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Kinetics of Substitution and Oxidative Elimination Reactions of Pentacarbonylruthenium(0)

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The substitution reactions of pentacarbonylruthenium(0) with a number of phosphorus donor ligands have been shown to proceed by a simple carbon monoxide dissociative mechanism in cyclohexane at 30–50 °C. $\Delta H^{\neq} = 27.62 \pm 0.40$ kcal mol^{-1} and $\Delta S^{\neq} = 15.2 \pm 1.3$ cal K^{-1} mol^{-1}. The $Ru(CO)_4$ intermediate generated by CO dissociation is stable towards reaction with oxygen in the presence of triphenylphosphine but trimerises to form $Ru_3(CO)_{12}$ in decalin at 125 °C under an atmosphere of 5% CO in a CO–N_2 mixture. Unlike $Fe(CO)_4$, reaction of $Ru(CO)_4$ with PPh_3 does not lead to any direct formation of a bis phosphine product.

The reaction of iodine with $Ru(CO)_5$ in cyclohexane to form cis-*$Ru(CO)_4I_2$ was studied in a stopped-flow apparatus and shown to proceed via essentially the same mechanism as the corresponding reaction of $Fe(CO)_5$ but at rates* ca. *10^3 times faster. Reaction of I_2 with tricarbonylbis(triphenylphosphine)ruthenium(0) is not appreciably faster than that with $Ru(CO)_5$. $Ru(CO)_5$ was prepared quantitatively* in situ *by photochemically induced reaction of dodecacarbonyltriruthenium with CO.*

Introduction

The comparative chemistry of the binary carbonyls $M(CO)_6$ (M = Cr, Mo, and W) and their derivatives is well known and includes extensive kinetic studies of their substitution and oxidative elimination reactions [1–3]. The same cannot be said of the binary carbonyls $M(CO)_5$ (M = Fe, Ru, and Os). The substitution reactions of $Fe(CO)_5$ are so slow, and the complex is so volatile, that a study of its substitution reactions would be difficult at the elevated temperatures required [4]. Acceleration of its substitution reactions is possible by protonation [5] and, more conventionally, by irradiation [6] but no studies of its unassisted substitution reactions appear to have been made. A kinetic study of an oxidative elimination reaction (with I_2) has been reported [7]. No studies of kinetics of reactions of $Ru(CO)_5$ or $Os(CO)_5$ have been described, partly, perhaps, because the impression has been given that $Ru(CO)_5$ and $Os(CO)_5$ are unstable towards formation of their trinuclear analogues [8]. In fact $Ru(CO)_5$ is readily preparable, *in situ* at least [9], and we report here a study of examples of its substitution and oxidative elimination reactions.

Experimental and Results

$Ru(CO)_5$ was prepared photochemically *in situ* in cyclohexane. Thoroughly degassed solutions of $Ru_3(CO)_{12}$ (Strem Chemicals, Inc.) were irradiated under an atmosphere of CO in bright sunlight or with a high-pressure u.v. lamp. Reaction was continued for 30 min or more until all the infrared bands of the $Ru_3(CO)_{12}$ (2065s, 2035s, and 2012 m cm^{-1}) were replaced by those due to $Ru(CO)_5$ (2037s and 1998vs cm^{-1}). No other infrared bands were observed and there was no evidence of decomposition so the yields were concluded to be virtually quantitative and the concentrations of $Ru(CO)_5$ calculated accordingly. This was not the case in solvents such as acetone, chloroform or dimethyl sulphoxide where reaction, if it occurred, led mainly to decomposition.

Solutions for the study of substitution reactions were thoroughly degassed by several freeze–pump–thaw cycles before addition of solutions of the appropriate phosphorus donor ligand. The ligands were received and used as described previously [10]. The substitution reactions were carried out in Schlenk tubes sealed with rubber septum caps through which stainless steel needles were inserted to provide a means of taking samples and maintaining the atmosphere of gas above the reacting solutions. Reactions were carried out under atmospheres of pure CO (CP grade, 99.5%; Union Carbide of Canada, Ltd.) or under a mixture of CO and N_2 (5% CO; Matheson of Canada). Reactions were followed by monitoring the infrared band at 2037 cm^{-1} due to the $Ru(CO)_5$. Bands due to the monosubstituted

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TABLE I. Rate Constants for Reaction: $Ru(CO)_5 + L \rightarrow Ru(CO)_4L$ in Cyclohexane under 1 atm CO. $[Ru(CO)_5]_o = 8 \times 10^{-4}$ *M*.

