Kinetic Studies on the Reactions of the Tricarbonyl(1—3,6-η-cyclo-octadiene)-iron and -ruthenium Complexes with Tertiary Phosphines and Phosphites

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The complex [(1—3,6-η-C_8H_{12})Fe(CO)$_3$] (1—3,6-η-C_8H_{12} = 1—3,6-η-cyclo-octadiene), (Ia), when treated with tertiary phosphines L (L = triphenylphosphine or triphenyl phosphite) in n-heptane (40—70 °C) produces the monosubstituted derivative [(1—3,6-η-C_8H_{12})Fe(CO)$_2$L], (IIa), *via* a CO-dissociative mechanism. Observed pseudo-first-order rate constants for reaction with a range of more nucleophilic phosphorus ligands (for example triethyl phosphite) are given by the relation $k_{obs} = k_1 + k_2[L]$. The ligand-independent term corresponds to formation of the carbonyl-substituted derivative and the ligand-dependent term to formation of the complexes [Fe(CO)$_2$L$_3$], (IIa), and the *trans*-annular ketone $C_9H_{12}O$, (III). Studies of the analogous ruthenium system show that dissociation of CO (at 40 °C) is *ca.* 40 times greater than that of the iron complex. This results from a more favourable enthalpy of activation. However, no second-order reaction of this complex has been detected.

In two other papers [1,2] we described the preparation of M(CO)$_3$ (M = Fe or Ru) derivatives of cyclo-octa-1,5-diene in which the organo-group was bound in a σ,π-allyl manner. A preliminary examination [3] of the reactions of the iron complex with tertiary phosphines and phosphites led to the conclusion that one of two processes can occur. The first, in which the organo-group remains bound to the metal ion, leads to substitution of one carbonyl group by the tertiary phosphine or phosphite,

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[1] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.

[2] A. J. Deeming, A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and S. S. Ullah, *J.C.S. Dalton*, to be submitted.

[3] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **52**, C31.

and the second to formation of trisubstituted complexes of the type $[Fe(CO)_2L_3]$ and liberation of the bicyclic ketone, bicyclo[4.2.1]-2-nonen-9-one, the course of the reaction depending on the nature of the tertiary phosphine or phosphite employed. We now report full details of this work together with studies on the analogous ruthenium complex.

EXPERIMENTAL

Pure samples of the ruthenium and iron complexes were provided by Dr. A. J. P. Domingos and M. Mitchell of this department. Although moderately stable, they were stored prior to use under an atmosphere of argon at −10 °C. Triphenylphosphine (Koch–Light) was recrystallized from absolute ethanol, and dried under vacuum for several days. Liquid alkyl phosphites (B.D.H.) were distilled under an atmosphere of argon [$P(OMe)_3$ 110—112 °C, 758 mmHg; $P(OEt)_3$ 147—149 °C, 751 mmHg; $P(OPr^i)_3$ 77—79 °C, 28 mmHg]. $P(OCH_2)_3CEt$ (Aldrich Chemical Co. Inc.) was sublimed (40 °C, 0·01 mmHg). Other ligands were obtained from Maybridge Research Chemicals, and were used as received. n-Heptane (B.D.H. reagent grade) was distilled from sodium under a nitrogen atmosphere.

Kinetics.—For each kinetic run, with solid ligands, the appropriate quantities of complex and ligand were weighed into a 10 cm³ volumetric flask. Freshly distilled n-heptane was added and, after the reactants had dissolved, the volume of the solution was made up to 10 cm³ by further additions of solvent. In reactions involving liquid ligands the ligand and complex were weighed into separate volumetric flasks. After making the ligand solution up to 10 cm³ with heptane, the solution was transferred to the other flask and the complex dissolved. Typically, the complex concentration was *ca.* 1×10^{-3}M and that of the ligand 1×10^{-2}—2×10^{-1}M. The solution of complex and ligand was then transferred to a Pyrex reaction tube, having a side arm and tap and fitted with a rubber Subaseal cap. After degassing the solution, the reaction tube was filled with pure argon (99·998%) and then immersed in a constant-temperature bath containing poly(arylalkylglycol). Temperature control (±0·05 °C) was achieved by a ' circotherm II ' circulator unit in conjunction with cooling coils and stirrers. Aliquot portions were removed from the reaction tube through a stainless steel tube by applying a pressure of argon. A positive pressure of argon was maintained in the reaction tubes throughout the runs.

