Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part VIII.[1] Substitution Reactions of *cyclo*-Tris(tetracarbonylruthenium)(3*Ru–Ru*)

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Reactions of *cyclo*-tris(tetracarbonylruthenium)(3*Ru–Ru*), (I), with some phosphorus- and arsenic-donor ligands (L), mainly in decalin, have been studied over a range of temperature. Observed pseudo-first-order rate constants obey the rate equation $k_{\text{obs}} = k_1 + k_2[\text{L}]$ and activation parameters have been obtained. Values of log k_2 obey a moderately good linear free-energy relation when plotted against corresponding values of Δ(h.n.p.) (the relative half-neutralization potentials for titration of the nucleophiles with perchloric acid in nitromethane), but those for triphenyl- and tricyclohexyl-phosphine lie well below the line. The use of such relations, and of deviations from them, in indicating the relative contributions of bond making in reactions of a wide variety of metal carbonyl complexes is described and compared with other methods. Reactions of complex (I) appear to involve an exceptionally high degree of bond making. The relative strengths of carbonyl and phosphorus-donor ligands as nucleophiles in attacking vacant co-ordination sites in several complexes are also considered.

ALTHOUGH bimolecular substitution reactions of substituted metal carbonyl complexes are becoming increasingly common, it appears that it is the nature of the substituent that facilitates these reactions.[2] Indeed, many of the reactions involve displacement of co-ordinated polydentate ligands, and it has been shown, in some cases at least, that reversible dissociation of one end of the ligand occurs before attack at the metal atom by the nucleophile.[3] Bimolecular reactions of octahedral metal carbonyl complexes that unambiguously involve rate-determining nucleophilic attack at the metal atom to form a seven-co-ordinate transition state are, therefore, still quite rare, and such reactions of binary metal carbonyls seem to be restricted almost entirely to those of octahedral Group 6A hexacarbonyls.[4] Some reactions of *cyclo*-tris(tetracarbonylruthenium)(3*Ru–Ru*), (I), reported recently by Candlin and Shortland[5] appear to provide an additional set of examples since each metal atom forms six bonds in a roughly octahedral arrangement. However, two of these are metal–metal bonds so, although it is technically a binary metal carbonyl complex, it could also be regarded as a substituted metal carbonyl in a very real sense. Since the data reported were not very extensive, and since we are generally interested in reaction mechanisms of metal–metal bonded carbonyl complexes, we have studied the kinetics of substitution reactions of (I) in considerably greater detail in order to determine how susceptible it is to nucleophilic attack, to compare its behaviour with similar reactions of other metal carbonyls, and to see if one can infer the relative degrees of bond making in the transition states involved.

EXPERIMENTAL AND RESULTS

cyclo-Tris(tetracarbonylruthenium)(3*Ru–Ru*) (Strem Chemicals, Inc.) was used as received. Liquid phosphorus ligands (triphenyl phosphite, triethyl phosphite, and tri-n-butylphosphine) were obtained from commercial sources and were purified by distillation under low pressures of argon or nitrogen [$P(OPh)_3$, 172—174 (0·4); $P(OEt)_3$, 21—22 (0·85); and PBu^n_3, 94—95 °C (3·2 mmHg)] immediately before use. Their refractive indices agreed well with published values.[6] Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), and triphenylarsine were recrystallized from absolute ethanol, and tricyclohexylphosphine (Strem Chemicals, Inc.) from hexane, samples being dried *in vacuo* for several days before use. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [$P\{(OCH_2)_3CEt\}$, (etpb)] (Strem Chemicals, Inc.) was sublimed (50 °C, 0·12 mmHg) immediately before use. Decalin (J. T. Baker, Analysed Reagent) was dried over molecular sieves, or used as received. 1,4-Dioxan (B.D.H., Reagent Grade) was used as received.

Kinetics.—Reactions with pseudo-first-order excesses of nucleophiles in decalin were followed by standard spectrophotometric techniques. Those involving triphenyl-phosphine and -arsine were monitored continuously in thermostatted stoppered cells in Perkin-Elmer 402 or Cary 16K spectrophotometers. Those involving the other nucleophiles were followed by standard sampling techniques followed by measurement of i.r. spectra. To prevent oxidation of nucleophiles particular care was taken to ensure that air was excluded when preparing solutions. Complex (I) was shown to decompose at conveniently measureable rates under an atmosphere of oxygen in decalin and in the dark at temperatures above *ca.* 100 °C, but kinetic measurements were not very reproducible. Decomposition rates under the conditions of our kinetic runs were quite insignificant, even in 1,4-dioxan in which decomposition was somewhat faster than in decalin. The intensity of the i.r. bands of complex (I) (2 065s, 2 035s, and 2 012m cm^{-1}) decreased steadily during substitution reactions and rate plots were derived from the absorbance of the band at 2 065 cm^{-1} which usually decreased to zero. Excellent pseudo-first-order rate plots, linear to at least 80% completion of reaction, were obtained in all cases.