T, °C	10^2 [PPh_3], *M*	10^4 k_{obsd}, s^{-1}
30.4	6.00	1.64, 1.65[a], 1.61
35.0	6.00	3.36, 3.41, 3.48[a]
40.6	0.969	6.47
	0.792	5.81
	1.00	6.15
	1.01	6.31
	1.23	6.63
	1.42	7.05
	1.52	7.16
	1.92	7.69
	3.20	8.17
	6.00	8.54
	13.8	7.80[b]
	100	8.33
	1.48	8.17[a]
	2.48	8.27[a]
	3.20	8.17[a]
	3.72	8.11[a]
44.8	6.00	13.7[a], 12.9 12.9
50.4	6.00	30.3[a], 30.2
40.6	2.26[c]	8.13
	9.04[c]	8.22
	11.3[c]	8.34
	6.22[d]	8.16
	51.3[d]	8.24

$\Delta H^{\ddagger} = 27.62 \pm 0.40$ kcal mol^{-1}; $\Delta S^{\ddagger} = 1.52 \pm 1.3$ cal K^{-1} mol^{-1}; $\sigma(k_{obsd}) = 5.3$ %.

[a] Under 5% CO in CO–N_2 mixture. [b] Under 1 atm O_2. [c] L = $P(OMe)_3$. [d] L = PBu^n_3.

products were seen to grow, *e.g.*, 2061s, 1986 m, and 1954 vs cm^{-1} for $Ru(CO)_4(PPh_3)$. Only very weak bands due to disubstituted products were observed by the time all the $Ru(CO)_5$ had just disappeared. Plots of log A_t *vs.* t were linear for up to 3 half-lives. Kinetic data for these reactions are given in Table I.

Reaction with PPh_3 under an atmosphere of O_2 proceeded to form $Ru(CO)_4(PPh_3)$ in 100% yield and at a rate unaffected by the O_2. No loss of $Ru(CO)_5$ was detectable at 41 °C, under an atmosphere of CO and in the absence of any phosphorus donor ligand, over a period comparable to the duration of the substitution reactions. No evidence for decomposition or reaction to form other ruthenium carbonyl species was observed under an atmosphere of CO at more elevated temperatures. However, under an atmosphere of 5% CO in a CO–N_2 mixture, reaction to form $Ru_3(CO)_{12}$ was almost quantitative after *ca.* 2 h at 125 °C in a sealed tube.

Reaction of $Ru(CO)_4(PPh_3)$ in decalin under an atmosphere of CO was slow even at 170 °C and the products were not clearly defined.

Activation parameters were obtained by a least squares analysis, all values of k_{obs} being assumed to have the same intrinsic uncertainty measured by the standard deviation $\sigma(k_{obs})$. All uncertainties quoted are estimates of standard deviations corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them.

Reactions of $Ru(CO)_5$ with iodine were followed in a 'Canterbury' stopped-flow spectrophotometer [11] Solutions of I_2 (Baker Analysed Reagent) were made up by weighing. No particular care was taken to exclude O_2 from the reactant solutions.

The product of the reaction showed infrared bands at 2151m, 2100vs, 2089s, and 2066s cm^{-1} which characterised it as *cis*-$Ru(CO)_4I_2$ [8]. In all cases the absorbance of the solutions at 350 nm increased to a final constant value characteristic of the $Ru(CO)_4I_2$ product. This increase was, however, preceded by a finite induction period during which almost no change in absorbance occurred. The overall increase in absorbance was always <*ca.* 0.2 absorbance units so that simple plots of $\log(T_t - T_\infty)$ against t were linear and equivalent, as far as their gradients were concerned, to plots of $\log(A_\infty - A_t)$ [11]. Good plots, linear for up to *ca.* 2 half-lives, were obtained from the data obtained after the induction period. The occurrence of an induction period was important in a practical sense. Although the second stage of the reaction showed half-lives down to *ca.* 2 ms the solutions were thoroughly mixed by the time measurements of the second stage began. In order to check the effect, if any, of the spectrophotometer light reactions were carried out with a series of monochromator slit widths from 0.5 to 5.0 mm. Some reactions were carried out in the presence of 'Galvinoxyl'. The rate constants obtained are reported in Table II. The induction periods were roughly constant at $\lesssim$20 ms irrespective of slit-width.