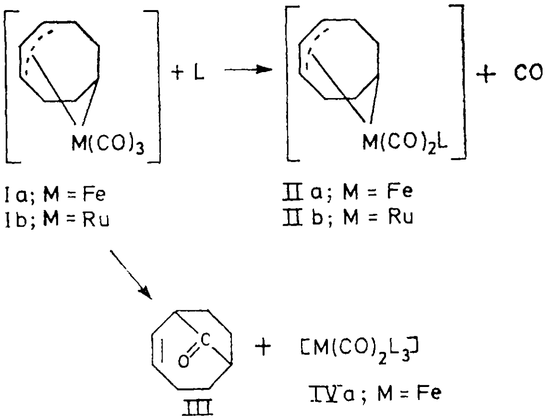
I.r. spectra, in the carbonyl-stretching region, of the cooled samples were obtained in 1·0 mm cells (NaCl windows with solvent reference) on a Perkin-Elmer 257 instrument. Unless otherwise stated, reactions were monitored by the loss of intensity of the highest-frequency carbonyl band of the reactant complex. Except where noted, excellent pseudo-first-order rate plots were obtained (to *ca.* 95% completion of reaction). Pseudo-first-order rate constants were reproducible to within ±5%, and similar data, within experimental error, were obtained when light was totally excluded from the reaction tube. In reactions under an atmosphere of carbon monoxide, this gas, obtained directly from a cylinder, was used in place of argon. Temperatures were measured with mercury-in-glass thermometers and the usual stem corrections were made when partial-immersion thermometers were not used.

Preparation of Dicarbonyltris(triethyl phosphite)iron.—The complex $[(1—3,6\text{-}\eta\text{-}C_8H_{12})Fe(CO)_3](1—3,6\text{-}\eta\text{-}C_8H_{12}$ = 1—3,6-η-cyclo-octadiene), (Ia), (0·1 g) and $P(OEt)_3$ (0·6 g) were dissolved in n-heptane (10 cm³) and the solution thoroughly degassed. After 46 h under an atmosphere of argon at 22 °C, solvent and excess of ligand were removed under reduced pressure (25 °C, 0·05 mmHg) leaving a pale brown moist solid from which a small quantity of the colourless *trans*-annular ketone (III), having a camphor-like odour, was condensed on to a cold finger (25 °C, 0·01 mmHg); ν(C=O) 1 743 cm⁻¹ (heptane) [Found: C, 79·1; H, 8·8; *M* (mass spectrometry) 136. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·9%; *M* 136]. The 2,4-dinitrophenylhydrazone derivative was prepared by the usual procedure, m.p. 163—166 °C [Found: C, 56·4; H, 5·1; N, 17·6; *M* (mass spectrometry) 316. Calc. for $C_{15}H_{16}N_4O_4$: C, 56·9; H, 5·1; N, 17·7%; *M* 316]. After removal of ketone from the product mixture the residue dissolved in heptane had no absorption at 1 743 cm⁻¹. Filtration of this solution through silica gel removed soluble brown impurities and, after partial removal of solvent, the complex $[Fe(CO)_2\{P(OEt)_3\}_3]$ (60%) separated as an off-white micro-crystalline powder [Found: C, 39·1; H, 7·5; P, 15·5; *M* (mass spectrometry) 610. Calc. for $C_{20}H_{45}FeO_{11}P_3$: C, 39·4; H, 7·45; P, 15·2%; *M* 610].

Microelemental analyses were carried out in this department.

RESULTS AND DISCUSSION

The reactions of the complexes $[(1—3,6\text{-}\eta\text{-}C_8H_{12})Fe(CO)_3]$, (Ia), and $[(1—3,6\text{-}\eta\text{-}C_8H_{12})Ru(CO)_3]$, (Ib), investigated in this study are summarised in the Scheme.



