Tetracarbonyl(phosphine)ruthenium Complexes: Synthesis and Kinetics of Carbonyl Substitution

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The complexes $[Ru(CO)_4L]$ and *trans*-$[Ru(CO)_3L_2]$ ($L = PPh_3$, $PMePh_2$, or $PBu^n{}_3$) have been obtained on photolysis of $[Ru_3(CO)_{12}]$ in the presence of an excess of ligand. High-pressure carbonylation of readily available *trans*-$[Ru(CO)_3(PPh_3)_2]$ provides a further convenient route to $[Ru(CO)_4PPh_3]$. Unlike the corresponding iron complex, solid $[Ru(CO)_4PPh_3]$ forms $[Ru_3(CO)_9(PPh_3)_3]$ when heated, while in solution the tetracarbonyl complexes react with excess of ligand to form *trans*-$[Ru(CO)_3L_2]$. The kinetics of this reaction have been studied and the results are compared with those for $[Fe(CO)_4PPh_3]$.

PREVIOUSLY the complex $[Ru(CO)_4PPh_3]$ has been prepared[1] by carbonylation of $[Ru_3(CO)_9(PPh_3)_3]$ (150 °C, 80 atm), and by u.v. irradiation of $[Ru(CO)_5]$ in the presence of PPh_3 (ref. 2).† During our studies[3] on photochemical reactions of $[Ru_3(CO)_{12}]$ we discovered that solutions containing $[Ru(CO)_4L]$ and *trans*-$[Ru(CO)_3L_2]$ (molar ratio 2 : 1; $L = PBu^n{}_3$, $PMePh_2$, or PPh_3) are rapidly produced by photolysis of $[Ru_3(CO)_{12}]$ in the presence of an excess of the appropriate ligand. These results prompted us to investigate other routes to $[Ru(CO)_4L]$ complexes and to examine their carbonyl-substitution reactions in order to compare their reactivity with the iron analogues.

EXPERIMENTAL

Materials.—The complex $[Ru_3(CO)_{12}]$, prepared from ruthenium chloride by the method of Bruce and Stone,[4] was recrystallised from benzene; *trans*-$[Ru(CO)_3(PPh_3)_2]$ was obtained directly from ruthenium chloride in 94% yield by reaction with formaldehyde in the presence of PPh_3.[5] Methyldiphenylphosphine (Maybridge Chemicals) was distilled under nitrogen (138—140 °C/2.5 mmHg), and PPh_3 (B.D.H.) was recrystallised from absolute ethanol and dried for several days *in vacuo*. n-Heptane (B.D.H.)

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† 1 atm = 101 325 Pa, 1 mmHg ≈ 13.6 × 9.8 Pa, 1 lbf in^{-2} ≈ (9.8 × 4536)/6.45 Pa, 1M = 1 mol dm^{-3}, and 1 cal = 4.184 J.

[1] F. Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, 1968, **7**, 1815; R. Whyman, *J. Organometallic Chem.*, 1973, **56**, 339.

[2] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1968, **7**, 1290.

[3] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organometallic Chem.*, 1974, **67**, C75.

[4] M. I. Bruce and F. G. A. Stone, *Chem. Comm.*, 1966, 684; *J. Chem. Soc. (A)*, 1967, 1238.

[5] N. Ahmad, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843.

was distilled from sodium under nitrogen. Before use, decalin was passed through a column of alumina.

Photochemical Reactions.—These were generally made on a 10 cm^3 scale, with the Pyrex reaction tubes used for the kinetic studies (see below). Saturated (*ca.* 10^{-3}M) solutions of $[Ru_3(CO)_{12}]$ in either n-heptane or decalin containing the appropriate phosphine (*ca.* 0.1M) were degassed (freeze–pump–thaw cycles) and the tubes filled with high-purity argon (or carbon monoxide, 10 lbf in^{-2}, as required). They were then exposed to bright sunlight or to light from six 2 ft fluorescent tubes at 25 °C. After further degassing these solutions were used for most of the kinetic experiments. Identical rate constants were obtained when pure solid complex was used.