Reactions of $Ru(CO)_5$ with Br_2 were complicated by overlap of the uv–vis spectra of reactants and products and the absorbance changes were so small as to make kinetic measurements unpromising. Reactions of $Ru(CO)_3(PPh_3)_2$ with I_2 and Br_2 were also studied briefly. $Ru(CO)_3(PPh_3)_2$ was prepared by heating a saturated solution $Ru_3(CO)_{12}$ in decalin with a large excess of PPh_3 under 5%CO (in a CO–N_2 mixture) at 160 °C overnight. On reduction of the volume under reduced pressure and addition of a small amount of MeOH the product precipitated. It was recrystallised from THF–pentane. Reaction with I_2 in cyclohexane was followed at 300 nm and proceeded in a similar way to that of $Ru(CO)_5$. There was an initial stage, lasting *ca.* 5 ms, during which little absorbance change occurred and this was followed by a further reaction, involving an increase in absorbance, with $k_{obs} = ca.$ 100 s^{-1} ($[I_2] = 2.2 \times 10^{-4}$ *M*). Reaction in the presence of Tenox, a commercial radical inhibitor, followed essentially

TABLE II. Observed Pseudo-First-Order Rate Constahts for Reaction of I_2 with $Ru(CO)_5$ at 25.3 °C in Cyclohexane. $[Ru(CO)_5]_o = 5 \times 10^{-5}$ *M*.

10^4 $[I_2]$, *M*	10^{-2} k_{obsd}, s^{-1}			
	0.5^a	1.0^a	3.0^a	5.0^a
0.52				1.80
5.12		2.21		
5.15	2.23		2.28	2.11
5.97	2.20		2.42	2.39
6.03				2.39^b
6.97		2.61		
7.00	2.30		3.22	3.03
8.40		2.64		
8.44	3.15		3.34	3.67
8.52				3.74^b
10.0		3.06		
10.1	2.87		3.31	4.13
11.9	2.88	3.72	4.05	4.73
12.1				4.44^b
13.9		4.01		
14.0	3.75			4.28
14.1				4.59^b
15.0	3.73	4.56	4.95	5.23

^{a}Monochromator slit width in mm. ^{b}Reaction in the presence of galvinoxyl, [galvinoxyl] = [complex].

the same path. The solubility of the product in cyclohexane was not sufficient to obtain an infrared spectrum but a good spectrum was obtained immediately after reaction of more concentrated solutions in CH_2Cl_2 (ν_{CO} = 2080vs, 2060s, and 1995m).

Discussion

The Substitution Reactions

These reactions show all the characteristics of a simple CO-dissociative mechanism of the type shown in equations 1 and 2. The reaction proceeds at the same limiting rate irrespective of the nature of the

$$Ru(CO)_5 \underset{k_{+CO}}{\overset{k_{-CO}}{\rightleftharpoons}} CO + Ru(CO)_4 \qquad (1)$$

$$Ru(CO)_4 + PPh_3 \xrightarrow{K_{+PPh_3}} Ru(CO)_4(PPh_3) \qquad (2)$$

substituting ligand and the concentration of CO. An excellent linear plot of $1/k_{obs}$ against $1/[PPh_3]$ is obtained from the data under an atmosphere of CO at 40.6 °C as expected from rate equation (3).

$$k_{obs} = (k_{-CO}k_{+PPh_3}[PPh_3]/k_{+CO}[CO])/$$
$$(1 + k_{+PPh_3}[PPh_3]/k_{+CO}[CO]) \qquad (3)$$

A weighted least squares analysis leads to $\sigma(k_{obs})$ = 4.6% and the ratio of the gradient to the intercept leads to a value of $k_{+PPh_3}/k_{+CO} = 1.3$ when [CO] is taken as 6×10^{-3} *M* [12].