SCHEME

Reactions of Complex (Ia) *with Phosphorus Ligands.*—(a) PPh_3 *and* $P(OPh)_3$. The product of the reaction between complex (Ia) and PPh_3 in hydrocarbon solvents has been shown [1] to be (IIa) with the triphenylphosphine ligand *trans* to the metal–carbon σ-bond. Pseudo-first-order rate constants obtained at 60 °C for this reaction over a range of ligand concentration are shown in Figure 1. The order of the reaction with respect to $[PPh_3]$ is complex. At low $[PPh_3]$ the reaction is first order in ligand and at high $[PPh_3]$ it is zero order in ligand. At low $[PPh_3]$ rate plots were slightly curved, the observed rate constant decreasing during the latter stages of the reaction. A similar reaction took place with $P(OPh)_3$ and the i.r. spectrum of the product indicated that it is (IIa) [L = $P(OPh)_3$]. The kinetics of this reaction are similar to that with PPh_3 except that the reaction becomes zero order in ligand at a much lower ligand concentration (see Figure 1). However, the limiting rate constant is, within experimental error, the same for both reactions. These data suggest that the mechanism of these reactions is simple CO-dissociative in nature:

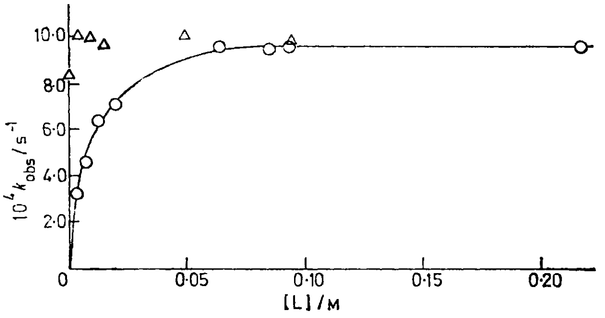


FIGURE 1 Ligand dependence of the rate of substitution of CO by PPh_3 (○) and $P(OPh)_3$ (△) in complex (Ia) at 60 °C

$$\begin{tikzcd} \begin{matrix}[(C_8H_{12})Fe(CO)_3] \\ \text{(Ia)}\end{matrix} \arrow[r, shift left, "k_1"] & \begin{matrix}[(C_8H_{12})Fe(CO)_2] + CO \\ \text{(V)}\end{matrix} \arrow[l, shift left, "k_{-1}"] \arrow[d, "{k_2[L]}"] \\ & \begin{matrix}[(C_8H_{12})Fe(CO)_2L] \\ \text{(IIa)}\end{matrix} \end{tikzcd}$$

Assuming stationary-state kinetic conditions for the intermediate (V), the following expression is obtained for the pseudo-first-order rate constant:

$$k_{obs} = \frac{k_1 k_2[L]}{k_{-1}[CO] + k_2[L]}$$

This expression quantitatively describes (see below) the rise of k_{obs} with increasing ligand concentration to a limiting value that is independent of the nature of the ligand. The curvature of the rate plots for reactions at low [PPh_3] can be explained by a significant increase in the value of k_{-1}[CO] relative to k_2[L] as CO is liberated during the reaction. From a plot of $1/k_{obs}$ against $1/[PPh_3]$, which was linear, a value of $(1·02 \pm 0·02) \times 10^{-3}$ s^{-1} was obtained for k_1 which is in good agreement with the average limiting value obtained for reaction with $P(OPh)_3$ [$(0·99 \pm 0·02) \times 10^{-3}$ s^{-1}], and k_2/k_{-1} was estimated to be *ca.* 0·1 assuming [CO] to be 1×10^{-3}M. A satisfactory linear plot of $1/k_{obs}$ against $1/[P(OPh)_3]$ was not obtained because of the rapid rise to the limiting rate with increasing ligand concentration. However, k_2/k_{-1} was estimated to be *ca.* 1 from the concentration of $P(OPh)_3$ required to produce limiting rate constants. The greater reactivity of complex (V) towards $P(OPh)_3$, compared with PPh_3, may be due to reduced steric interaction.[4]

In order to obtain activation parameters for loss of CO from complex (Ia), kinetic runs were undertaken at different temperatures. At higher temperatures (65 °C and above) observed rate constants for reaction with PPh_3 (*ca.* 0·1M) were less than predicted by the low-temperature results and a non-linear Arrhenius plot was produced. This was found to be due to the significantly higher PPh_3 concentrations needed to obtain limiting rates at the higher temperatures. This problem was not encountered with the more reactive $P(OPh)_3$. Limiting-rate data for reaction with these ligands over the temperature range 40—70 °C are collected in Table 1.

