	>100	>100	2.87	16.19[c]	0.017[c]	4.24	—	—
10^4k_{obsd} at 43.6 °C, s^{-1}	21.8[c]	>>100	>>100	—	—	—	18.93	4.11	0.31
Rel k_{obsd} at 20 °C	1.0	>30.	>30.	0.8	4.4	0.005	1.1	0.9[d]	0.014[d]

[a] Measured under 1 atm of CO in tetrachloroethane solution. [b] Cis isomer. [c] Extrapolated value. [d] Estimated assuming same $\Delta E^{\ddagger}$ as found for 25.

Table IV. The Effect of Halogen on k_{obsd}[a]

Compound	 3	 8	 11
10^4k_{obsd} at 43.2 °C, s^{-1}	1.15	1.86	10.7
Compound	—	 4	 9
10^4k_{obsd} at 2.3 °C, s^{-1}	—	35.	28.
Compound	 58	 59	 60
10^4k_{obsd} at 2.3 °C, s^{-1}	22.	22.	30.–98.[b]

[a] Measured under 1 atm of CO in tetrachloroethane solution. [b] First-order rate constants increased with time.

Further comparison of complexes differing only in the halogen attached to the metal is shown in Table IV. The largest factor observed was about 9, between chloride **3** and iodide **11**. The iodonickel complex **60** failed to give good first-order kinetics but it is clearly not very much more reactive than the related chloro and bromo derivatives.

In order to determine if dissociative or associative reaction paths were involved in the carbonylation reactions, rates were measured in the presence of tetraethylammonium halides and also in the presence of an excess of the phosphine ligand contained in the complexes. Relatively large amounts of tetraethylammonium halides had no significant effect upon the carbonylation rates as judged by results obtained with complexes **4**, **25**, and **30**. Other related experiments, to be described below, also showed no halide ion effect on the rates. Excess common ligand, however, did appreciably decrease rates in all of the 13 cases examined including complexes of Pd, Pt, and Ni. The kinetics of the carbonylations with excess common ligand were also pseudo first order in starting complex under 1 atm of CO. Increasing concentrations of the ligand had a decreasing effect upon the rate constants and finally at about 0.03–0.30 M ligand, depending upon the complex, the constants no longer decreased with increasing ligand concentration. The totally depressed rate constants varied from at least 0.3 to about 0.03 times the rate constants obtained in the absence of excess ligand. Figure 1 illustrates the effect of adding triphenylphosphine to complex **4**, on the carbonylation rates. The totally depressed rate is about 26 times slower than without excess ligand. The exact rate constant without ligand added was too fast to measure in this instance with our apparatus, but was estimated by assuming $\Delta E^{\ddagger}$ was approximately the same as found for the excess ligand-depressed reaction.

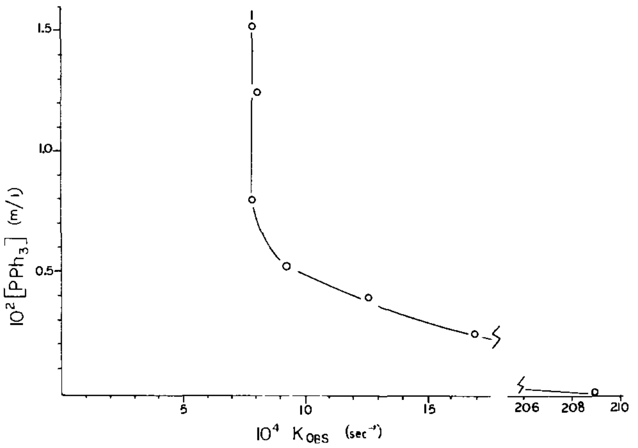
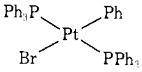
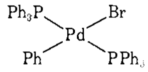
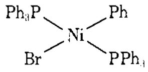


Figure 1. The effect of triphenylphosphine upon the rate of carbonylation of 0.0026 M **4** in tetrachloroethane solution at 20 °C.

This assumption was shown to be valid in the case of the related platinum complex **25**. The products obtained in the presence of excess ligand were the same as obtained in its absence for the platinum and palladium complexes. The nickel complexes, however, absorbed less CO, approaching 3 mol per mole of complex forming acyl halide and essentially only the dicarbonylbistriphenylphosphinenickel(0) product with the highest excess ligand concentrations. It was shown that dicarbonylbis(triphenylphosphine)nickel(0) does not react with CO under those conditions in the absence of excess ligand.

$$X(PPh_3)_2(Ph)Ni + 3CO \xrightarrow{+L} PhCOX + (CO)_2(PPh_3)_2Ni$$

Table V. The Effect of the Metal upon k_{obsd}[a]

Compound	 **26**	 **4**	 **59**
$10^4 k_{\mathrm{obsd}}$ at 2.3°, s^{-1}	0.19[b]	35.	22.
k_{obsd} rel	1.	184.	115.
$10^4 k_{\mathrm{obsd}}$ at 2.3° with excess PPh_3, s^{-1}	0.014[c]	1.1	7.2
k_{obsd} rel with excess PPh_3	1.	79.	514.

[a] Measured under 1 atm of CO in tetrachloroethane solution. [b] Extrapolated value. [c] Extrapolated value assuming the same $\Delta E^{\ddagger}$ as obtained without excess PPh_3.

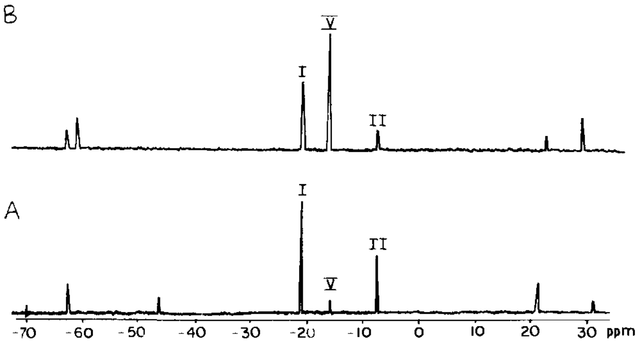


Figure 2. $^{31}P[^1H]$ Spectra of partially carbonylated solutions of complex **40**: (A) a 0.1 M solution of **40** in 3:1 tetrachloroethane–benzene-d_6 at −10° after bubbling CO through at −10° for 10 min; (B) same sample as A after warming to 25° for 15 min and then cooling to −10°. I = complex **40**, II = five-coordinated intermediate **66**, V = acylplatinum complex **57**.

