Chalcogen Derivatives of Iron Carbonyls. Part 7.[1] Kinetics and Mechanism of Carbonyl Replacement in a Nonacarbonylthiodicobaltiron

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The kinetics of ^{14}CO exchange and CO replacement in $[FeCo_2(CO)_9S]$ have been studied with a variety of ligands. The rate equation is $k_{obs.} = k_1 + k_2[L]$, in which the ligand-independent path is often negligible, except with very poor nucleophiles such as CO or $AsPh_3$. The ligand-dependent path indicates the very high electrophilicity and great discriminating power among the ligands of the co-ordination site, suggesting that bond making plays an important role in the transition state. The probable mechanism is discussed in terms of steric accessibility of the co-ordination site and in terms of a bonding model for the cluster complex. The rates of the successive CO substitutions with PBu_3 indicate that the ligand already bonded to the cluster affects the reactivity of the adjacent metal atom, *i.e.* CO dissociation is practically unaffected, whereas ligand co-ordination is greatly decreased.

ALTHOUGH the kinetics of substitution reactions of mono- and bi-nuclear carbonyl complexes have been studied in great detail,[2] there are few data on the reactions of carbonyl clusters containing three or more metal atoms. Results have been reported for the CO-exchange mechanism of $[M_3(CO)_{12}]$ (M = Fe,[3] Ru, or Os [4]) and of $[Co_4(CO)_{12}]$,[3] and on the replacement of CO by other ligands in $[Ru_3(CO)_{12}]$,[5] $[Ru_3(CO)_{10}(NO)_2]$,[6] and $[Ir_4(CO)_{12}]$.[7] Two series of metal carbonyl clusters containing heteroatoms have been studied in some detail: $[Co_3(CO)_9(CR)]$ [8] and $[Fe_3(CO)_9XY]$ [9] (X and Y = S, Se, Te, or NR). This lack of experimental data limits the knowledge of the interaction between the metal atoms in clusters, whose chemistry seems to be different from that of mononuclear complexes. For example, in the case of $[Ir_4(CO)_{12}]$, the rate of the successive CO substitution is accelerated, contrary to what is observed with mononuclear complexes.[7]

These facts prompted us to investigate the rate and the mechanism of substitution reactions on the $[FeCo_2(CO)_9S]$ complex. The interesting feature of this complex is that the first [equation (1)] and the second [equation (2)] substitutions occur on the cobalt centres, whereas the Fe atom is only involved at the third stage [equation (3)].[1,10] We report the results on the mechanism of reaction *e.g.* (1) with several ligands L and of (2) and (3) when L = PBu^n_3. To our knowledge, this is the first example of a kinetic study on a cluster complex containing different, competing, metal centres.

$$[FeCo_2(CO)_9S] + L \longrightarrow [FeCo_2(CO)_8(L)S] + CO \quad (1)$$

$$[FeCo_2(CO)_8(L)S] + L \longrightarrow [FeCo_2(CO)_7L_2S] + CO \quad (2)$$

$$[FeCo_2(CO)_7L_2S] + L \longrightarrow [FeCo_2(CO)_6L_3S] + CO \quad (3)$$

EXPERIMENTAL

Compounds and Solvents.—The complex $[FeCo_2(CO)_9S]$ was prepared by reaction [11] between $[Co_2(CO)_8]$ and $[Fe_2(CO)_6S_2]$ in light petroleum at room temperature and subsequent purification by t.l.c. (adsorbent, silica gel G; eluant, light petroleum). Its purity was checked by i.r. and mass spectroscopy. The complex $[Co_2(CO)_8]$ was purchased from Alfa Inorganics; $[Fe_2(CO)_6S_2]$ was prepared according to the literature.[12] The compounds $AsPh_3$ and PPh_3 (Aldrich Chemical) were crystallized before use from n-heptane; $P(OPh)_3$ (Fluka AG), $P(OEt)_3$, PEt_2Ph, and PBu^n_3 (Strem Chemicals) were distilled at reduced pressure and carefully stored under nitrogen. Radioactive ^{14}CO was purchased from the Amersham Radiochemical Centre and diluted with high-purity carbon monoxide. All the solvents (reagent grade) were dehydrated by use of molecular sieves and stored under an inert atmosphere.

The reaction of $[FeCo_2(CO)_9S]$ with the ligands L gives rise in general to a complex mixture of substituted products. It is possible to increase the yield of a particular product by means of an appropriate complex : ligand ratio and a suitable temperature and reaction time, but it is best to replace only one CO in each preparation by using a less-substituted product as the starting reagent. Trace amounts of other complexes eventually formed were removed by t.l.c. When appropriate, the required product was crystallized from n-heptane. All the reactions were performed under a nitrogen atmosphere in light petroleum or in n-heptane. Experimental conditions and i.r. data are summarized in Table 1; the analytical data are in good agreement with the calculated compositions.