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[1] Part VII, M. Basato, J. P. Fawcett, S. A. Fieldhouse, and A. J. Poë, preceeding paper.

[2] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 2nd edn., 1967, pp. 571—578.

[3] See, for example, G. R. Dobson and A. J. Faber, *Inorg. Chim. Acta*, 1972, **6**, 507; F. Zingales, F. Canziani, and F. Basolo, *J. Organometallic Chem.*, 1967, **7**, 461.

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

[5] J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289.

[6] L. Maier, *Progr. Inorg. Chem.*, 1963, **5**, 27.

Values of k_{obs} increased with increasing concentration of nucleophile L and were fitted to the rate equation $k_{obs} = k_1 + k_2[L]$ by least-squares analysis. It was assumed that all values of k_{obs} at a given temperature had the same percentage uncertainty. Values of $\sigma(k_{obs})$ showed no systematic trends with temperature and data for each nucleophile at all temperatures were therefore treated by the method of pooled variances so as to increase substantially the numbers of degrees of freedom and provide a more reliable single estimate of $\sigma(k_{obs})$ for a given nucleophile. Values of $\sigma(k_{obs})$ and of the standard deviations of k_1 and k_2 were adjusted according to the number of degrees of freedom so that good estimates of the various confidence levels can be obtained by multiplying by the appropriate value of Student's t for an infinite number of degrees of freedom. All activation parameters were calculated by a weighted least-squares analysis.

TABLE 1

Pseudo-first-order rate constants for reaction of the complex $[Ru_3(CO)_{12}]$ with PPh_3

(*a*) In decalin

t/°C	$[PPh_3]$/mM	$10^5\ k_{obs}/s^{-1}$
39·7	9·9	1·57
	53·7	3·92
	124	7·92
	187	11·2
	251	14·5
	293	16·7
	361	19·9
	397	21·9
50·1	10·8	7·06
	47·7	11·4
	98·5	17·8
	153	25·7
	208	32·8
	266	38·7
	308	45·6
	351	50·3
	388	53·4
	398	55·7
60·4	6·2	26·9
	63·4	41·6
	128	58·6
	192	77·4
	238	90·4
	296	103
	366	124
	424	142
69·8	5·18	104
	17·5	109
	39·7	124
	53·5	129
	80·7	140
	114	164
	147	172
	160	186
	193	191
	230	213
	267	240
	288	260
	311	254
	350	283

(*b*) In 1,4-dioxan

t/°C	$[PPh_3]$/mM	$10^5\ k_{obs}/s^{-1}$
34·5	120	4·77
	204	7·85
	314	12·2
	411	16·3
41·9	49·5	3·63
	79·0	5·56
	190	13·7
	291	21·6
	365	27·2
57·8	64·0	44·6
	107	53·8
	202	75·0
	286	97·5
	345	112
64·6	116	121
	152	133
	208	158
	251	178
	254	183
	349	236
	366	220

Reaction with Triphenyl-phosphine and -arsine.—Changes in i.r. spectra during reaction with triphenylphosphine showed loss of complex (I) and formation of $\{Ru(CO)_3PPh_3\}_3$, characterized by bands at 1 985s, 1 975s, and 1 958m cm^{-1}, without any sign of intermediate species even when $[PPh_3] = 0{\cdot}05$M and reaction occurred under an atmosphere of carbon monoxide. Reaction with triphenylarsine showed growth of i.r. bands at frequencies close to those reported[7] for the complex $[Ru_3(CO)_{10}(AsPh_3)_2]$ with a subsequent much slower growth of bands at lower frequencies. Since neither triphenyl-phosphine nor -arsine is sensitive to oxygen under conditions of these reactions, and since there were no signs of intermediates, rate data were obtained by measuring the growth of absorbance at 506 (ε 1·21 × 10^{-4} l mol^{-1} cm^{-1}) and 470 nm, respectively. Reaction with triphenylphosphine was also followed in the more polar solvent 1,4-dioxan, where yields were low at lower values of $[PPh_3]$ but quantitative at higher values. Values of k_{obs} are shown in Tables 1 and 2, derived values of k_1 and k_2 in Table 6, and activation parameters for the second-order path in Table 7. It is clear that the reason why Candlin *et al.*[5] did not detect the bimolecular contribution to the rate law when L = PPh_3 was that not high enough concentrations were used.