The finding that excess common ligand decreased the reaction rates raised the question of how the relative depressed rates would compare with the relative "normal" rates. Table V illustrates the changes in relative reactivities which may occur. The three examples shown are particularly interesting because they compare reactivities of a Pt, Pd, and Ni complex with identical ligands. Without the excess ligand, PPh_3, the relative reactivities are 1:184:115 and the totally depressed rate ratios are 1:79:514, respectively. Thus, palladium is the most reactive without and nickel is with excess ligand added. It is of considerable interest that the only other rate measurements reported with this complete triad with identical ligands, the reaction of *trans*-chlorobis(triethylphosphine)-*o*-tolylmetal(II) complexes with pyridine, showed the reactivities to be 1:10^4:5 × 10^6,[11] respectively.

Information on possible interactions of PPh_3 with the complexes was obtained from $^{31}P[^1H]$ NMR data. The ^{31}P NMR spectra of complexes **2, 4, 5, 6, 7, 9, 12, 25, 30, 33, 36, 37, 38, 40,** and **59** in the presence of added phosphine failed to show any significant interactions between complex and ligand as evidenced by lack of peak broadening, chemical shift changes, or coalescence of peaks up to 45° or in three cases, **4, 25,** and **30,** up to 75°. Both ligand and complex resonances were separated and sharp even in examples measured at 75°, a temperature well above that used in the kinetic measurements. Chloro(bismethyldiphenylphosphine)phenylplatinum(II) (**61**), however, with excess methyldiphenylphosphine, formed the ionic product, tris(methyldiphenylphosphine)phenylplatinum(II) chloride. Addition of tetrabutylammonium iodide did not change the ^{31}P spectrum as would be expected for the ionic formulation.

Reaction Intermediates. Some complexes behaved differently from the above examples in the carbonylation reaction. Complexes **38, 39, 40, 41, 42** and **43** all absorbed a fraction of 1 equiv of CO initially and then more slowly absorbed the remaining part of the 1 equiv per mole of complex. As usual the final products were at least largely the expected acylmetal complexes. After the first stage of the reactions, the ^{31}P NMR and infrared spectra showed that a new intermediate complex was formed in each case, which on standing changed into the usual acylmetal complexes. For example, iodobis(tri-*p*-anisylphosphine)phenylplatinum(II) (**38**) at 45° rapidly absorbed 10.3% of the theoretical 1 mol of CO and then much more slowly absorbed 90.1% more. After the initial stage the ir spectrum showed two characteristic terminal carbonyl absorptions at 2092 and 2112 cm^{-1}. In the second part of the reaction these two absorptions decreased simultaneously with the appearance of the acyl carbonyl absorption at 1620 cm^{-1}. The terminal carbonyls were still visible at the completion of the gas absorption suggesting there was an equilibrium between product and the intermediate(s). Only acyl complexes could be isolated from the reaction mixtures, however.

Further evidence for the structure of the carbonyl intermediate was derived from ^{31}P NMR examination of **37, 38,** and **40.** The $^{31}P[^1H]$ spectra, from −10 to +35, of a partially carbonylated solution of **38** and **40** showed three well-separated, sharp singlet resonances due to starting complex, intermediate, and acyl complex product. The spectra obtained for **40** are shown in Figure 2. The resonances due to starting complexes I and intermediate II decreased with time as the resonance due to acyl metal complex V increased. Upon completion of the reaction the ^{31}P NMR showed only acyl product present indicating little of the intermediate is in equilibrium with the product at the concentrations necessary to obtain spectra. The amount of the intermediate formed depends markedly upon the ligands present in the complex and upon the reaction temperature. The percentage of intermediate formed in equilibrium with starting complex and CO under the same conditions at 43.6 °C increases from 27 to 39 to ~100% as the triarylphosphine ligands are changed from tri-*p*-tolyl- to tri-*p*-anisyl- to tri-*p*-dimethylaminophenylphosphines (complexes **40, 38,** and **37**). The intermediate from the last complex, **37**, was stable enough to be isolated and analyzed and, in contrast to the other complexes, showed no tendency to rearrange to the acylmetal complex even at elevated temperatures with long reaction times. Analyses showed the carbonylated product to be a complex of **37** with one CO molecule. The $^{31}[^1H]$ NMR resonance of this intermediate showed only one sharp resonance up to 45° at δ −11.0 with $J_{\mathrm{Pt-P}}$ = 2454 Hz.

Addition of excess common phosphine ligand to a solution of **37** results in a spectrum consisting of sharp resonances due to **37** and the free ligand. No line broadening or change in δ was observed up to 45°. Similarly, solutions of **38, 40,** and **42** revealed no exchange with free ligand on the NMR timescale. No phosphine exchange with the five-coordinated CO complex from **37** was observed either up to 45°.

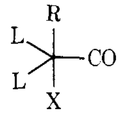
A partially carbonylated solution of chlorobis(tri-*p*-anisylphosphine)phenylplatinum(II) at −10° showed three, well-separated, sharp, singlet, $^{31}P[^1H]$ resonances due to starting complex, the intermediate, and acylmetal complex product. When tetrabutylammonium iodide was added to this mixture of the three chloroplatinum complexes, the $^{31}P[^1H]$

Table VI. $^{31}P[^1H]$ NMR and Ir Spectra of Complexes Producing Detectable Five-Coordinated Intermediates, of the Intermediates, and of the Acyl Products

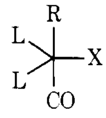
		$(R^1{}_3P)_2PtRI$			$(R^1{}_3P)_2Pt(CO)RI$				$(R^1{}_3P)Pt(CO)RI$		$(R^1{}_3P)_2PtC(=O)RI$			
R^1	R	No.	δP^a	J_{Pt-P} (Hz)	No.	δP^a	J_{Pt-P} (Hz)	νCO (cm^{-1})	No.	νCO (cm^{-1})	No.	δP^a	J_{Pt-P} (Hz)	νCO (cm^{-1})
p-$Me_2NC_6H_4$	Ph	37	−17.4	2966	**64**	−11.0	2554	2117 2088						
p-$MeOC_6H_4$	Ph	38	−18.3	2037	65	−6.8	2760	2114 2090			53	−13.3	3231	1625
p-MeC_6H_4	Me				68			2109 2097	69	1103				
p-MeC_6H_4	Ph	40	−20.7	3057	66	−8.2	2835	2112 2095			57	−15.8	3288	
Ph	Ph	25	−21.8	3088							46	−16.9	3325	1612
p-MeC_6H_4	p-MeC_6H_4	**42**			67			2115 2093						
Ph	Ph				70^b			2120 2115 2089 2079	71^b	[2120 2115 2089 2079]				1618

^{a} δP vs. 85% H_3PO_4, downfield shifts are negative. ^{b} $(AsPh_3)_2PtPhI$, νCO possibly due to 70 and 71.