TABLE 1

Rate data for the reaction of the complex [(1—3,6-η-C_8H_{12})$Fe(CO)_3$], (Ia), (1—2·5mM) with PPh_3 and $P(OPh)_3$ in n-heptane under an atmosphere of argon

t/°C	L	[L]/M	k_{obs}/s^{-1}	k_{calc} [a]/s^{-1}
70·0	$P(OPh)_3$	0·201	$3·84 \times 10^{-3}$	$3·66 \times 10^{-3}$
70·0	$P(OPh)_3$	0·130	$3·62 \times 10^{-3}$	$3·66 \times 10^{-3}$
69·9	$P(OPh)_3$	0·0864	$3·65 \times 10^{-3}$	$3·61 \times 10^{-3}$
65·0	$P(OPh)_3$	0·139	$2·04 \times 10^{-3}$	$1·92 \times 10^{-3}$
65·0	$P(OPh)_3$	0·238	$2·03 \times 10^{-3}$	$1·92 \times 10^{-3}$
60·0	PPh_3	0·0928	$9·60 \times 10^{-4}$	$9·84 \times 10^{-4}$
60·0	$P(OPh)_3$	0·00429	$1·01 \times 10^{-3}$	$9·84 \times 10^{-4}$
60·0	$P(OPh)_3$	0·0091	$1·00 \times 10^{-3}$	$9·84 \times 10^{-4}$
60·0	$P(OPh)_3$	0·0145	$9·68 \times 10^{-4}$	$9·84 \times 10^{-4}$
60·0	$P(OPh)_3$	0·0485	$1·01 \times 10^{-3}$	$9·84 \times 10^{-4}$
60·0	$P(OPh)_3$	0·0938	$9·70 \times 10^{-4}$	$9·84 \times 10^{-4}$
59·9	PPh_3	0·0640	$9·55 \times 10^{-4}$	$9·70 \times 10^{-4}$
59·9	PPh_3	0·0844	$9·45 \times 10^{-4}$	$9·70 \times 10^{-4}$
59·9	PPh_3	0·216	$9·52 \times 10^{-4}$	$9·70 \times 10^{-4}$
55·1	PPh_3	0·0906	$4·73 \times 10^{-4}$	$5·02 \times 10^{-4}$
55·1	PPh_3	0·164	$4·84 \times 10^{-4}$	$5·02 \times 10^{-4}$
50·0	PPh_3	0·0761	$2·31 \times 10^{-4}$	$2·44 \times 10^{-4}$
50·0	PPh_3	0·0777	$2·34 \times 10^{-4}$	$2·44 \times 10^{-4}$
50·0	PPh_3	0·0796	$2·40 \times 10^{-4}$	$2·44 \times 10^{-4}$
45·0	PPh_3	0·112	$1·14 \times 10^{-4}$	$1·18 \times 10^{-4}$
45·0	PPh_3	0·150	$1·17 \times 10^{-4}$	$1·18 \times 10^{-4}$
39·8	PPh_3	0·0730	$5·46 \times 10^{-5}$	$5·36 \times 10^{-5}$
39·8	PPh_3	0·105	$5·45 \times 10^{-5}$	$5·36 \times 10^{-5}$
39·8	PPh_3	0·143	$5·66 \times 10^{-5}$	$5·36 \times 10^{-5}$
39·8	PPh_3	0·193	$5·52 \times 10^{-5}$	$5·36 \times 10^{-5}$

Derived activation parameters: $\Delta H^‡ = 29·21 \pm 0·16$ kcal mol^{-1}, $\Delta S^‡ = 15·2 \pm 0·5$ cal K^{-1} mol^{-1}.