TABLE 2

Pseudo-first-order rate constants for reaction of the complex $[Ru_3(CO)_{12}]$ with $AsPh_3$ in decalin

t/°C	$[AsPh_3]$/mM	$10^5\ k_{obs}/s^{-1}$
50·6	163	6·74
	209	6·99
	248	6·97
	288	7·16
	339	7·66
60·2	42·7	26·0
	77·4	25·5
	121	26·8
	167	26·7
	214	27·5
	245	27·6
	291	28·3
	324	28·2
69·8	43·4	102
	82·9	103
	128	104
	147	104
	164	106
	236	105
	294	108
	350	106

Values of k_1 for L = PPh_3 in 1,4-dioxan were much less precise than those for reaction in decalin since the reaction went to completion only at higher values of $[PPh_3]$. Comparable values of k_1 when L = PPh_3 and $AsPh_3$ were the

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

same within the limits of error. $\Delta H_1^\ddagger = 133·5 \pm 0·8$ kJ mol^{-1} ($31·81 \pm 0·19$ kcal mol^{-1}) and $\Delta S_1^\ddagger = 84·5 \pm 2·5$ J K^{-1} mol^{-1} ($20·2 \pm 0·6$ cal K^{-1} mol^{-1}) when L = PPh_3, values for $AsPh_3$ being virtually identical but slightly less precise. These values compare well with those ($\Delta H^\ddagger = 31·8 \pm 1·0$ kcal mol^{-1} and $\Delta S^\ddagger = 21 \pm 3$ cal K^{-1} mol^{-1}) calculated from data reported [8] for the exchange of ^{14}CO with complex (I) in benzene.

Reaction with Triphenyl Phosphite and 4-*Ethyl*-2,6,7-*trioxa*-1-*phosphabicyclo*[2.2.2]*octane*.—Although, under preparative conditions, no evidence for mono- and bis-substituted triphenyl phosphite complexes has been reported,[9] we found evidence for successive formation and decay of intermediates. When L = $P(OPh)_3$, i.r. bands at 2 055s and 2 022s cm^{-1}, and at 2 037s and 2 017s cm^{-1}, successively grew and decayed before the tris-substituted complex (2 002s and 1 982s cm^{-1}) [9] was finally formed. The corresponding pairs of bands when L = etpb were 2 053s and 2 025s, 2 038ms and 2 018s, and 1 988m and 1 978m cm^{-1}. The tris(etpb) complex tended to precipitate from solution at the end of the reaction, but good rate plots were obtained for reactions with both nucleophiles with the i.r. technique described. Kinetic data are reported in Tables 3, 4, 6, and 7. Values of k_1 were not very precise since the lowest values of [L] were considerably higher than before and values of k_2 were relatively larger. Reaction with $P(OPh)_3$ under an atmosphere of carbon monoxide was also followed (Table 3). At higher values of [$P(OPh)_3$], k_2 was identical with that found for reactions under a nitrogen atmosphere, and the lower rates at lower [$P(OPh)_3$] can be ascribed to retardation of the path governed by k_1 in the absence of carbon monoxide.

TABLE 3

Pseudo-first-order rate constants for reaction of the complex [$Ru_3(CO)_{12}$] with $P(OPh)_3$ in decalin

t/°C	[$P(OPh)_3$]/mM	$10^5\ k_{obs}$/s^{-1}
41·0	45·8	4·72
	126	11·3
	210	17·2
	310	26·1
	429	36·4
50·3	76·4	18·3
	153	29·8
	230	44·1
	318	60·2
	432	80·4
59·6	57·9	36·4
	91·0	46·1
	186	79·0
	278	108
	366	126
68·4	92·4	120
	189	175
	262	214
	318	248
	417	302
68·4 [a]	7·6	25·1
	16·7	45·4
	43·4	75·0
	60·6	88·6
	111	118
	171	160
	253	210

[a] Under 1 atm carbon monoxide.

Reactions with Triethyl Phosphite and Tri-n-butylphosphine.—Changes in i.r. spectra during reaction were quite complex, substituted five-co-ordinate mononuclear products being indicated together with substituted trinuclear complexes. A detailed examination of the kinetics and course of the reaction with PBu_3 will be reported elsewhere,[10] although derived kinetic parameters are reported here (Table 7) for comparison. Values of k_1 were again very imprecise (as expected from the small value of k_1/k_2) and also suffered from systematic errors, perhaps because of the loss of small amounts of nucleophile at low concentrations by reaction with traces of oxygen. The precision of k_2,

TABLE 4

Pseudo-first-order rate constants for reaction of the complex [$Ru_3(CO)_{12}$] with P{$(OCH_2)_3CEt$} (etpb) in decalin

t/°C	[etpb]/mM	$10^5\ k_{obs}$/s^{-1}
40·0	35·3	29·2
	56·8	44·6
	94·9	73·7
	107	83·7
	153	119
50·0	37·2	66·5
	67·8	116
	114	190
	134	227
	152	246
60·0	34·0	145
	57·7	224
	77·7	276
	109	362
	122	423
70·0	13·2	210
	19·6	228
	27·8	289
	38·7	345
	45·5	370