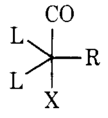
NMR spectrum showed the appearance of a second set of three singlets no doubt due to the presence of the corresponding iodo derivatives. The fact that the resonance due to the intermediate was doubled showed that halogen was attached to the metal and the complex was not ionic. The lack of phosphine exchange between free ligand and intermediate and the lack of observation of free ligand in the presence of the intermediate rule out the presence of large amounts (>5%) of $X(CO)(PR^1{}_3)(R)Pt$ in the solutions we have observed. The intermediate must therefore be a five-coordinate complex having a halo, two phosphines, a CO, and an organic group directly attached to the metal. Seven geometric isomers are possible for such an intermediate assuming a trigonal bipyramidal arrangement of ligands (A–G). Since the infrared spectrum at room temperature shows two strong terminal carbonyl absorptions it appears that at least two major isomers are present which do not exchange on the ir timescale at 30° but which do undergo intramolecular exchange at −10° on the NMR timescale. The isomers could not be "frozen out" because of low solubility of the complexes. The chemical shift values and coupling constants observed in the $^{31}P[^1H]$ NMR spectra of complexes which gave detectable intermediates are listed in Table VI along with the corresponding values found for the intermediates and the acylmetal products. The stability of the intermediates appears related to the J_{Pt-P} values; the smaller the coupling constant the more stable the complex. The ^{31}P chemical shifts in the starting complexes may also indicate which ones will form the most stable five-coordinate complexes since δ decreases with increasing tendency to form the intermediates in the few examples we have.



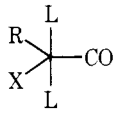
A



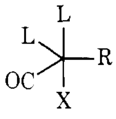
B



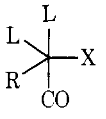
C



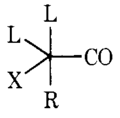
D



E



F



G

We have succeeded in measuring rates of formation, k_1, and the equilibrium constants K_1 between starting complexes, CO, and the intermediate in several instances. We have used the extrapolated initial values for the first reaction stage of a plot of ln (A_0/A) vs. time to obtain k_1. The addition of excess tetrabutylammonium halide to these reactions (complexes **38** and **40**) did not appreciably change the k_1 or K_1 values. Addition of excess triphenylphosphine likewise did not effect the initial k_1. A minor complication did appear in several instances, however, when it was observed that after an initial absorption of CO, ca. 10% was reevolved more slowly, before the second stage became significant. This, we believe, was due to a minor amount of reaction of I with excess ligand to form tris- or tetrakisphosphineplatinum(0) and organic halide, thus removing some I from equilibrium with II causing CO evolution.

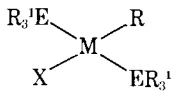
$$\underset{\text{I}}{X(PR^1{}_3)_2(R)Pt} + PR^1{}_3 \rightleftharpoons (PR^1{}_3)_3Pt + RX$$

This side reaction was effectively suppressed by adding 0.02 M organic halide to the solutions. The excess phosphine added, however, did affect the equilibrium constant K_1, decreasing it significantly in the case of complexes **38, 40, 41,** and **42.** We believe this difference between the amount of CO absorbed in the absence of and the presence of excess phosphine to be due to the presence of a second intermediate which reacts with the excess phosphine. We propose that the second intermediate is the product obtained by phosphine dissociation from the five-coordinated intermediate, a four-coordinate complex with halo, phosphine, CO, and the organic group attached to the metal. A complex of this structure was isolated, as noted above, in the case of the carbonylation of the bis(tricyclohexylphosphine) complex **32,** where the product presumably was favored because the loss of one phosphine ligand significantly decreased the strain due to ligand crowding. The terminal carbonyl ir absorptions of this complex (mixture of isomers) were at 2119 and 2087 cm^{-1}, very close to those found in the five-coordinate intermediates (see Table VI). On closer examination in the carbonylation of complex **39** we were able to detect the slow appearance of a third terminal carbonyl absorption at 2103 cm^{-1} between the other two which we believe is from the second intermediate. Likewise the ^{31}P NMR spectrum at −10° of partially carbonylated complex **40** after a few hours reveals the presence of a small (ca. <5%) amount of free ligand indicating the slower development of another complex presumably

$$X(PR^1{}_3)_2(R)M + CO \overset{K_1}{\rightleftharpoons} X(PR^1{}_3)_2(CO)(R)M$$