[a] Calculated from activation parameters.

Activation parameters calculated from these data, $\Delta H^‡ = 29·2 \pm 0·2$ kcal mol^{-1} and $\Delta S^‡ = 15·2 \pm 0·5$ cal K^{-1} mol^{-1}, are typical[5] for a CO-dissociative mechanism.

(b) $P(OEt)_3$. Reactions of complex (Ia) with this ligand produced the monosubstituted complex (IIa) together with (IVa) [L = $P(OEt)_3$] and a ketone tentatively assigned the bicyclo[4.2.1] structure (III). The physical properties of the latter compound and its derivatives clearly demonstrate that it is not the previously reported[6] bicyclo[3.3.1]-2-non-9-one. Semiquantitative experiments suggested that the formation of (III) and (IVa) are associated and that more of these products relative to (IIa) are formed at high ligand concentrations. Under pseudo-first-order conditions, excellent rate plots were obtained and observed rate constants increased with [$P(OEt)_3$]. At three temperatures, plots of k_{obs} against

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[4] A. J. Poë and M. V. Twigg, *J. Organometallic Chem.*, 1973, **50**, C39.

[5] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173.

[6] S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6; C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.

$[P(OEt)_3]$ were linear (Figure 2) with positive intercepts.

$$k_{obs} = k_1' + k_2'[P(OEt)_3]$$

Values of k_1' and k_2' were calculated using a least-mean-squares treatment in which each rate constant was assumed to have the same percentage of uncertainty. These data are collected in Table 2, together with values of the rate constants (k_1) for loss of CO from complex (Ia), at the appropriate temperatures, calculated from data for the reactions with PPh_3 and $P(OPh)_3$ (see above). The values of k_1' and k_1 agree to within one standard deviation.

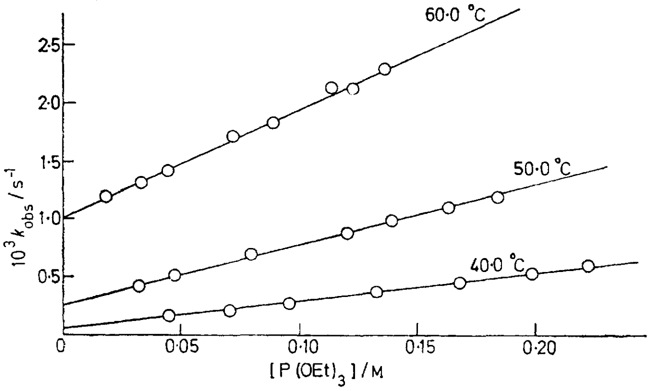

FIGURE 2 Plots of k_{obs} against $[P(OEt)_3]$ for the reaction of complex (Ia) with $P(OEt)_3$

TABLE 2

Derived values of k_1' and k_2' (see text) for reaction of complex (Ia) with $P(OEt)_3$

t/°C	$10^3k_2'$ [a]/ l mol^{-1} s^{-1}	k_1'/s^{-1}	k_1(calc) [b]/ s^{-1}
60·0	9·50 ± 0·32	(1·01 ± 0·03) × 10^{-3}	0·98 × 10^{-3}
50·0	5·19 ± 0·16	(2·57 ± 0·14) × 10^{-4}	2·44 × 10^{-4}
40·0	2·38 ± 0·09	(4·86 ± 0·94) × 10^{-5}	5·36 × 10^{-5}

[a] Activation parameters: $\Delta H^{\ddagger} = 13{\cdot}7 \pm 0{\cdot}5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27{\cdot}0 \pm 1{\cdot}6$ cal K^{-1} mol^{-1}. Quoted errors are standard deviations corrected for the appropriate number of degrees of freedom so that doubling them produces 95% confidence limits. [b] Calculated from data for the reaction of complex (Ia) with PPh_3 and $P(OPh)_3$.