Kinetic Measurements.—These were made on a 10 cm^3 scale using techniques previously described.[6,7] Temperature control of the bath used was better than ± 0.1 °C, and reactions were monitored by measuring the absorption of the highest-frequency i.r. CO-stretching band of cooled samples in 1 mm NaCl cells on a Perkin-Elmer 257 instrument. Excellent pseudo-first-order rate plots were obtained up to 90% completion of reaction.

Carbonylation of trans-$[Ru(CO)_3(PPh_3)_2]$.—The complex (0.36 g) and benzene (250 cm^3) were heated (100 °C) in a stirred autoclave under carbon monoxide (80 atm) for 9 h. After removal of solvent under reduced pressure the residue was chromatographed on alumina (No. 5) and eluted with cyclohexane to give pure $[Ru(CO)_4PPh_3]$ (0.23 g, 98%). Further elution with toluene gave a very small quantity of *trans*-$[Ru(CO)_3(PPh_3)_2]$.

RESULTS AND DISCUSSION

Under an atmosphere of carbon monoxide (10 lbf in^{-2}) irradiation of n-heptane solutions of $[Ru_3(CO)_{12}]$ with bright sunlight or fluorescent tubes ($\lambda_{max.}$ *ca.* 390 nm) produced quantitative conversion into colourless $[Ru(CO)_5]$. In the presence of an excess of PPh_3, under an atmosphere of argon, irradiation rapidly converted $[Ru_3(CO)_{12}]$ into a mixture of $[Ru(CO)_4PPh_3]$ and *trans*-$[Ru(CO)_3(PPh_3)_2]$ in a molar ratio of *ca.* 2 : 1. Similar results were obtained with PBu^n_3 and $PMePh_2$. This reaction provides a more convenient route to $[Ru(CO)_4PPh_3]$ than that previously used involving preparation of $[Ru_3(CO)_9(PPh_3)_3]$ and its high-temperature high-pressure carbonylation.* Under an atmosphere of CO, irradiation of $[Ru_3(CO)_{12}]$ and PPh_3 produced considerably more $[Ru(CO)_4PPh_3]$ than under Ar, together with some $[Ru(CO)_5]$ and *trans*-$[Ru(CO)_3(PPh_3)_2]$.

Since no reaction between *trans*-$[Ru(CO)_3(PPh_3)_2]$ and CO was observed under these circumstances it seems likely that two paths are involved: (*a*) 'direct' formation of $[Ru(CO)_4PPh_3]$ from $[Ru_3(CO)_{12}]$; and (*b*) formation of $[Ru_3(CO)_{11}PPh_3]$ which then undergoes metal–metal bond fission to give $[Ru(CO)_4PPh_3]$ and *trans*-$[Ru(CO)_3(PPh_3)_2]$ in the observed stoicheiometry. Production of $[Ru_3(CO)_{11}PPh_3]$ is expected to be inhibited by CO, and this accounts for the reduced yield of *trans*-$[Ru(CO)_3(PPh_3)_2]$ in the presence of CO. Further, CO and PPh_3 will compete for any intermediate formed 'directly' from $[Ru_3(CO)_{12}]$ to form $[Ru(CO)_5]$ and $[Ru(CO)_4PPh_3]$ respectively. On this basis the discrimination of the intermediate(s), k_2/k_{-1} (see below), was estimated to be *ca.* 0.9 at 25 °C, a value reminiscent of those for thermally generated $[Ru(CO)_3L]$ species (see below). Perhaps this suggests that similar species are formed by the photochemical process. The similarity between these photochemical reactions and the thermal reaction[8] of $[Ru_3(CO)_{12}]$ with PBu^n_3 to give monomeric species may indicate that this reaction involves bimolecular attack of PBu^n_3 on $[Ru_3(CO)_{11}PBu^n_3]$, and that the orbitals used in this process are antibonding with respect to a metal–metal bond.