TABLE 5

Pseudo-first-order rate constants for reactions of the complex [$Ru_3(CO)_{12}$] with $P(OEt)_3$ in decalin

t/°C	[$P(OEt)_3$]/mM	$10^5\ k_{obs}$/s^{-1}
30·0	19·9	7·05
	46·6	17·6
	93·3	35·2
	132	50·9
	154	58·3
40·0	21·7	18·3
	62·4	54·3
	81·8	70·6
	123	109
	141	123
50·0	29·7	56·5
	76·7	151
	124	240
	149	282
	187	352
60·0	41·6	167
	54·8	216
	108	405
	121	457
	184	684

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[8] G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.* (*Torino*), 1967, **101**, 855.

[9] F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1389.

[10] A. J. Poë and M. V. Twigg, *Inorg. Chem.*, in the press.

$\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ was excellent (Tables 6 and 7), indicating good reproducibility of the second-order rate constants.

Reaction with Tricyclohexylphosphine and 1,2-*Bis*(*diphenylphosphino*)*ethane*.—Low solubility of these nucleophiles in decalin prevented a thorough study of their reactions. Groups of product bands at 2 020—2 050 and 1 920—2 000 cm^{-1} were observed when L = $P(C_6H_{11})_3$ and a maximum value of k_2 at 50·0 °C of *ca.* 10^{-4} l mol^{-1} s^{-1} was obtained from k_{obs} = 6·3 × 10^{-5} s^{-1} {[$P(C_6H_{11})_3$] = 0·116M}. Reaction with dppe produced the complex [$Ru(CO)_3$(dppe)] (2 009s, 1 944s, and 1 929vs cm^{-1}),[11] and a broad band at *ca.* 1 900 cm^{-1} and a shoulder on the high-energy side of the 1 944 cm^{-1} band also appeared. The complex [$Ru_3(CO)_{10}$(dppe)] has been reported [7] as a minor product (3%) of this reaction under slightly milder conditions. No evidence of a second-order term in the rate law was obtained.

TABLE 6

Values of k_1 and k_2, for reactions in decalin, obtained from the rate equation $k_{obs} = k_1 + k_2[L]$ by least-squares analysis

L	t/°C	10^5 k_1/s^{-1}	10^5 k_2/ l mol^{-1} s^{-1}	$\sigma(k_{obs})$/ % [a]
PPh_3	39·7	1·05 ± 0·04	5·35 ± 0·06	
	50·1	5·62 ± 0·15	12·7 ± 0·1	
	60·4	24·9 ± 0·5	27·0 ± 0·4	
	69·8	101·2 ± 1·0	50·9 ± 1·0	2·3
PPh_3 [b]	34·5	0·07 ± 0·26	3·89 ± 0·14	
	41·9	−0·09 ± 0·15	7·36 ± 0·17	
	57·8	28·9 ± 1·6	23·7 ± 1·0	
	64·6	67·9 ± 5·0	44·3 ± 2·3	3·0
$AsPh_3$	50·6	5·95 ± 0·19	0·46 ± 0·08	
	60·2	25·3 ± 0·3	0·96 ± 0·15	
	69·8	102·0 ± 1·2	1·54 ± 0·55	1·5
$P(OPh)_3$	41·0	1·03 ± 0·20	8·04 ± 0·19	
	50·3	4·80 ± 0·83	17·2 ± 0·5	
	59·6	18·6 ± 1·4	30·9 ± 1·0	
	68·4	68·2 ± 5·4	56·2 ± 2·5	3·2
$P\{(OCH_2)_3CEt\}$	40·0	2·2 ± 1·3	75·8 ± 2·1	
	50·0	6·9 ± 2·9	161 ± 4	
	60·0	43·3 ± 6·4	303 ± 10	
	70·0	136 ± 8	526 ± 30	2·8
$P(OEt)_3$	30·0	−0·62 ± 0·2	38·7 ± 0·4	
	40·0	−0·9 ± 0·4	88·2 ± 0·9	
	50·0	0·7 ± 1·2	191 ± 2	
	60·0	16·6 ± 3·7	362 ± 5	1·5

[a] Obtained by pooling data at all temperatures. [b] In 1,4-dioxan.