$$\overset{K_3}{\rightleftharpoons} X(PR^1{}_3)(CO)(R)M + PR^1{}_3$$

Table VII. Kinetic Data Obtained from Rates of Carbon Monoxide Absorption



No.	E	R^1	M	X	R	Concn (mol/l.) $\times 10^2$	Other reagents $\times 10^2$ mol	Temp, °C	K, mol/l.^{f}	$10^4\,k_{obsd}$, s^{-1} (under 1 atm of CO)	$\Delta E^‡$, kcal/mol	$\Delta S^‡$, eu
2	P	C_6H_5	Pd	Cl	$4\text{-}CNC_6H_4$	2.78		43.2		2.10 ± 0.18^b		
3	P	C_6H_5	Pd	Cl	$4\text{-}NO_2C_6H_4$	2.66		43.2		1.15 ± 0.05		
4	P	C_6H_5	Pd	Br	C_6H_5	2.44		2.3		35 ± 3^b		
						2.31	38.9 $(Et_4N)Br$	2.3		32.8 ± 2.6		
						2.44	3.06 L	2.3		1.10 ± 0.06	15.8	−23.9
						2.44	3.05 L	20.0		8.00 ± 0.03^e		
5	P	C_6H_5	Pd	Br	$4\text{-}MeC_6H_4$	1.67		2.3		>100		
						1.61	6.10 L	2.3		10.8 ± 1.0		
6	P	C_6H_5	Pd	Br	$4\text{-}CNC_6H_4$	2.61		20.0		0.36 ± 0.02	17.7	−22.8
						2.70		43.2		4.10 ± 0.13^b		
7	P	C_6H_5	Pd	Br	$4\text{-}CF_3C_6H_4$	2.32		20.0		1.20 ± 0.02	15.4	−29.7
						2.32		43.2		9.6 ± 1.7^b		
						2.17	5.29 L	43.2		1.70 ± 0.02^e		
8	P	C_6H_5	Pd	Br	$4\text{-}NO_2C_6H_4$	2.37		43.2		1.86 ± 0.14		
9	P	C_6H_5	Pd	I	C_6H_5	2.41		2.3		28 ± 2^b		
10	P	C_6H_5	Pd	I	$4\text{-}MeOC_6H_4$	2.56		2.3		>100		
						3.29	6.00 L	2.3		20.7 ± 0.1	3.25	−61.2
						2.64	6.11 L	20.0		31.1 ± 1.9		
11	P	C_6H_5	Pd	I	$4\text{-}NO_2C_6H_4$	2.29		43.2		10.7 ± 0.5		
12	P	C_6H_5	Pd	I	Me	2.50		2.3		>100		
						2.38	9.62 L	2.3		34.3 ± 1.3		
13	P	C_6H_5	Pd	Br	$C_6H_5CH_2$	1.30		2.3		>100		
						1.21	2.00 L	2.3		47.6 ± 2.9^b		
14	P	C_6H_5	Pd	Br	$p\text{-}NO_2C_6H_4CH_2$	2.36	4.61 L	2.3		22.5 ± 0.8		
15	P	CH_3CH_2	Pd	Br	C_6H_5	2.30		48.3		1.10 ± 0.02	30.5	+2.3
						2.32		67.9		14.7 ± 1.0		
16	P	$4\text{-}CH_3C_6H_4$	Pd	I	C_6H_5	1.82		2.3		79.7 ± 2.8		
25	P	C_6H_5	Pt	I	C_6H_5	1.11	25.43 $(Bu_4N)I$	20.0		3.65 ± 0.29		
						1.07		20.0		3.72 ± 0.19	13.6	−34.6
						1.17	2.46 L	20.0		0.13 ± 0.02	15.8	−32.5
						1.09	2.68 L	43.2		1.12 ± 0.10^e		
						1.10		41.5		15.4 ± 1.4		
26	P	C_6H_5	Pt	Br	C_6H_5	2.02		38.0		3.45 ± 0.28	14.8	−28.5
						1.88		25.0		1.21 ± 0.13		
27	P	C_6H_5	Pt	I	$4\text{-}MeOC_6H_4$	0.78		2.3		3.47 ± 0.31^b		
						0.82	3.37 L	20.0		0.97 ± 0.08		
29	P	C_6H_5	Pt	I	$4\text{-}NO_2C_6H_4$	0.89		72.6		0.57 ± 0.04		
30	P	C_6H_5	Pt	Br	$C_6H_5CH_2$	2.23		20.0		64.8 ± 2.9^b		
						2.30	5.50 L	20.0		$4.50 \pm 0.05^{b,e}$		
						2.40	30.51 $(Bu_4N)Br$	20.0		67.5 ± 3.4		
33	P	OC_6H_5	Pt	Cl	C_6H_5	2.00		43.2		4.11 ± 0.59		
34	P	$4\text{-}CF_3C_6H_4$	Pt	I	C_6H_5	1.41		20.0		3.29 ± 0.14^b		
35	P	$4\text{-}CF_3C_6H_4$	Pt	Cl	CH_3	1.36		20.0		4.24 ± 0.64		
36	P	$4\text{-}CF_3C_6H_4$	Pt	I	CH_3	1.59		20.0		2.87 ± 0.21		
37	P	$4\text{-}Me_2NC_6H_4$	Pt	I	C_6H_5	0.83		2.3	K_1 >3350	k_1 $>100^c$		
						1.54		20.0	K_1 3350	k_1 $>100^c$		
						1.69	8.32 L	20.0	K_1 3350	k_1 $>100^c$		
						1.64		43.6	K_1 335	k_1 $>100^c$		

38	P	4-MeOC$_6$H$_4$	Pt	I	C$_6$H$_5$	0.84		−18.2		Insoluble		
						0.87		2.3	K_1 770	k_1 78.8 ± 4.8		
						0.86	24.2 (Et$_4$N)I	2.3	K_1 720	k_1 76.1 ± 2.7		
						0.52	4.62 L	2.3	K_1 756	k_1 82.5 ± 3.9		
						0.93	3.54 L	2.3	K_1 772	k_1 81.5 ± 5.6		
						1.54		15.0	K_3 0.0013			
						0.75		15.0	K_3 0.0012			
						1.64	3.5 L	15.0	K_1 171			
						0.72	3.6 L	15.0	K_1 157			
						1.92	4.1 L	20.0	K_1 123			
						0.84						
						1.44	3.9 L	30.0	K_1 39.7	k_2 1.79 ± 0.16	23.2	−6.1
						0.75	2.8 L	30.0	K_1 38.0	k_2 2.09 ± 0.18		
						1.67		43.6	K_3 0.013	k_4k_5/k_{-4} 19 ± 3		
						0.82		43.6	K_3 0.014	k_3 185 ± 15		
						1.62	4.2 L	43.6	K_1 18.5	k_2 10.45 ± 0.82		
						1.24	3.6 L	43.6	K_1 18.1	k_2 10.39 ± 0.64		
						0.75	3.1 L	43.6	K_1 16.8	k_2 9.8 ± 0.8		
						0.93	4.3 L	62.2	K_1 6.9	k_2 68.0 ± 3.5		
39	P	4-MeC$_6$H$_4$	Pt	I	CH$_3$	0.94		−18.2	K_1 315	k_1 86 ± 4^c		
						0.89	3.25 L	−18.2	K_1 350	k_1 86 ± 5^c		
						0.86		+2.3	K_1 196	>100		
						1.89	3.40 L	+20.0	K_1 86.8			
40	P	4-MeC$_6$H$_4$	Pt	I	C$_6$H$_5$	0.88	4.77 L	−18.2	K_1 5987	k_1 31.7 ± 2.8^{c,b}	6.39	−45.5
						2.07		2.3	K_1 604	k_1 78.4 ± 4.8^c		
						1.71	3.8 L	2.3	K_1 642	k_1 83.8 ± 7.0^c		
						0.91	4.9 L	2.3	K_1 696	k_1 81.5 ± 6.5^c		
						1.78	8.56 L	20.0	K_1 77	k_2 = slow		
						0.81	5.20 L	20.0	K_1 86	k_2 = slow		
						1.67	4.6 L	43.6	K_1 19.6	k_2 7.5 ± 0.6		
						0.80	4.6 L	43.6	K_1 17.6	k_2 7.2 ± 0.5	22.0	−3.5
						1.65	4.3 L	62.2	K_1 12.8	k_2 49.4 ± 1.4	22.0	−3.5
						0.92	3.9 L	62.2	K_1 10.1	k_2 50.7 ± 0.8		
41	P	4-MeC$_6$H$_4$	Pt	I	4-MeOC$_6$H$_4$	0.80	3.40 L	−18.2	K_1 527	k_1 62.3 ± 4.7^c		
						1.75	4.21 L	−18.2	K_1 560	k_1 58.4 ± 3.9^c		
						0.83	3.71 L	2.3	K_1 270	k_1 >100^c		
						1.71	7.63 L	20.0	K_1 79	k_2 >0.5		
						1.69	7.92 L	43.6	K_1 9	k_2 12.03 ± 0.93	25.8	+1.0
						0.90	6.83 L	43.6	K_1 11	k_2 12.18 ± 0.76		
						1.54	5.62 L	63.2	K_1 5	k_2 122 ± 8		
42	P	4-MeC$_6$H$_4$	Pt	I	4-MeC$_6$H$_4$	0.84	3.90 L	−18.2	K_1 500	k_1 47.3 ± 3.9^c	3.77	−54.5
						0.56	4.10 L	−18.2	K_1 506	k_1 50.1 ± 3.1^c		
						0.89	1.04 L	+2.3	K_1 335	k_1 85.4 ± 4.6^c		
						0.89	1.18 L	20.0	K_1 95	k_2 <0.5		
						0.47		30.0	K_1 61	k_3 20 ± 5		
						1.73	3.89 L	43.6	K_1 23	k_2 8.2 ± 0.9	29.6	+5.4
						1.13	3.85 L	43.6	K_1 25	k_2 8.3 ± 0.8		
						1.80	5.72 L	63.2	K_1 8	k_2 110 ± 8		
						1.02	5.51 L	63.2	K_1 10	k_2 103 ± 7		
43	P	4-MeC$_6$H$_4$	Pt	I	4-ClC$_6$H$_4$	1.64	3.4 L	43.6	K_1 9.0	k_2 6.42 ± 0.37		
						0.82	3.7 L	43.6	K_1 7.8	k_2 6.59 ± 0.42		
44	As	C$_6$H$_5$	Pt	I	C$_6$H$_5$	1.39	4.0 L	20.0		>100		
						1.46		20.0		>100		
45	Sb	C$_6$H$_5$	Pt	I	C$_6$H$_5$	1.11		20.0		>100		