TABLE 3

Rate constants (obtained by monitoring loss of reactant and appearance of products), product ratios, and rate constant ratios for reaction of complex (Ia) with $P(OEt)_3$ at 50·0 °C in n-heptane under an atmosphere of argon

[L]/mM	[Complex]/mM	10^4k/s^{-1} *a*	*b*	*c*	[(IVa)] : [(IIa)]	$(k^a - k_1) : k_1$
32·8	1·53	4·14	4·27	4·80	0·72	0·70
47·4	1·01	5·17	4·91	4·96	1·11	1·12
79·4	0·97	6·88	6·54	6·55	2·01	1·82
120	1·67	8·74	8·82	8·74	2·68	2·52
139	1·77	9·81	9·45	9·71	3·03	3·02
163	1·53	11·0	11·5	10·9	3·76	3·51
184	2·10	11·9	12·4	11·8	4·72	3·98

k = Observed pseudo-first-order rate constant; reaction monitored at *a*, 2 048, *b* 1 930, and *c* 1 866 cm^{-1}.

The k_2 term may be associated with a bimolecular reaction of complex (Ia), and activation parameters for this process ($\Delta H^{\ddagger} = 13{\cdot}7 \pm 0{\cdot}5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27{\cdot}0 \pm 1{\cdot}6$ cal K^{-1} mol^{-1}) are typical for a bimolecular reaction of a complex of this type in a non-polar solvent. Since no evidence for conversion of (IIa) into (IVa) [L = $P(OEt)_3$, PPh_3, or $P(OPh)_3$] was obtained at 80 °C, it is tempting to suggest that the k_1 path corresponds to a CO-dissociative reaction forming complex (IIa) with the bimolecular reaction producing (III) and (IVa). Indeed no (IIa) was formed at room temperature with a high ligand concentration. There was no reaction, even at 60 °C, between complex (Ia) and CO (1 atm) during reaction times used with phosphorus ligands. Over extended periods (2 days), some ketone (III) and iron carbonyl species were formed * from complex (Ia) but not from (IIa) in the presence of free ligand.

With two concurrent reactions of the type suggested, the same observed rate constant ($k_1 + k_2$[L]) will be obtained if the reaction is monitored by following the loss of reactant, or the appearance of either product. Moreover, the ratio ($k_{obs} - k_1$) : k_1 should equal the product concentration ratio, in this case [(IVa)] : [(IIa)]. Table 3 contains these data for a series of experiments at 50 °C. In some cases only small absorbance changes were used to monitor the appearance of one product, but even so the three observed rate constants (one reactant and two metal carbonyl products) are in satisfactory agreement, as are the product and rate constant ratios. This is consistent with complex (IVa) being formed exclusively by the bimolecular reaction and (IIa) by the CO-dissociative path.

(c) *With a variety of phosphorus ligands.* The kinetics of reactions of complex (Ia) with a variety of substituted phosphines and phosphites at 60 °C were studied to obtain information about the factors determining the contribution of the bimolecular path, and whether this reaction always leads to formation of a ketone. In all cases, plots of k_{obs} against [L] were linear with a common intercept corresponding to the rate of CO dissociation and formation of complex (IIa). Table 4 contains second-order rate constants and i.r. spectroscopic data for the various products. Inspection of these data suggests that both steric and electronic factors are important in determining the value of k_2. The sterically crowded PPh_3 and the less hindered, but less basic, $P(OPh)_3$ have

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* The ketone is also formed at room temperature with higher carbon monoxide pressures.

no detectable second-order reaction. The increased second-order reactivity of PMe_2Ph over that of PEt_2Ph may be assigned to steric factors, as may be the decrease of k_2 along the series $P(OR)_3$ (R = Me, Et, or Pr^i). On this basis the cage phosphite $(POCH_2)_3CEt$ might be expected to be more reactive than $P(OMe_3)$ but this is not the case. This phosphite is also unusual because no (III) or (IVa) is formed from the reaction with complex (Ia), although there is a second-order reaction. This might indicate that the incoming ligand must have a minimum ' bulkiness ' for completion of the bimolecular ketone-producing process, and perhaps this could be interpreted in terms of a carbonyl-insertion rather than an alkyl-migration reaction.[7] However, it is not clear why the second-order rate constant for reaction with $P(OCH_2)_3CEt$ is less than that for reaction with $P(OMe)_3$.