TABLE 7

Kinetic parameters for bimolecular substitution reactions of the complex [$Ru_3(CO)_{12}$] in decalin

L	$\Delta H_2^{\ddagger}$/ kJ mol^{-1}	$\Delta S_2^{\ddagger}$/ J K^{-1} mol^{-1}	10^4 k_2 (50 °C)/ l mol^{-1} s^{-1}	Δ(h.n.p.)/ mV [a]
$AsPh_3$	51 ± 14	−147 ± 43	0·5	
PPh_3	64·6 ± 0·6	−102 ± 2	13	573
PPh_3 [b]	60·5 ± 1·5	−100 ± 5	14	573
$P(OPh)_3$	60·5 ± 1·4	−112 ± 4	17	875
$P\{(OCH_2)_3CEt\}$	56·4 ± 1·5	−107 ± 5	161	650
$P(OEt)_3$	60·5 ± 0·4	−91·5 ± 1·3	191	520
PBu^n_3	50·5 ± 0·8	−115 ± 0·3	456	131

[a] Relative values of half-neutralization potential for titration of the ligand L with perchloric acid in nitromethane.[2] [b] In 1,4-dioxan.

DISCUSSION

Reaction Products.—The absence of detectable intermediate mono- and bis-(triphenylphosphine) complexes during reaction shows that these react more rapidly than the parent carbonyl. Reactions with triphenyl phosphite and etpb show clear evidence for successive formation of intermediates, the trends of the i.r. spectra being the same as those shown by the mono-, bis-, and tris-(dimethylphenylphosphine) complexes isolated by Stone and his co-workers.[7] Similarly the complex [$Mn_2(CO)_9$(PPh_3)] undergoes further substitution, in xylene [12] or decalin,[13] more rapidly than [$Mn_2(CO)_{10}$], whereas [$Mn_2(CO)_9\{P(OPh)_3\}$] reacts in xylene [12] less rapidly. Reactions with triethyl phosphite and tri-n-butylphosphine do not proceed simply through successive formation of mono- and bis-substituted intermediates and monomeric five-co-ordinate complexes are formed under some conditions. Similarly, one of the products of reaction with dppe appears to be [$Ru(CO)_3$(dppe)] but it is not known at which stage fission of the Ru–Ru bond occurs.

Mechanism of the First-order Path.—The path governed by k_1 is most reasonably assigned a simple dissociative mechanism. Retardation by carbon monoxide when L = $P(OPh)_3$ is consistent with this and suitable graphical analysis [14] of the data (Table 3) leads to k_1 = 6·9 × 10^{-4} s^{-1} (in excellent agreement with the value from reaction under an argon atmosphere) and $k_{P(OPh)_3}$: k_{CO} = 0·34 : 1 when [CO] is taken as 5·6 × 10^{-3}M,[15] the ratio being a measure of the relative rate constants for nucleophilic attack on the co-ordinatively unsaturated complex [$Ru_3(CO)_{11}$]. This value is compared with some other competition parameters in Table 8. Hyde and Darensbourg [16] reported several competition parameters for the complex [$Mo(CO)_4$(PPh_3)], only one of which is quoted here. Steric effects are of major importance as might be expected for co-ordinatively unsaturated reactive intermediates that should be electronically not very discriminating. The highest values are obtained for simple four-co-ordinate d^8 cobalt intermediates, whereas much lower values are obtained for various bridged or cluster intermediates. Substitution of a phosphine group into a fully co-ordinated metal atom also decreases the competitive power of a phosphine in attack at the other, co-ordinatively unsaturated, metal atom.

Complex (I) is considerably more labile than molybdenum hexacarbonyl [17] but this is due to a more

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[11] F. Faraone, F. Cusmano, and R. Pietropaolo, *J. Organometallic Chem.*, 1971, **26**, 147.

[12] H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113.

[13] J. P. Fawcett, Ph.D. thesis, London University, 1973.

[14] M. Basato and A. J. Poë, *J.C.S. Dalton*, 1974, 456.

[15] M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1974, 350.

[16] C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 1973, **12**, 1286.

[17] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173; H. Werner, *Angew. Chem. Internat. Edn.*, 1968, **7**, 930.

favourable value of $\Delta S_1^\ddagger$, the values of $\Delta H_1^\ddagger$ being virtually equal. Respective values of 286 and 220 N m^{-1} for the Ru–CO(equatorial) and Ru–CO(axial) stretching force constants [18] are both significantly greater than that (181 N m^{-1}) for the Mo–CO stretch,[19] exemplifying again the lack of correlation between kinetic and spectroscopic parameters already shown even by the closely related hexacarbonyl complexes of chromium, molybdenum, and tungsten.[17,19]

TABLE 8

Values of k_L/k_{CO} for nucleophilic attack on co-ordinatively unsaturated intermediates in decalin

Intermediate	L	t/°C	k_L/k_{CO}	Ref.
$[Ru_3(CO)_{11}]$	$P(OPh)_3$	50	0·34	This work
$[Ru_3(CO)_{11}]$	PPh_3	50	*ca.* 0·2	*a*
$[(OC)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_2]$	PBu_3	70	0·5	14
$[(Bu_3P)(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2]$	PBu_3	70	0·1	14
$[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3]$	PBu_3	30	45	1
$[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3]$	PPh_3	30	22	1
$[(Ph_3P)(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_3]$	PPh_3	120	1·7	1
$[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2]$	PPh_3	30	0·5	1
$[Mo(CO)_4(PPh_3)]$	PPh_3	28	*ca.* 3 [b]	16

[a] M. J. Lang and A. J. Poë, unpublished work. [b] Corrected for solubility of carbon monoxide of 6×10^{-3}M.