Kinetic Measurements.—The reaction rates are very different and require different measurement techniques. Slow reactions (half-life $\geqslant$1 h) were followed by point-to-point measurements of the i.r. absorption of a significant CO stretching band of the starting complex. Fast reactions required continuous measurement of the absorbance of the solution at a fixed wavelength in the visible region by normal

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[1] Part 6, S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Inorg. Chim. Acta*, 1977, **25**, 103.

[2] D. A. Brown, *Inorg. Chim. Acta Rev.*, 1967, **1**, 35; R. J. Angelici, *J. Organometallic Chem. Rev.*, 1968, **3**, 173; J. P. Fawcett and A. Poë, *J.C.S. Dalton*, 1976, 2039 and refs. therein.

[3] G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Ricerca Sci.*, 1967, **37**, 430.

[4] G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Atti Accad. Sci. Torino*, 1966–1967, **101**, 1.

[5] J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289; A. Poë and M. V. Twigg, *Inorg. Chem.*, 1974, **12**, 2982; M. V. Twigg, *Inorg. Chim. Acta*, 1977, **21**, L7.

[6] J. R. Norton and J. P. Collman, *Inorg. Chem.*, 1973, **12**, 476.

[7] K. J. Karel and J. R. Norton, *J. Amer. Chem. Soc.*, 1974, **96**, 6812.

[8] G. Cetini, R. Ercoli, O. Gambino, and G. A. Vaglio, *Atti Accad. Sci. Torino*, 1965, **99**, 1123; O. Gambino, G. Cetini, L. Milone, G. Gervasio, and G. A. Vaglio, *ibid.*, 1968—1969, **103**, 885; A. Cartner, R. G. Cunninghame, and B. H. Robinson, *J. Organometallic Chem.*, 1975, **92**, 49.

[9] G. Cetini, P. L. Stanghellini, R. Rossetti, and O. Gambino, *Inorg. Chim. Acta*, 1968, **2**, 443; R. Rossetti, P. L. Stanghellini, O. Gambino, and G. Cetini, *ibid.*, 1972, **6**, 205; R. Rossetti and P. L. Stanghellini, *J. Co-ordination Chem.*, 1974, **3**, 217.

[10] K. Burger, L. Korecz, and G. Bor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1527.

[11] S. A. Khattab, L. Marko, G. Bor, and B. Marko, *J. Organometallic Chem.*, 1964, **1**, 373.

[12] W. Hieber and J. Gruber, *Z. anorg. Chem.*, 1958, **296**, 91.

u.v.-visible spectroscopy, and in the case of very fast reactions (half-life <1 min) a stopped-flow technique was necessary. Finally, the radioactivity in solution was monitored in the case of the ^{14}CO isotopic exchange reaction.

The rates of consecutive reactions were largely different and kinetically well separated; *e.g.* when L = PBu^n_3, $t_{\frac{1}{2}}$ = 10—100 ms for reaction (1), 1—10 min for reaction (2), and 1—5 h for reaction (3).

Details of the experimental techniques are as follows.

(a) *Infrared technique.* A solution of the complex and of the ligand was placed in a glass vial having a serum cap and argon was bubbled through the solution. The vial was sealed and placed in a thermostatted bath (±0.1 °C). Samples of solution were withdrawn by a syringe *via* the serum cap at fixed times and examined by i.r. spectroscopy. The absorbances of appropriate CO stretching bands were measured at 2 112 cm^{-1} for [$FeCo_2(CO)_9S$] and at 2 044 cm^{-1} for [$FeCo_2(CO)_7(PBu^n_3)_2S$], which are well separated from the bands of the reaction products. Plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ against time gave good straight lines during 2—3 half-lifes, where A_0, A_t, and A_∞ are the absorbance at $t = 0$, t, and ∞, respectively (A_∞ is practically the absorbance of the solvent and the ligand). Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the gradients of these plots by means of the least-squares method: the uncertainty was always $< 5\%$.