Owing to the high volatility of $Fe(CO)_5$ coupled with the high temperatures required no substitution kinetics appear to have been studied. This, in itself, shows that the behaviour of $Fe(CO)_5$ and $Ru(CO)_5$ parallels that of $Cr(CO)_6$ and $Mo(CO)_6$. $Cr(CO)_6$ requires a temperature *ca.* 50 °C higher than $Mo(CO)_6$ to react at a comparable rate and its activation enthalpy is *ca.* 10 kcal mol^{-1} higher. A similar relationship holds for $Fe(CO)_4(PPh_3)$ and $Ru(CO)_4(PPh_3)$ [9]. The introduction of a PPh_3 ligand into $Ru(CO)_5$ reduces the rate of CO dissociation at 50 °C by a factor of *ca.* 20 which is mainly due to a higher value of $\Delta H^{\ddagger}$. An increase in inertness also results from the introduction of PPh_3 into $Mn(CO)_5Br$ although the effect is much smaller [13]. $Ru(CO)_5$ falls into a series of increasing lability $Mo(CO)_6$, $Ru(CO)_5$, and $Pd(CO)_4$, the last being stable only at low temperatures and having much weaker metal-CO bonds than those in $Ni(CO)_4$ [14]. $Ru_3(CO)_{12}$ undergoes dissociation [15] at a rate 50 times slower than $Ru(CO)_5$ at 50 °C, and this is associated with a 4 kcal mol^{-1} higher value of $\Delta H^{\ddagger}$. This could be indicative of the lower stability of what can be regarded as a 5-coordinate d^6 Ru atom in $Ru_3(CO)_{11}$ compared with the 4-coordinate d^8 Ru in $Ru(CO)_4$. Such 4-coordinate Ru atoms have been shown to be quite stable since trimerization of $Ru(CO)_3(PBu_3)$ to form $Ru_3(CO)_9(PBu_3)_3$ can compete with addition of PBu_3 provided the ratio $[complex]/[PBu_3]$ is high enough [16]. The case of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ is not comparable since the bridging carbonyls in $Fe_3(CO)_{12}$ appear to induce a much greater degree of lability into the system compared with an unbridged form. A similar labilizing effect of bridging carbonyls is shown by $Ir_4(CO)_{12}$ and $Ir_4(CO)_{11}(PPh_3)$ [17], as well as $Co_2(CO)_8$ and $Co_2(CO)_6(PBu_3)_2$ [18]. The competition between PPh_3 and CO for $Ru(CO)_4$ is at least 3 times [9, 12] more favourable to PPh_3 than is the case for $Ru(CO)_3(PPh_3)$ and steric factors may play a role in this.

The fact that $Ru(CO)_5$ does not react with PPh_3 to form $Ru(CO)_3(PPh_3)_2$ directly contrasts with the direct formation of $Fe(CO)_3(PPh_3)_2$ by reaction of PPh_3 with $Fe(CO)_4ol$ (ol = various olefines) [19]. This is believed [19, 20] to be due to dissociation of CO from $Fe(CO)_4$ at a rate competitive with the addition of PPh_3. An alternative explanation in terms of dissociation of CO from a binuclear $Fe_2(CO)_8$-intermediate has also been suggested [21]. Evidently neither of these processes can occur with $Ru(CO)_4$. The stability of $Ru(CO)_4$ towards O_2 is similar to that of $Ru(CO)_3(PPh_3)$ [22].

The great difficulty of displacing the PPh_3 in $Ru(CO)_4(PPh_3)$ by CO is a measure of the stability

TABLE III. Kinetic Data for the Reaction $Ru(CO)_5 + I_2 \rightarrow$ *cis*-$Ru(CO)_4I_2$ + CO Analysed According to the Rate Equation $k_{obs} = k_1 + k_2[I_2]$.

Slit width, mm	10^{-2} k_1, s^{-1}	10^{-5} k_2, M^{-1} s^{-1}	$\sigma(k_{obs})$, %
0.5	1.28 ± 0.26	1.61 ± 0.30	10.6
1.0	1.25 ±0.35	1.99 ±0.41	11.8
3.0	1.02 ±0.33	2.56 ±0.43	12.6
5.0	1.35 ±0.22	2.32 ±0.29	14.6

of the Ru–P bond and is paralleled by the difficulty of removing PPh_3 from $Ru_3(CO)_{11}(PPh_3)$. By contrast PPh_3 in $Ru_3(CO)_9(PPh_3)_3$ and $Ru_3(CO)_{10}(PPh_3)_2$ is easily displaced by CO [23].

The Oxidative Elimination Reactions

The reaction of $Ru(CO)_5$ with I_2 is a straightforward oxidative elimination reaction. The reaction is preceded by an induction period after which the reaction follows rate equation (4).

$$k_{obs} = k_1 + k_2[I_2] \quad (4)$$

Values of k_1 and k_2 obtained by a weighted least squares analysis are given in Table III.