No.	E	R'	M	X	R	Concn (mol/L.) ×10²	Other reagents ×10² mol	Temp, °C	*K*, mol/L.[f]	$10^4 k_{\text{obsd}}$, s^{-1} (under 1 atm of CO)	Δ*E*‡, kcal/mol	Δ*S*‡, eu
58	P	C_6H_5	Ni	Cl	C_6H_5	1.72		2.3		22.3 ± 1.3		
						1.81	15.3 L	2.3		6.24 ± 0.05		
59	P	C_6H_5	Ni	Br	C_6H_5	1.58		2.3		19.6 ± 1.0		
						1.65		2.3		23.2 ± 1.7		
						1.58	7.83 L	2.3		10.91 ± 1.04		
						1.67	12.0 L	2.3		7.53 ± 0.53		
						1.72	30.5 L	2.3		7.21 ± 0.71		
60	P	C_6H_5	Ni	I	C_6H_5	1.59		2.3		30.0–98[d]		
61	$Cl(PPh_2Me)_2(C_6H_5)Pt$					1.72		43.6		0.31 ± 0.04		

[a] Also contains 20 × 10^{-2} M aryl halide when PR_3 was added. [b] Average of two or more separate determinations. [c] Second-order rate constants, l. mol^{-1} s^{-1}. [d] First-order constants increased with time. [e] Rate depression with L determined over a series of L concentrations. The concentration of L appearing here being greater than or equal to the experimentally determined amount. [f] K_1 = [II]/[I] [CO]; K_3 = [III]/[II] [L].

$I[P(C_6H_4Me)_3](CO)PhPt$ although δP of this complex is not detected directly due to low concentration or overlap with other δP's. Thus, if this explanation is correct we can obtain both K_1 and K_3 by measuring the CO absorbed in the initial reaction with and without excess ligand.

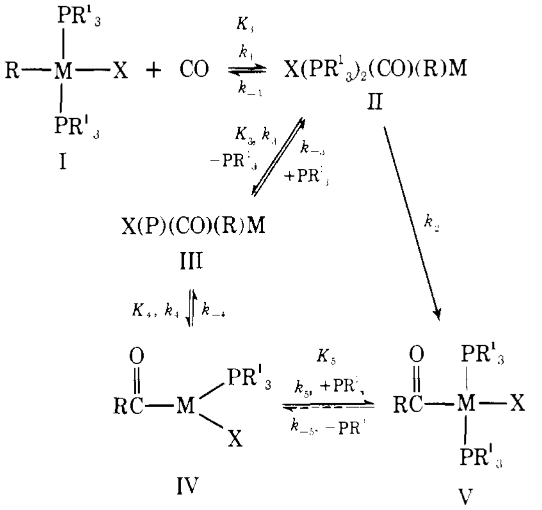
We can now return to the effect of temperature on the concentration of the five-coordinated intermediate. The data determined by CO absorption for a typical complex, **42,** are shown in Figure 3. The percent of the five-coordinate intermediate in equilibrium with the uncarbonylated complex varies from about 9% at 62° up to about 73% at −18°. Other complexes gave similar data. The ^{31}P NMR signal due to the intermediate likewise decreases in intensity as the temperature of the sample is raised from −10 to 35°.

In two favorable cases, with complexes **42** and **38,** we were able to measure the rates of formation of the second intermediate, k_3, because the subsequent reaction forming acyl complex was relatively slow and the formation of the five-coordinate intermediate was relatively fast compared with k_3. Again k_3 was obtained by extrapolating a plot of ln (A_0/A) vs. time to zero time for the second part of the initial reaction. Only in the case of **38** were we able to obtain K_3 accurately. With K_3 then we were able to measure the rate and calculate a rate constant of the final reaction for the formation of V from III. Unfortunately, we could not vary concentrations or temperatures appreciably with **38** or **42** without reducing the differences between the rates of the last two stages to the point where we could not definitely distinguish them. Figure 4 shows plots of milliliters of CO absorbed vs. time in the examples where the stages were clearly separated for **38** and **42.** The kinetic data and thermodynamic parameters calculated from the data for all of the complexes studied are given in Table VII.