Recently a rapid single-stage synthesis of *trans*-$[Ru(CO)_3(PPh_3)_2]$ from ruthenium chloride was described.[5] In an attempt to utilise this efficient reaction as a stage in the preparation of ruthenium carbonyl clusters we investigated the carbonylation of this complex and found that at 100 °C and 80 atm it is almost quantitatively converted into $[Ru(CO)_4PPh_3]$. This is a convenient route to this complex from ruthenium chloride. The iron complex $[Fe(CO)_4PPh_3]$ is readily purified[9] by sublimation at 180 °C, and can be stored in air for long periods with only slight decomposition. In contrast, the analogous ruthenium complex, on standing in the dark over a period of weeks, forms a black surface deposit that is insoluble in common solvents. The instability of $[Ru(CO)_4PPh_3]$ was further demonstrated during attempts to purify samples by sublimation. During 15 min at 125 °C *in vacuo* it darkened to a deep red colour. The visible spectrum of this substance dissolved in acetone had $\lambda_{max.}$ = 510 nm, identical with an authentic[6] sample of $[Ru_3(CO)_9(PPh_3)_3]$, while its i.r. spectrum in CH_2Cl_2 contained bands in the carbonyl-stretching region attributable to this complex and its pyrolysis products.[10] These observations suggest Scheme 1. Similarly, the mass spectra of these complexes suggest that CO is lost more readily from $[Ru(CO)_4PPh_3]^+$ than from $[Fe(CO)_4PPh_3]^+$. Relative to their respective parent ions, fragments due to $[Ru(CO)_nPPh_3]^+$ (n = 1—3) were about three times more intense than those of the iron analogue.

$$3[Ru(CO)_4PPh_3] \longrightarrow [Ru_3(CO)_9(PPh_3)_3] \longrightarrow \text{pyrolysis products}$$

SCHEME 1

Results of a kinetic study have been reported[11] for

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* We found that deep red $[Ru_3(CO)_9(PPh_3)_3]$ can be carbonylated photochemically under ambient conditions using an intense quartz–iodine visible light source.

[6] A. J. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

[7] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1974, 241.

[8] A. J. Poë and M. V. Twigg, *Inorg. Chem.*, 1974, **13**, 2982.

[9] A. F. Clifford and A. K. Mukherjie, *Inorg. Synth.*, 1966, **8**, 185.

[10] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[11] E. E. Siefert and R. J. Angelici, *J. Organometallic Chem.*, 1967, **8**, 374.

reaction (1). The corresponding reaction of $[Ru(CO)_4PBu^n_3]$ with PBu^n_3 has recently been investigated,[8] and

$$[Fe(CO)_4PPh_3] + PPh_3 \longrightarrow trans\text{-}[Fe(CO)_3(PPh_3)_2] + CO \quad (1)$$

in agreement with the above observations this complex * is considerably more reactive than $[Fe(CO)_4PPh_3]$ towards carbonyl substitution. Since $[Ru(CO)_4PPh_3]$ was available, kinetic results for its reaction with PPh_3 were obtained so that a direct comparison with $[Fe(CO)_4PPh_3]$ could be made. Convenient rates were obtained in the temperature range 45—70 °C, and pseudo-first-order rate constants for this reaction in n-heptane are in Table 1, together with data for the reaction of $[Ru(CO)_4PMePh_2]$ with excess of $PMePh_2$.