The value of k_1 appears to be independent of the intensity of the light passing into the solution during the reaction whereas k_2 appears to increase slightly with increasing intensity. However, although the parameters in Table III are the most probable ones in statistical terms, the possibility that it is k_1 that is light sensitive, and not k_2, cannot be excluded. Thus, as the slit width increases from 0.5 to 5.0 mm, k_1 could increase from 102 to 157 s^{-1} while k_2 remains constant at $(2.0 \pm 0.1) \times 10^5$ M^{-1} s^{-1}. This would conform to the covariance of the two parameters, k_1 most probably being high when k_2 is low and vice versa, and does not require any value being more than about one standard deviation from the least squares value. In any case the effect of slit width is sufficiently small that the 'thermal' values for k_1 and k_2 must be greater than *ca.* 100 s^{-1} and 2×10^5 M^{-1} s^{-1}, respectively. Further, the absence of any effect due to galvinoxyl shows that no thermal chain reaction is involved.

This reaction therefore shows very similar behaviour to that of I_2 with $Fe(CO)_5$ [7]. When the reaction of $Fe(CO)_5$ with a pseudo-first-order excess of I_2 was followed at 410 nm an induction period was followed by a slower reaction also following equation (4). Reaction with a pseudo-first-order excess of $Fe(CO)_5$ was followed at 475 nm and the first stage of reaction shown to be first order in $[I_2]$. Reaction of I_2 with $Ru(CO)_5$ is very much faster than with $Fe(CO)_5$ and we have no kinetic data for the first stage of our reaction. However, we assume it to involve formation of a $Ru(CO)_5 \cdot I_2$ adduct by analogy with the $Fe(CO)_5$ reaction. Also as with the $Fe(CO)_5$ reaction, this adduct can then react spontaneously, or under the influence of another I_2 molecule, to form *cis*-$Ru(CO)_4I_2$. This requirement of two I_2 molecules for reaction by one of the paths is also shown by reactions of I_2 with several axially disubstituted derivatives of group 7B dimetal decacarbonyls such as $Mn_2(CO)_8L_2$ [24]. The most common reaction path is second order in $[I_2]$. However, a transition state containing as many as four I_2 molecules was found for reaction of $Re_2(CO)_9(PPh_3)$ [25]. The overall third-order rate constants for reactions were found to be dependent on the basicity of the substituents in such a way that reaction was concluded to involve initial electrophilic attack at the O atoms of the CO ligand to form a series of adducts, this being followed by relatively slow oxidation of the metal [24, 25, 11]. Rates increased by two orders of magnitude as M_2 in the complexes $M_2(CO)_8(PPh_3)_2$ changed from Mn_2 to Re_2 in parallel with an increasing ease of oxidation. Although the nature of the initial adducts in the reaction of $Fe(CO)_5$ [26, 27] and $Ru(CO)_5$ is almost certainly somewhat different from those in the reactions of the group 7B metal carbonyls, the much greater rates with $Ru(CO)_5$ compared with $Fe(CO)_5$ (k_1 is 10^3 times bigger, and k_2 is 2×10^3 times bigger) are also in accord with a growing ease of oxidation with increasing atomic weight of the metal.

The presence of P- or As-donor substituents in the group 7B dimetal carbonyls leads to an acceleration in the rate of reaction with I_2 of at least seven orders of magnitude [24, 25, 28]. Our studies on $Ru(CO)_3(PPh_3)_2$ suggest that no such increase occurs in this mononuclear 5-coordinate system since an observably slow reaction is detected. This is likely to be due to steric effects which have been shown to be pronounced in the reactions of the disubstituted dimanganese carbonyl complexes [11, 25]. The reaction with I_2 in benzene [29] has been shown to form the ionic species $[Ru(CO)_3I(PPh_3)_2]I$ (ν_{CO} = 2135w, 2075vs, and 2054s cm^{-1} in CH_2Cl_2) which precipitates slowly out of solution. It reacts further in refluxing $CHCl_3$ [29] to form $Ru(CO)_2I_2(PPh_3)_2$ (ν_{CO} = 2053vs and 1994 vs cm^{-1} in CH_2Cl_2). The product of the very rapid reaction which we observe in CH_2Cl_2 showed bands at 2080vs, 2060s, and 1995m cm^{-1}. It therefore appears that a mixture of $[Ru(CO)_3I(PPh_3)_2]I$ and $Ru(CO)_2I_2(PPh_3)_2$ was formed very rapidly and Kuhen's results may simply be explained by the slow precipitation of the former from an equilibrium mixture in benzene and the need to use refluxing conditions in $CHCl_3$ to drive off all CO and displace the equilibrium towards formation of pure $Ru(CO)_2I_2(PPh_3)$. Whether the reactions of $Fe(CO)_5$ and $Ru(CO)_5$ with iodine involve formation of ionic intermediates of a similar kind is still not clear [7, 26, 27].