TABLE 4

Second-order rate constants for reactions of complex (Ia) with phosphorus ligands in n-heptane at 60 °C, and i.r. spectra of the products

Ligand (L)	$\dfrac{10^3 k_2{}^a}{\text{l mol}^{-1}\,\text{s}^{-1}}$	ν(CO)/cm⁻¹			
		$[(C_8H_{12})Fe(CO)_2L]$		$[Fe(CO)_2L_3]$	
CO		2 048	1 978		
$P(OCH_2)_3CEt$	*ca.* 5	2 004	1 952		
$P(OPh)_3$	*b*	1 999	1 945		
$P(OMe)_3$	10·2	1 986	1 932	1 874	*c*
$P(OEt)_3$	9·5	1 984	1 930	1 866	1 926 *d*
$P(OPr^i)_3$	5·4	1 980	1 925	1 851	*c*
PPh_3		1 977	1 923		
$PMePh_2$	1·5	1 976	1 922	1 834	*c*
PMe_2Ph	7·0	1 974	1 919	1 820	1 876
PEt_2Ph	2·4	1 972	1 918	1 814	1 871
$P(Bu^t)_3$	4·7	1 972	1 918	1 814	1 873

[a] k_2 Values estimated from plots of k_{obs} against [L]; uncertainties are *ca.* ±5%. [b] Estimated upper limit 0·2 × 10^{-3} l mol⁻¹ s⁻¹. [c] Obscured by other absorptions. [d] Isolated from reaction (see Experimental section).

Reactions of Complex (Ib) *with Phosphorus Ligands*.— Observed pseudo-first-order rate constants for reaction of the ruthenium complex (Ib) with several phosphorus ligands under an atmosphere of argon showed no dependence on the nature or concentration of the ligand (Table 5). In each case, only one ruthenium-containing product (IIb) was observed. (I.r. spectra of these products are given in Table 6.) These observations and the values of the activation parameters, $\Delta H^\ddagger = 26{\cdot}5 \pm 0{\cdot}1$ kcal mol⁻¹ and $\Delta S^\ddagger = 13{\cdot}8 \pm 0{\cdot}5$ cal K⁻¹ mol⁻¹, are consistent with a CO-dissociative mechanism. At 35 °C it was necessary to use low concentrations of the poor nucleophile PPh_3 under 1 atm CO to observe the expected rise of k_{obs} to the limiting value with increasing $[PPh_3]$. [Like (Ia), the ruthenium complex (Ib) does not react over convenient reaction periods with CO.] The plot of $1/k_{obs}$ against $1/[PPh_3]$ was linear, and from its intercept a value of $(1{\cdot}06 \pm 0{\cdot}03) \times 10^{-3}$ s⁻¹ for k_1, was obtained which agrees with that calculated ($1{\cdot}09 \times 10^{-3}$ s⁻¹) from the data for reaction under an atmosphere of argon. The competition ratio $k_{-1} : k_2$ for reaction of ' C_8H_{12}-$Ru(CO)_2$ ' with CO and PPh_3 at 35 °C was estimated to be 0·9 from the gradient of this plot and the known value of k_1. The value of this ratio for the iron complex (see above) is *ca.* 10 at 60 °C, suggesting that ' $C_8H_{12}Ru(CO)_2$ ' is less selective than ' $C_8H_{12}Fe(CO)_2$.' However, the effect of the temperature difference cannot be completely evaluated from the data available, although there is evidence (see above) that $k_{-1} : k_2$ is smaller for the iron complex at lower temperatures.

TABLE 5

Rate data for reaction of complex (Ib) with phosphorus ligands in n-heptane under an atmosphere of argon