TABLE 9

L.f.e.r. data for some bimolecular substitution reactions of metal carbonyl complexes with phosphorus-donor ligands

Complex	Solvent	t/°C	$-[\log k_2/\Delta(\text{h.n.p.})]/\text{V}^{-1}$	$\Delta(PPh_3)$ [a]	$\Delta[P(C_6H_{11})_3]$ [a]	Ref.
$[Co(NO)(CO)_3]$	Toluene	25	4·8	0	−1·7	22
$[Fe(NO)_2(CO)_2]$	Toluene	25	6·0	0	−1·7	24
$[Mn(NO)(CO)_4]$	*p*-Xylene	50	3·7	0		25
$[(cp)Rh(CO)_2]$	Toluene	40	*ca.* 2·5	0	−2·0	23
$[W(CO)_6]$	Decalin	166	1·5	−0·25		4
$[Mo(CO)_6]$	Decalin	112	1·5	−0·4		4
$[Cr(CO)_6]$	Decalin	131	0·7	0		4
$[(OC)_3Fe(\mu\text{-}S_2C_6H_3Me)Fe(CO)_3]$	Toluene	35	3·4	0	−2·0	29
$[Ru_3(CO)_{12}]$	Decalin	50	*ca.* 2·5	*ca.* −1	*ca.* −3	This work; 26

[a] Deviation of log k_2 from the l.f.e.r.

Mechanism of the Second-order Path.—Very few substitution reactions of unsubstituted binary metal carbonyl complexes show rate laws that include a term dependent on the concentration of the entering ligand. However, a rapidly increasing number is accumulating for reactions of substituted metal carbonyl complexes in which the metal atom has an ill defined oxidation state brought about by the presence, particularly, of co-ordinated nitrogen oxide or of unsaturated hydrocarbon ligands.[20] These ligands provide flexibility in the electronic structure of the complexes that enables them to respond readily to the approach of a nucleophile.[2] Although the nucleophile is definitely present in the transition state, the dependence of rate parameters on the natures of the complex and entering nucleophiles must be examined to determine the degree of which the incoming group determines the energy of the transition state by bond formation. Such data can also enable one to draw inferences as to the site of nucleophilic attack. Thus, reaction of Group 6A hexacarbonyl complexes with azide ion shows a pattern of reactivity quite different from that of reactions with phosphorus-donor ligands, and attack by azide is believed to occur at the carbon atom of a co-ordinated carbonyl group,[21] attack by the phosphorus ligands most probably occurring at the metal atom.[17]

Basolo and his co-workers [2,22–25] have shown that good linear free-energy relations (l.f.e.r.) with positive gradients are often obtained when values of log k_2 are plotted against a quantitative measure of basicity, provided by the relative half-neutralization potentials, $-\Delta$(h.n.p.),[24,22] for titration of the nucleophile with perchloric acid in nitromethane, the standard base being

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NN′-diphenylguanidine. Data obtainable from such l.f.e.r. are shown in Table 9. The gradients, —log k_2/Δ(h.n.p.), should be a measure of the ability of the complexes to discriminate electronically between nucleophiles, and it can be argued that larger gradients imply greater relative importance of bond making in the transition states. Deviations from such l.f.e.r. can also be informative.[2] Thus, $\Delta(PPh_3)$ and $\Delta[P(C_6H_{11})_3]$ measure the extent to which values of log k_2 for reactions with triphenyl- and tricyclohexyl-phosphine deviate from the values expected from the l.f.e.r. The negative values of the deviations and the much larger [26] deviations for tricyclohexyl- than for triphenyl-phosphine strongly suggest that the deviations are steric in origin, cone angles [27] for these nucleophiles being 145 ± 2 and 179 ± 10°, respectively.