TABLE 1

Kinetic data for reaction of $[Ru(CO)_4L]$ with excess of L ($L = PPh_3$ and $PMePh_2$) [a]

θ_c/°C	L	[L]/mol l^{-1}	$10^5k_{obs.}/s^{-1}$ Expt.	$10^5k_{obs.}/s^{-1}$ Calc.[b]
74.1	$PMePh_2$	0.120	187	191
		0.206	190	191
		0.215	193	191
69.6	PPh_3	0.209	264	269
		0.257	252	269
69.4	$PMePh_2$	0.060	104	105
69.05		0.145	102	100
66.3		0.069	69.4	69.7
		0.070	72.4	69.7
		0.097	70.4	69.7
65.05	PPh_3	0.189	149	147
		0.136	150	147
62.7		0.184	107	106
		0.136	111	106
60.0		0.041	76.4	73.3
	$PMePh_2$	0.091	29.2	29.8
		0.096	29.2	29.8
55.0		0.064	15.0	14.8
		0.111	14.8	14.8
	PPh_3	0.118	35.8	36.1
		0.165	36.2	36.1
50.0		0.150	16.9	17.4
		0.167	17.6	17.4
45.0		0.146	8.16	8.20
		0.223	8.09	8.20

[a] In each run $[Ru(CO)_4L]$ *ca.* 10^{-3} mol l^{-1}. Results for $L = PPh_3$ were obtained in n-heptane and for $PMePh_2$ in decalin. [b] From the derived activation parameters (see Table 2).

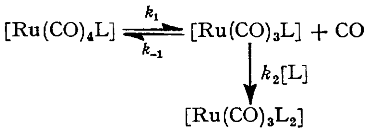
TABLE 2

I.r. data for some $[M(CO)_4L]$ complexes (M = Fe or Ru; $L = PPh_3$, $PMePh_2$, or PBu^n_3) and kinetic parameters for loss of CO

M	L	$\tilde{\nu}(CO)/cm^{-1}$			$10^5k/s^{-1}$ at 60° C	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}	Ref.
Ru	PPh_3[a]	2 061s	1 987m	1 955vs	76	30.10 ± 0.25	17.3 ± 0.8	*b*
Ru	$PMePh_2$	2 058s	1 983m	1 942vs	29	29.66 ± 0.22	14.1 ± 0.6	*b*
Ru	PBu^n_3	2 055s	1 977m	1 939vs	13	31.57 ± 0.18	18.3 ± 0.5	8
Fe	PPh_3	2 048s	1 976m	1 942vs	3[c]	42.5 ± 1.2	18.4 ± 2.8	11

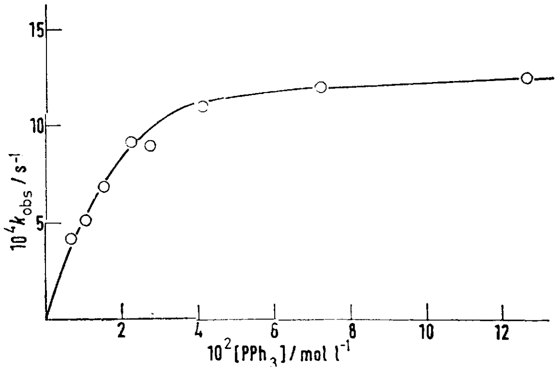
[a] In n-heptane, others in decalin. [b] This work. Quoted errors are standard deviations corrected for the number of degrees of freedom such that doubling them produces 95% confidence limits. [c] At 160 °C.

At a given temperature, rate constants for carbonyl substitution in these complexes are independent of the ligand concentration at the concentrations employed. This, together with the large enthalpies and positive entropies of activation (Table 2), suggests the dissociative mechanism in Scheme 2. For such a scheme the observed rate constant is given by $k_{obs.} = k_1k_2[L]/(k_{-1}[CO] + k_2[L])$, where k_1 is the rate constant for loss of CO from the complex, and k_{-1} and k_2 are second-order rate constants for attack by CO and L on the four-co-ordinate intermediate. At high ligand concentrations $k_2[L] > k_{-1}[CO]$ and $k_{obs.}$ is independent of [L], as observed, with $k_{obs.} = k_1$. As expected, the reaction of $[Ru(CO)_4PPh_3]$ with PPh_3 at low $[PPh_3]$ was inhibited under an atmosphere of CO (see Figure), and as predicted for a dissociative mechanism a plot of $1/k_{obs.}$ against $1/[PPh_3]$ was linear. From the intercept on the $1/k_{obs.}$ axis a value of $(1.49 \pm 0.03) \times 10^{-3}$ s^{-1} was obtained graphically for k_1 at 65 °C, in excellent agreement with that determined under argon (1.50×10^{-3} s^{-1}). From the gradient and intercept of this plot a value of 0.30 ± 0.04 was obtained for k_2/k_{-1} assuming the