Discussion

Reaction Mechanism. The experimental data obtained may be explained by the equations in the scheme shown below. Most

Scheme I



M = Pt, Pd, Ni; X = I, Br, Cl, OAc;
R = aryl, benzyl, Me; R' = aryl, ethyl

of the critical data have been obtained with platinum complexes because of their ease of preparation and generally higher stability. The data we have on Pd and Ni complexes, particularly the similar rate depressing effect of excess common ligand, suggest, at least, that their mechanisms of carbonylation are similar to those of the Pt complexes. Carbonylation of $I[P(p\text{-}CH_3C_6H_4)_3]_2PhPd$ in an attempt to separate k_1 and k_2 and observe II for a Pd reaction failed because the reaction rate

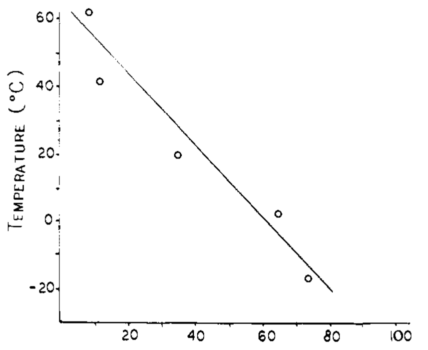
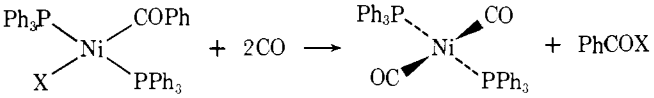


Figure 3. The effect of temperature on the percent of the five-coordinated intermediate **67** in the equilibrium mixture with complex **42**.



was too fast to measure being >100 s^{-1} at 2.3°. We could not go to lower temperatures because of low solubility of the compound. A final additional step in the nickel carbonylation reaction must be a reductive elimination of the acyl halide. We attribute the formation of some $(CO)_3(PPh_3)Ni$ in the carbonylation of nickel complexes in the absence of excess PPh_3 to capture some of the intermediate IV by CO followed by loss of RCOX and addition of two more CO's. With excess PPh_3, path k_2 is followed and the tricarbonyl product disappears. (The $(CO)_2(PPh_3)_2Ni$ does not react with CO under our reaction conditions.)

The arguments and evidence supporting the proposed mechanism in the scheme are the following. The formation of intermediate II appears firmly established in the five cases described from ir and NMR data and isolation in one instance. The equilibrium constant K_1 could be measured at a variety of concentrations of I and at different temperatures in the presence of excess common ligand to surpress formation of III. Rate constant k_1 was determined where rates were slow enough to measure, by extrapolation to zero time of a plot of ln (A_0/A) vs. time. Since excess common ligand depressed reaction rates to a constant (lower) value in the second stage of the reaction (after equilibration of I, II, and III) there must be two reaction paths: one which is inhibited by excess $PR^1{}_3$ and one which is not.

The reaction inhibited by excess $PR^1{}_3$ is consistent with formation of complex III in a reversible reaction. Increasing $PR^1{}_3$ concentration will decrease the amount of III in equilibrium with II and suppress reaction by path k_3 through k_4 and k_5. In the presence of sufficient $PR^1{}_3$, therefore, only path k_2 is followed producing the observed acyl product V. Values of k_2 have been measured (in the presence of excess common ligand) directly in cases where equilibrium K_1 is established rapidly compared with the rate of formation of V from II. Good first-order rate constants were obtained for k_2 using the rate expression:

$$-\frac{d(CO)}{dt} = k_2K_1[I][CO]$$

In all examples investigated, k_2, the direct migration route to product was less favorable than the indirect, dissociative route through k_3, k_4, and k_5.

The evidence for intermediate III includes preparation by a different method and isolation by others of a complex with the proposed structure, $[Cl(PPh_3)(CO)(Me)Pt]$.[6] Another complex of this structure was isolated in this work by carbonylation of the bis(tricyclohexylphosphine) complex **32**. We also see a CO absorption attributable to an intermediate of type III in the carbonylation of **39**. In all other cases III is assumed to be present but only in low concentrations. Even in the most favorable examples found, with complexes **38** and **42**, III is present only in minor amounts in equilibrium with II and I dependent both on the concentration of I and temperature. The inhibition of carbonylation is correctly predicted by III reacting with $PR^1{}_3$ and the decrease in the total initial CO absorption in the presence of $PR^1{}_3$ also can be explained by the decreased concentration of III. In the two cases where k_5K_4 is slow compared with k_3, and k_3 is appreciably faster than equilibration of I and II, the rate k_3 can be measured by extrapolating to zero time, a plot of ln (A_0/A) vs. time for the second CO absorption. Finally, then, we believe we are able to measure k_5K_4 when the third stage of CO absorption occurs. Since we can experimentally determine K_3 from the amounts of CO absorbed in the initial stage without and with phosphine, and we know k_3 as noted above we can calculate k_5K_4 from the following expression:

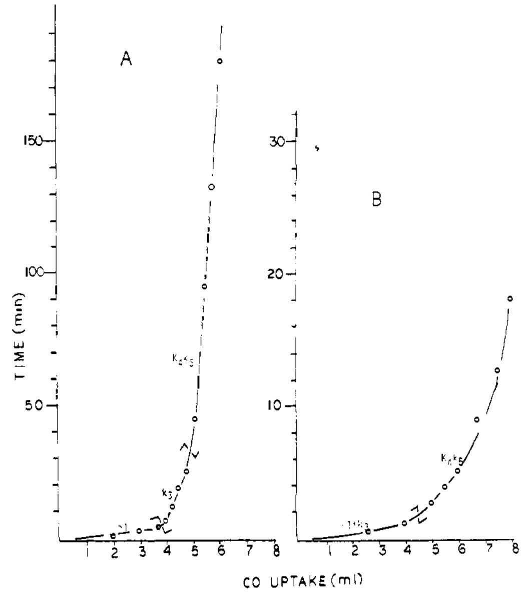


Figure 4. Carbonylation of complexes **42** and **38** showing the separate stages of the reactions: (A) carbonylation of 0.47 M **42** in tetrachloroethane at 30.0 °C; (B) carbonylation of 0.082 M **38** in tetrachloroethane at 43.6 °C.

$$\frac{d(V)}{dt} = -\frac{d(CO)}{dt} = k_5K_4[III][PR^1{}_3]$$

since $[III] = K_1K_3[I][CO]/[PR^1{}_3]$, then

$$-\frac{d(CO)}{dt} = k_5K_1K_3K_4[CO][I]$$

The equilibrium K_5 must be significant, however, in the absence of excess ligand, because even though I absorbs very close to 1 equiv of CO, we see by ir, after complete reaction, some (amount unknown) of II present in equilibrium with V and k_5K_4 decreases toward the end of the reaction. (Average initial values are shown in Table III.) Some III must also be present but not observed by ir due to low concentration and overlap of the ν_{CO} absorption with those of II. In the presence of excess ligand, the concentration of IV would be reduced by equilibrium K_5 and, as observed experimentally, III is not observed in carbonylated reaction mixtures containing excess common ligand.