The highest discrimination is shown by the tetrahedral complexes, as expected on steric grounds, and also, perhaps, because they both contain the NO^+ ligand which should greatly facilitate bond making.[2] The gradient for $[Fe(NO)_2(CO)_2]$ is greater than that for $[Co(NO)(CO)_3]$ and this may reflect a greater degree of bond making brought about for reactions of the former complex because of its greater number of NO^+ ligands. Even with these complexes, in which the metal atoms should be geometrically quite accessible, attack by tricyclohexylphosphine is quite strongly inhibited by steric effects. Although data are known only for three nucleophiles (including triphenylphosphine) reacting with $[Mn(NO)(CO)_4]$, they define an excellent l.f.e.r., the gradient of which is significantly less than those for the tetrahedral complexes. No value of $\Delta[P(C_6H_{11})_3]$ is available. A smaller, but still substantial, discrimination is shown by the formally five-co-ordinate complex $[(cp)Rh(CO)_2]$ (cp = η-cyclopentadienyl). Bond making must still be pronounced since the steric retardation of tricyclohexylphosphine is even larger than that for the tetrahedral complexes. The octahedral complexes $[W(CO)_6]$ and $[Mo(CO)_6]$ show a smaller discrimination and here the relatively bulky nucleophile triphenylphosphine shows significant steric retardation. Data for chromium hexacarbonyl are unusual. The only nucleophiles for which values of log k_2 are available are PPh_3, $P(OEt)_3$, and PBu_3, but the three points lie on a good straight line of low gradient. Triphenylphosphine is not anomalous in spite of the larger steric effects expected for the complex $[Cr(CO)_6]$ with its smaller metal atom. Evidently metal–nucleophile bond making is much less pronounced and the actual site of nucleophilic attack may even be different in this case.

Data for $[Mo(CO)_6]$ and (I) (which both contain isoelectronic, formally d^6, octahedrally co-ordinated metal atoms) suggest that bond making is much more important in reactions of the latter complex. Not only is the gradient greater, but steric retardation for reaction with triphenylphosphine is considerably greater in spite of the geometrically more accessible nature of the ruthenium atom brought about by the large OC–Ru–CO angle (106°) for carbonyl groups in the plane of the Ru_3 cluster.[28] Since tributylphosphine is also a relatively bulky nucleophile (cone angle 103 ± 4°) and is also highly basic, it is possible that values of log k_2 for this ligand are lowered by steric effects. If so, the gradient of the l.f.e.r. would be lower than if electronic effects alone were operating, and this would account for the apparently conflicting implications of the relatively low gradient and high steric retardation for reactions of complex (I). In general, the greater importance of steric effects in reactions of more highly co-ordinated complexes probably results in less satisfactory l.f.e.r.'s since there is no simple relation between nucleophile basicity and size.

Data [29] for the complex $[(OC)_3Fe(\mu\text{-}S_2C_6H_3Me)Fe(CO)_3]$ are very similar to those for $[(cp)Rh(CO)_2]$ and $[Mn(NO)(CO)_4]$ and suggest that bond making is relatively quite important. The absence of steric retardation for reaction with triphenylphosphine reflects the relatively accessible nature of the iron atoms in this complex but steric retardation was shown to be important in reactions of related, but sterically more hindered, mercapto-complexes.

Activation parameters can usefully supplement the above rate data. Values of $\Delta H_2^\ddagger$ for reactions of complex (I) are generally lower even than those for $[Co(NO)(CO)_3]$,[22] $[Fe(NO)_2(CO)_2]$,[24] and $[(cp)Rh(CO)_2]$.[23] Values of $\Delta H_1^\ddagger$ do not seem to suggest a greater ease of bond breaking in complex (I), so it must be concluded that bond making must be very pronounced. Values of $\Delta S_2^\ddagger$ are significantly more negative, in keeping with the more restricted form of seven-co-ordinate transition states. Corresponding values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ for reactions of tributylphosphine and triphenyl phosphite with the complexes (I) and $[(OC)_3Fe(\mu\text{-}S_2C_6H_3Me)Fe(CO)_3]$ are virtually identical, whereas those for reactions of triphenylphosphine reflect significantly the steric inhibition found with (I) which is absent with $[(OC)_3Fe(\mu\text{-}S_2C_6H_3Me)Fe(CO)_3]$. Thus $\Delta H_2^\ddagger(PPh_3)$ is *ca.* 13 kJ mol^{-1} higher, and $\Delta S_2^\ddagger(PPh_3)$ is *ca.* 30 J K^{-1} mol^{-1} less negative, for reaction with complex (I). It would seem that steric effects show up here through a smaller extent of bond making offset by a somewhat less restricted form of the transition state, although in other cases they may show up through a similar extent of bond making offset by larger ligand–ligand repulsions and a similar, or more highly restricted, transition state. The activation energy, $\Delta H_2^\ddagger$, for reaction of tributylphosphine with octahedrally co-ordinated complex (I) is very much lower than the 90·5 ± 5·4 kJ mol^{-1} for reaction [4] with octahedral $[Mo(CO)_6]$, and the respective values of $\Delta S_2^\ddagger$ (−120 ± 5 and −60 ± 14 J K^{-1} mol^{-1}) indicate a much more restricted transition state in the reaction