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References

1 R. J. Angelici, *Organometal. Chem., Rev., 3,* 173 (1968).

2 H. Werner, *Angew. Chem., Internat. Edn., 7,* 930 (1968).

3 J. W. McDonald and F. Basolo, *Inorg. Chem., 10,* 492 (1971); R. T. Jernigan and G. R. Dobson, *ibid., 11,* 81 (1972); M. N. Memering, A. Moradi-Araghi, and G. R. Dobson, *J. Co-ordination Chem., 2,* 271 (1973).

4 W. Reppe and W. Schweckendiek, *Ann. Chem., 560,* 104 (1948).

5 F. Basolo, A. T. Brault, and A. J. Poë, *J. Chem. Soc.,* 676 (1964).

6 J. Lewis, R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.,* 2825 (1964).

7 G. R. Dobson, R. T. Jernigan, and P.-T. Chang, *J. Organometal. Chem., 54,* C33 (1973).

8 F. Calderazzo and F. L'Eplattenier, *Inorg. Chem., 6,* 1220 (1967).

9 B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Chem. Soc. Dalton,* 1876 (1975); E. E. Siefert and R. J. Angelici, *J. Organometal. Chem., 8,* 374 (1967).

10 M. A. Cobb, B. Hungate, and A. J. Poë, *J. Chem. Soc. Dalton,* 2226 (1976).

11 G. Kramer, J. Patterson, and A. J. Poë, *J. Chem. Soc. Dalton,* 1165 (1979).

12 This is the value of [CO] at 40 °C in decalin (M. Basato, J. P. Fawcett, and A. J. Poë, *J. Chem. Soc. Dalton,* 1350 (1974)) which is approximately equal to the solubility in 1,4-dichlorobutane, 1,2-dichloroethane, chloroform, and toluene (W. J. Knebel and R. J. Angelici, *Inorg. Chem., 13,* 632 (1974)). Values about double this have been obtained for non-cyclic paraffins (G. Bor, U. K. Dietler, P. Pino, and A. J. Poë, *J. Organometal. Chem., 154,* 301 (1978) and references therein). If the latter values were appropriate here then k_{+PPh_3}/k_{+CO} would be 2.5.

13 R. J. Angelici and F. Basolo, *J. Am. Chem. Soc., 84,* 2495 (1962); *idem, Inorg. Chem., 2,* 728 (1963).

14 The Pd–C force constant in $Pd(CO)_4$ is much less than that of the Ni–C bond in $Ni(CO)_4$ (E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc., 95,* 7234 (1973)) and the average Pd–CO bond energy is slightly less than the average Ni–CO bond energy in $Ni(CO)_4$ (M. Moskovits and G. A. Ozin, *J. Mol. Str., 32,* 71 (1976)). It is also of interest that $Pd[P(OMe)_3]_4$ has a lower activation energy for ligand dissociation than those for the corresponding Ni and Pt complexes (M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem., 8,* 795 (1969)).

15 A. J. Poë and M. V. Twigg, *J. Chem. Soc. Dalton,* 1860 (1974).

16 A. J. Poë and M. V. Twigg, *Inorg. Chem., 13,* 2982 (1974).

17 K. J. Karel and J. R. Norton, *J. Am. Chem. Soc., 96,* 6812 (1974).

18 M. Basato and A. J. Poë, *J. Chem. Soc. Dalton,* 607 (1974).

19 G. Cardaci, *Inorg. Chem., 13,* 368, 2974 (1974).

20 G. Cardaci, *J. Am. Chem. Soc., 97,* 1412 (1975).

21 I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem. Internat. Edn., 14,* 54 (1975).

22 D. P. Keeton, S. K. Malik, and A. J. Poë, *J. Chem. Soc. Dalton,* 1392 (1977).

23 S. K. Malik and J. Poë, *Inorg. Chem., 17,* 1484 (1978).

24 G. Kramer, L. Ng, and A. J. Poë, *Chem. Commun.,* 265 (1977).

25 G. Kramer, J. Patterson, and A. J. Poë, unpublished observations.

26 K. Noak, *J. Organometal. Chem., 13,* 411 (1968).

27 M. F. Farona and G. R. Camp, *Inorg. Chim. Acta, 3,* 395 (1969).

28 W. R. Cullen and G. L. Hou, *Inorg. Chem., 14,* 3121 (1975).

29 H. B. Kuhen, *J. Organometal. Chem., 105,* 357 (1976).