t/°C	L	[L]/M	k_{obs}/s⁻¹	$k_{calc}{}^a$/s⁻¹
20·0	$P(OEt)_3$	0·0441	$1{\cdot}11 \times 10^{-4}$	$1{\cdot}14 \times 10^{-4}$
20·0	$P(OEt)_3$	0·400	$1{\cdot}12 \times 10^{-4}$	$1{\cdot}14 \times 10^{-4}$
25·0	$P(OEt)_3$	0·0588	$2{\cdot}52 \times 10^{-4}$	$2{\cdot}48 \times 10^{-4}$
25·0	$P(OEt)_3$	0·288	$2{\cdot}50 \times 10^{-4}$	$2{\cdot}48 \times 10^{-4}$
30·0	$P(OEt)_3$	0·0245	$5{\cdot}30 \times 10^{-4}$	$5{\cdot}26 \times 10^{-4}$
30·0	$P(OEt)_3$	0·0736	$5{\cdot}26 \times 10^{-4}$	$5{\cdot}26 \times 10^{-4}$
35·0	$P(Bu^n)_3$	0·160	$1{\cdot}14 \times 10^{-3}$	$1{\cdot}09 \times 10^{-3}$
35·0	$P(OEt)_3$	0·0736	$1{\cdot}06 \times 10^{-3}$	$1{\cdot}09 \times 10^{-3}$
40·0	PPh_3	0·0830	$2{\cdot}24 \times 10^{-3}$	$2{\cdot}21 \times 10^{-3}$
40·0	$P(OPh)_3$	0·0898	$2{\cdot}17 \times 10^{-3}$	$2{\cdot}21 \times 10^{-3}$
40·0	$P(OEt)_3$	0·0246	$2{\cdot}27 \times 10^{-3}$	$2{\cdot}21 \times 10^{-3}$
40·0	$P(OEt)_3$	0·228	$2{\cdot}18 \times 10^{-3}$	$2{\cdot}21 \times 10^{-3}$
45·0	$P(OEt)_3$	0·0555	$4{\cdot}34 \times 10^{-3}$	$4{\cdot}39 \times 10^{-3}$
45·0	$P(OEt)_3$	0·216	$4{\cdot}36 \times 10^{-3}$	$4{\cdot}39 \times 10^{-3}$

Derived activation parameters: [b] $\Delta H^\ddagger = 26{\cdot}5 \pm 0{\cdot}14$ kcal mol⁻¹, $\Delta S^\ddagger = 13{\cdot}8 \pm 0{\cdot}5$ cal K⁻¹ mol⁻¹.

[a] Calculated from the derived activation parameters. [b] Quoted errors are corrected for the appropriate number of degrees of freedom so that doubling them produces 95% confidence limits.

TABLE 6

I.r. data for some substituted ruthenium complexes, (IIb)

L	ν(CO) */cm⁻¹	
CO	2 067	1 998
$P(OPh)_3$	2 020	1 967
$P(OEt)_3$	2 006	1 951
PPh_3	2 002	1 946
$P(Bu^t)_3$	1 996	1 940

* In n-heptane.

As a result of a more favourable enthalpy of activation, the rate of CO dissociation from the ruthenium complex (Ib) at 40 °C is about 40 times faster than that from the iron complex (Ia). Enhanced reactivity of second-row transition-metal carbonyl complexes over their first-row counterparts in reactions of this type is well established.* Enhanced bimolecular reactivity might be expected from the increased atomic radii and the greater stability of seven-co-ordinate complexes of the second and third transition series.[8,9] If this is correct, the important bimolecular reactions of the iron complex (Ia), which were not detected for the ruthenium complex (Ib), suggest that

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* Exceptions are known, *e.g.* the rate of CO dissociation from $[M(CO)_4LL]$ (LL = 2,2′-bipyridine and 1,10-phenanthroline) follows the order Cr > Mo > W.

[7] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.

[8] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 1967, **6**, 2082.

[9] R. J. Angelici and J. R. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 5586, 5590.

bonding between iron and the organo-group is significantly weaker than that between ruthenium and the organo-group.

There is a general tendency of the $M(CO)_3$ (M = Fe or Ru) unit to favour the 1—3,6-η mode of bonding in preference to the more generally observed 1,2,5,6-η form. As might be anticipated from the formal oxidation states of the metal ion in these systems, (II) and (0) respectively, a marked change in substitution behaviour is observed. Thus with the former the carbonyl ligand *trans* to the σ-bond is readily substituted, while at the higher temperatures required for reaction of the latter, replacement of the diene occurs. Since there is some evidence that the two isomers are thermally interconvertible these reactions offer some synthetic potential.

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