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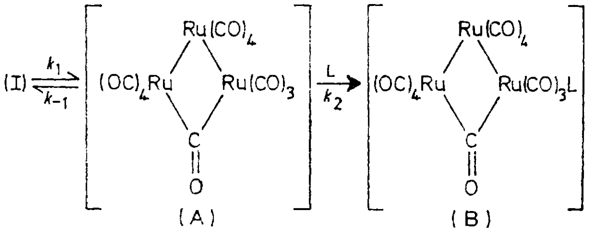
with (I). Finally, Covey and Brown[30] have pointed out that $\Delta H_1^\ddagger - \Delta H_2^\ddagger$ is governed in part by the lower extent of bond breaking in the transition state for the bimolecular process, and that unless this difference is substantial the strength of the metal–nucleophile bond in the transition state could be quite small. However, no explicit consideration was given to the extent to which $\Delta H_1^\ddagger - \Delta H_2^\ddagger$ is reduced by different ligand–ligand repulsion effects and this could also be quite substantial.

Other criteria have been used to infer the relative importance of nucleophilic attack at the metal atom. Graham and Angelici[4] considered relative values of the quantity k_2/k_1 for reactions of PBu^n_3 with the complexes $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$; these are 0·7, 10, and 35 l mol^{-1}, respectively, at 112 °C in decalin and this was taken to reflect decreasing steric inhibition of the bimolecular reaction along the series. The value of k_2/k_1 for reaction of tributylphosphine with complex (I) in decalin is 80 l mol^{-1} at 50 °C. The major disadvantage of this parameter is that it is very temperature dependent. Thus k_2/k_1 drops to *ca.* 0·5 l mol^{-1} for complex (I) at 112 °C while it rises to 75 l mol^{-1} for molybdenum hexacarbonyl at 50 °C. The ruthenium complex would then be concluded to be much less (at 112 °C) or about equally (at 50 °C) susceptible to nucleophilic attack compared with molybdenum hexacarbonyl.

The absence, or relatively small value, of an observable second-order rate constant does not necessarily imply that the complex is intrinsically reluctant to undergo nucleophilic attack. It may equally well be that it is exceptionally ready to undergo the alternative dissociative process. Such an explanation possibly accounts for the absence of a second-order term for reactions of the complex $[Cr(CO)_4(phen)]$ (phen = 1,10-phenanthroline). Replacement of two carbonyl groups in the complex $[M(CO)_6]$ by phen increases the value of k_1 for dissociative loss of a remaining carbonyl by a factor of 10^2—10^3 more when M = Cr than when M = Mo.[31] The value of the quantity $\{k_2 \text{ for } [Cr(CO)_4(phen)]\}/\{k_2 \text{ for } [Mo(CO)_4(phen)]\}$ could be 10—100 times larger than that of $\{k_2 \text{ for } [Cr(CO)_6]\}/\{k_2 \text{ for } [Mo(CO)_6]\}$ and k_2 for the complex $[Cr(CO)_4(phen)]$ would still be undetectable.

A similar point applies to substitution reactions of the complex $[Ru_3(CO)_{10}(NO)_2]$. Compared with (I) this complex contains two bridging nitrosyl groups in place of a Ru–Ru bond and a carbonyl ligand on each of these two ruthenium atoms.[32] Reaction with triphenylphosphine[33] produces the complex $[Ru_3(CO)_8(NO)_2(PPh_3)_2]$, where substitution appears to have occurred at the NO-bridged ruthenium atoms. The rate of reaction is much greater than that for the dissociative path of complex (I) and does not depend on the concentration of the phosphine.

The reasons for the much greater susceptibility of complex (I) to nucleophilic attack compared with that of $[Mo(CO)_6]$ may lie in the two extra protons in the nucleus of the six-co-ordinate d^6 ruthenium atom which is isoelectronic with octahedral d^6 molybdenum. It could also be due to some special property of the Ru–Ru bonds. One extra proton in the nucleus or one metal–metal bond does not seem to be sufficient to bring about this high susceptibility since $[Tc_2(CO)_{10}]$ reacts with PPh_3 at a rate independent of $[PPh_3]$.[13] The bent nature of the Ru–Ru bonds may be important and the second-order reaction could be envisaged as in (1) with $k_{-1} \gg k_2$. Loss of a carbonyl ligand from the $Ru(CO)_3L$ group in (B) followed by reformation of the Ru–Ru bond would complete the reaction. [Alternatively (B) could be formed by concerted nucleophilic attack and migration.] However, steric effects would be much smaller in such a scheme and there is no compelling reason to suppose that anything other than straightforward nucleophilic attack at a ruthenium atom is occurring.



(1)

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