The isomeric structures of intermediates II and III remain uncertain and in fact our data indicate at least two of the possible seven isomers of II are present under our reaction conditions (two ν_{CO} bands), probably both possible isomers of

III are present (two ν_{CO} absorptions in complex **63**). Probable intermediate II from the $AsPh_3$ complex **44** shows four ν_{CO} bands indicating at least four compounds are present. It would, of course, be very useful to know which of these isomers is undergoing the subsequent reaction or indeed if one or more isomers of II take path k_2 and others take k_3. Intuitively, having the migrating group 90° from the CO ligand in complex II would seem to be a preferred structure for path k_2. If this is correct and the PR^1_3 ligands prefer to be equivalent as is usually the case, then isomers A or C are likely structures for following paths k_2. Similarly, the isomers of III with R and CO cis to each other would be required for formation of IV if the transition state is planar. These isomer problems have been discussed previously by Osborn.[12]

A tricoordinated complex analogous to IV has been proposed as an intermediate by Mawby[6] in the reaction of $Cl(CO)(PPh_3)MePt$, an anologue of III, with various triarylarsines since reaction rates were independent of the arsine concentration.

$$Cl(CO)(PPh_3)(Me)Pt \rightleftharpoons (Cl)(PPh_3)(MeC{=}O)Pt \xrightarrow{AsR_3} Cl(AsR_3)(PPh_3)(MeC{=}O)Pt$$

Entropies of Activation. The accuracy in measuring k_1 by extrapolation is probably only about ±10%. The average errors are somewhat less for the k_2 values. Using data at different temperatures, at least 20° apart, entropies of activation for the k_1 and k_2 steps have been calculated. In the several instances where $\Delta S_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ were measured, "normal" values were obtained. Solvent effects are probably minimal for tetrachloroethane. The $\Delta S_1^{\ddagger}$ values obtained from **40** and **42**, the second-order reaction of I with CO, were -45.5 and -54.5 eu. The $\Delta S_2^{\ddagger}$ values (a first-order reaction) obatined from **38**, **40**, **41**, and **42** were -6.1, -3.5, 1.0, and 5.4 eu. The "normal" values obtained for the $\Delta S^{\ddagger}$ values of the two individual steps contrast with the wide range observed when $\Delta S^{\ddagger}$ was calculated from "one-stage" reactions using k_{obsd} values. We observed values of $\Delta S^{\ddagger}{}_{obsd}$ between -61 and $+2$ eu. On the basis of the proposed mechanism it is clear why such variable $\Delta S^{\ddagger}$ values are obtained: the equilibrium constants K_1 and K_3 vary greatly with temperature and therefore the relative contributions of k_1 and other k's to the total rate vary giving $\Delta S^{\ddagger}$ values which are complex combinations of the individual $\Delta S^{\ddagger}$'s.

Stability of the Five-Coordinated Intermediate. From the K_1 values obtained the effect of substituents on the stability of the five-coordinated intermediate(s), II, can be observed. In the series where the substituents in the para position of the two triarylphosphines are varied, the dimethylamino group in **37** stabilizes more than either the methoxyl, **38**, or methyl, **40**, the last two being very similar. Attempts to measure K_1 for the parent in the series, the triphenylphosphine complex **25**, indicate it is lower than for **38** or **40** but it is not sufficiently separated from k_2 to be measurable. The situation is worse with the tris-4-trifluoromethyl complex **34** where no initial CO absorption can be detected. Thus, electron supplying substitutents on the phosphines stabilize the five-coordinate intermediates relative to I. We are not certain that we are stabilizing the same isomeric form of II in every case, however.

It has been reasoned that removing electron density from the metal by π-bonding should stabilize the five-coordinate intermediate since then the metal can better accommodate another unshared pair from the new, fifth ligand.[13] A rationalization of our results is complicated by the unknown importance of p–d bonding between the aromatic ring and phosphorus, and the back-bonding between the metal and the phosphorus. A similar electronic effect is noted in four complexes when the para substituent in the aryl group σ-bonded to the metal is changed. Thus, the stability of II decreases as the para substituent is varied from CH_3 to H, OCH_3 to Cl (complexes from **42**, **40**, **41**, and **43**, respectively). These results suggest stabilization is primarily effected by the inductive rather than the resonance effect of the para substituent and that there is little p–d bonding between the aryl groups and the metal.

Relative Rate Comparisons. With the individual steps of the complex carbonylation reaction separable in some instances, it becomes possible to make more meaningful comparisons of substituent affects on reaction rates. One comparison of particular interest is how substituents affect the tendency for the organic group to migrate from metal to carbon monoxide. The effects can be seen in a comparison of k_2 values. Table VIII compares k_2 values for some pertinent complexes. From Table VIII it is clear that migration of aryl groups is facilitated by electron supplying substituents in the para positions. The effect, however, is not very large. There is only a factor of two in k_2 between *p*-chloro and *p*-anisyl while, for example, in the formolysis of β-arylethyl *p*-toluenesulfonates where aryl migration occurs the factor between phenyl and *p*-anisyl is 47.[14] A change of phosphine substituents from tri-*p*-tolylphosphine to tri-*p*-anisylphosphine causes a small increase in the rate of phenyl migration. The ρ calculated from the data using σ^+ values gives a value of -0.29. The accelerating effect of electron supplying para substituents on k_2 is in agreement with the rate accelerating effects noted for the same type substituents on k_{obsd} when the rate cannot be dissected (Table II).