$$\begin{tikzcd}[Ru(CO)_4L] \arrow[r, shift left, "k_1"] & {[Ru(CO)_3L] + CO} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2{[L]}"] \\ & {[Ru(CO)_3L_2]}\end{tikzcd}$$

SCHEME 2



Ligand dependence of the rate of substitution of CO in $[Ru(CO)_4PPh_3]$ by PPh_3 in n-heptane at 65.0 °C under carbon monoxide (1 atm)

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* The complex $[Ru(CO)_4PBu^n_3]$ was obtained from $[Ru_3(CO)_{12}]$ and excess of PBu^n_3.

solubility of n-heptane is 5×10^{-3} mol l^{-1} at 65 °C. This is about twice the value of the ratio for the competition of PBu^n_3 and CO for $[Ru(CO)_3PBu^n_3]$ at 80 °C in decalin.[8] The competition parameters for several co-ordinatively unsaturated ruthenium intermediates are now available, and it is interesting that the discrimination of $[Ru(CO)_3L]$ $[k_L/k_{CO} = 0.30$ at 65 °C (L = PPh_3), 0.17 at 80 °C (PBu^n_3) [8]] and $[Ru_3(CO)_{11}]$ are similar {k_L/k_{CO} *ca.* 0.2 (L = PPh_3), 0.34 at 50 °C [$P(OPh)_3$] [6]}. However, these results were obtained at different temperatures and the unknown temperature coefficients of these parameters may be significant.

The usual steric acceleration for dissociative reactions was observed for loss of CO from the $[Ru(CO)_4L]$ complexes. The rate constants decreased along the series L = $PPh_3 > PMePh_2 > PBu^n_3$, as did their i.r. carbonyl-stretching frequencies (Table 2). This suggests that the CO molecule ***trans*** to the ligand in $[Ru(CO)_4L]$ is more strongly bound the smaller the π-bonding ability of the ligand. However, these variations were not large. The ruthenium complexes are considerably more reactive than $[Fe(CO)_4PPh_3]$. This results from more favourable enthalpies of activation, and parallels the enhanced reactivity towards loss of CO from the iron and ruthenium tricarbonyl derivatives of 1-σ,4—6-η-cyclooctenediyl.[7] The present results are an extreme example of the general reactivity difference between first- and second-row complexes of this type. Similarly $[Ru(CO)_5]$ is considerably more reactive than $[Fe(CO)_5]$. In fact, we found that $[Ru(CO)_5]$ reacted with PPh_3 at room temperature with $t_{\frac{1}{2}}$ *ca.* 45 min.*

Few kinetic studies on substitution reactions of five-co-ordinate complexes have been reported. It is therefore interesting to note that, like the complexes studied here, the isoelectronic five-co-ordinate $[Ni(dtp)_2PBu^n_3]$ (dtp = diethyldithiophosphato) similarly reacts with bidentate ligands *via* a dissociative mechanism.[12] Electronic, rather than steric, effects control the reaction paths of these low-spin 18-electron complexes.

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* Similar reaction periods were used for the reaction under u.v. irradiation.[2] It appears the irradiation was not needed.

[12] D. A. Sweigart and P. Heidtmann, *J.C.S. Chem. Comm.*, 1973, 556.