As found in other organometallic systems, the sign and magnitude of ρ are a function of many factors and vary in an unpredictable manner.[15]

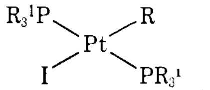
Conclusions

A comparison of the CO insertion reaction with ligand replacement reactions in square planar complexes suggests that some of the conclusions we have reached may be applicable to replacement reactions. The two types of reactions, of course, differ in the way the ligand being displaced is lost, but both apparently involve five-coordinate intermediates. In the carbonylation the ligand migrates to another ligand and in displacement it moves completely away. It can readily be seen, for example, why $\Delta S^{\ddagger}$ values measured for displacement reactions (from k_{obsd}) may be useless as indicators of reaction mechanism or solvation effects since K_1 may vary appreciably with temperature and structure. While we have not yet succeeded in dissecting the various rate constants for the carbonylation of Pd and Ni complexes we would expect some differences, perhaps large differences in K_1 values for example. Our k_{obsd} values show relative small differences in reactivity between members of the nickel triad in carbonylation (Table V), while Basolo et al.[11] found very large differences in the pyridine displacement reaction. This different effect could be due largely to differences in the K_1 values involved if equilibrium is reached. Since our data indicate the five-coordinated intermediates are fluxional, the question arises as to how the ligand displacement or the carbonylation reactions can be stereospecific since cis or trans starting complexes should give the same equilibrium mixture of five-coordinated intermediates? The only circumstance under which stereospecific reactions should occur, then, is when isomer equilibration in the intermediate is slow compared with ligand migration or dissociation.

Experimental Section

Materials. (*S*)-Tetrachloroethane (Fisher) was dried over the Linde 4A molecular sieves. Alkyl and aryl halides were used as purchased. The complexes $Pd(PPh_3)_2RX$,[16] $Ni(PPh_3)_3PhX$,[17] $Pt(PPh_3)_2RX$,[18] $Pd(PPh_3)_2PhCl$,[19] $Pd(PPh_3)_2Br(CH_2C_6H_4)$,[20] $Pt(PR_3)_2RX$,[21] $(COD)PtI_2$,[21] $(COD)PtR_2$,[21,22] and $(COD)PtRI$[21,22] were prepared by literature methods. New complexes are listed in Table I.

Table VIII. The k_2 Values at 43.6 °C



R	4-ClC_6H_4	C_6H_5	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	C_6H_5
R^1	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$
	43	**40**	42	**41**	38
10^4k_2, s^{-1}	6.5	7.4	8.3	12.1	10.4

Preparation of $Cl(CO)[P(C_6H_{11})_3](Ph)Pt$. A solution of 0.402 g of $Cl[P(C_6H_{11})_3]_2PhPt$ in 25 ml of tetrachloroethane was stirred under a CO atmosphere at 70°. The reaction was monitored by observation of the intensity of the carbonyl absorptions. After 4 days no further growth was noted and the solution was concentrated. The resulting oil was recrystallized from ethyl ether giving a colorless crystalline material.

Anal. Calcd: C, 48.54; H, 5.66; found: C, 48.33; H, 6.00.

Preparation of $Cl(CO)[P(p\text{-}Me_2NC_6H_4)_3]_2PhPt$. Carbon monoxide was bubbled through a solution containing 0.15 g of $Cl[P(p\text{-}Me_2NC_6H_4)_3]_2PhPt$ dissolved in 10 ml of CH_2Cl_2/5 ml of hexane at room temperature until sufficient CH_2Cl_2 evaporated to cause precipitation of the complex. The product appeared to be fairly air stable at room temperature but lost CO easily on heating.

Anal. Calcd: C, 55.00; H, 5.49; found: C, 54.67; H, 5.46.

General Procedure for the Carbonylation of $MRX(PR_3)_2$. In a 100-ml jacketed flask containing a magnetic stirring bar was hung a Teflon cup containing the complex. (The amount of complex used was calculated so that CO uptake would be ca. 10 ml. This usually represented 0.45–0.5 g of complex.) The flask was then attached to a thermostated microhydrogenation-type apparatus.[23] The apparatus was flushed several times with carbon monoxide; *s*-tetrachloroethane (generally 25–50 ml) was injected into the reaction flask by means of a hypodermic syringe through a side arm provided with a stopcock and rubber septum on the end. The reaction vessel was then brought to the proper temperature and allowed to come to equilibrium at 1 atm of pressure. The Teflon cup containing the complex was then dropped into the reaction flask by means of turning a stopcock. Gas volume changes and times were recorded periodically using a 10-ml micro gas buret with 0.05-ml markings, until gas absorption stopped. The acyl product could be recovered by removal of the solvent under vacuum followed by recrystallization of the resulting solid from ether/hexane solutions.

Analyses. Microanalyses were carried out by Chemalytics, Inc., Tempe, Ariz., and Gailbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer 180 spectrometer. ^1H NMR were obtained on a Perkin-Elmer R12B. ^{31}P NMR were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{31}P data were taken at operating frequencies of 36.43 MHz, chemical shifts are reported as referenced to external 85% H_3PO_4, downfield shifts being reported as negative. Samples were run as 0.1–0.2 M solutions in $CDCl_3$ with broadband ^1H decoupling. Spectra taken to observe the five-coordinated intermediate, II, were run in 4:15 tetrachloroethane:benzene-d_6.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Matthey Bishop, Inc., for the loan of the platinum and palladium salts used as starting materials in this study.

References and Notes

(1) R. F. Heck "Organotransition: Metal Chemistry", Academic Press, New York, N.Y., 1974, pp 201–261.
(2) A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).
(3) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).
(4) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, N.Y., 1971, p 19.
(5) A. Wojcick; *Adv. Organomet. Chem.*, **11**, 87 (1973).
(6) C. J. Wilson, M. Green, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1293 (1974).
(7) M. Hidai, T. Kashiwagi, and Y. Uchida, *J. Organomet. Chem.*, **30**, 279 (1971).
(8) P. Fitton and E. A. Rick, *J. Organomet. Chem.*, **28**, 287 (1971).
(9) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974).
(10) B. Corain and G. Favevo, *J. Chem. Soc., Dalton Trans.*, 283 (1975).
(11) F. Basolo, J. Chatt, H. Gray, R. Pearson, and B. Shaw, *J. Chem. Soc.*, 2207 (1961).
(12) J. R. Shapley and J. A. Osborn, *Acc. Chem. Res.*, **6**, 313 (1973).
(13) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1968, p 377.
(14) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).
(15) J. K. Stille and M. T. Regan, *J. Am. Chem. Soc.*, **96**, 1508 (1974), and references therein.
(16) P. Fitton and E. A. Rick, *J. Organomet. Chem.*, **28**, 287 (1971).
(17) M. Hidai, T. Kashiwagi, T. Ikenchi, and Y. Uchida, *J. Organomet. Chem.*, **30**, 279 (1971).
(18) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).
(19) D. R. Coulson, *Chem. Commun.*, 1530 (1968).
(20) P. Fitton, *Chem. Commun.*, 370 (1969).
(21) H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, **59**, 411 (1973).
(22) C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).
(23) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).