TABLE 1

Experimental data on the preparation of [$FeCo_2(CO)_{9-x}L_xS$] (x = 1—3) complexes

Reactants	Ratio	$\frac{\theta_c}{°C}$	t	T.l.c. eluant (light petroleum–diethyl ether)	Product	Colour	Yield (%)	I.r. spectra (cm^{-1}) in n-heptane
[$FeCo_2(CO)_9S$], $AsPh_3$	1:0.7	70	5 d	4:1	[$FeCo_2(CO)_8(AsPh_3)S$]	Brown	65	2 081s, 2 041s, 2 027s, 2 016s, 1 990m, 1 969m
[$FeCo_2(CO)_9S$], $P(OPh)_3$	1:1.5	20	30 min	9:1	[$FeCo_2(CO)_8\{P(OPh)_3\}S$]	Red	50	2 062s, 2 025s, 2 014s, 2 003s, 1 970m
[$FeCo_2(CO)_9S$], $P(OEt)_3$	1:0.8	8	1 min	9:1	[$FeCo_2(CO)_8\{P(OEt)_3\}S$]	Red-brown	90	2 084s, 2 036s, 2 018m, 1 988m, 1 967m
[$FeCo_2(CO)_9S$], PEt_2Ph	1:0.8	0	1 min	9:1	[$FeCo_2(CO)_8(PEt_2Ph)S$]	Red	80	2 082s, 2 036s, 2 027(sh), 2 015s, 1 987m, 1 971w, 1 959m
[$FeCo_2(CO)_8(PEt_2Ph)S$], PEt_2Ph	1:1	20	1 h	4:1	[$FeCo_2(CO)_7(PEt_2Ph)_2S$]	Red-brown	80	2 048s, 2 007s, 1 998s, 1 985m(sh), 1 974m, 1 954m
[$FeCo_2(CO)_9S$], PBu^n_3	1:0.8	0	1 min	1:0	[$FeCo_2(CO)_8(PBu^n_3)S$]	Red	90	2 080s, 2 035s, 2 026s, 2 015m, 2 004w, 1 983m, 1964m, 1 952m
$FeCo_2(CO)_8(PBu^n_3)S$], PBu^n_3	1:0.8	20	1 min	1:0	[$FeCo_2(CO)_7(PBu^n_3)_2S$]	Red	90	2 044s, 2 003s, 1 994m, 1 979m, 1 946m 1 933w
$FeCo_2(CO)_7(PBu^n_3)_2S$], PBu^n_3	1:1	50	2 h	9:1	[$FeCo_2(CO)_6(PBu^n_3)_3S$]	Red	90	2 006s, 1 948s, 1 935m, 1 893m

(b) *U.v.–visible technique.* Solutions of the complex and the ligand were placed in two large syringes immersed in a thermostatted bath. By pushing both the plungers of the syringes, equal volumes of the solutions were forced *via* a mixing chamber into the quartz cell of the spectrophotometer. The temperature of the cell was maintained by a continuous flow of thermostatted water from a circulating pump. Measurements were made continuously at a fixed wavelength (usually 380 nm) at which the absorbance of the ligand is zero and that of the starting complex differs greatly from that of the product. Treatment of the data as above gave the best values of the rate constants.

(c) *Stopped-flow technique.* Solutions of the ligand and of the complex were mixed in a stopped-flow mixing chamber and transferred to a thermostatted cell having a 2-cm optical path. The measurements were usually made at 380 nm. The variation of the solution transmittance as a function of the time was read from photographs of the reaction traces on an oscilloscope screen. Values of $k_{obs.}$ were obtained as above.

(*d*) ^{14}CO *Exchange technique.* Aliquot portions of a solution of the previously labelled [$FeCo_2(CO)_9S$] were placed in a series of glass vials and inactive CO (or an Ar–CO mixture) was bubbled in. The vials were sealed at a constant partial pressure of CO and kept in a thermostatted bath for fixed times. The specific activity was measured by liquid scintillation on a mixture of the reaction solution (1 cm^3) and of the scintillator solution (15 cm^3; 5 g dm^{-3} PPO + 0.2 g dm^{-3} POPOP dissolved in toluene) [PPO = 2,5-diphenyloxazole; POPOP = 1,4-bis(4-methyl-5-phenyloxazol-2-yl)benzene]. From the values of the specific activity at the beginning of the reaction, $(SA)_0$, at time t, $(SA)_t$, and at equilibrium, $(SA)_\infty$, the half-life of the exchange was obtained on plotting $\ln[(SA)_t - (SA)_\infty]/[(SA)_0 - (SA)_\infty]$ against time. By applying the McKay equation[13] it is possible to calculate the general rate of exchange R and the specific rate constant $k_{obs.}$, when the CO concentration in the solution and in the gas phase in each reaction vial is known. Details of the method of calculation are given elsewhere.[14] $(SA)_\infty$ was determined experimentally after 8—10 exchange half-times. Its agreement with the value calculated for the exchange of nine CO groups indicates that under these reaction conditions all the CO groups are equivalent.

Apparatus.—The following apparatus was used: i.r., Beckman 12 grating spectrophotometer; u.v.-visible, Unicam SP 1700 spectrophotometer with Techne C 100 Circulator; Durrum–Gibson stopped-flow spectrophotometer; Packard TRI-CARB model 2002 liquid-scintillation spectrometer; Hitachi–Perkin-Elmer RMU-6H single-focusing mass spectrometer.

RESULTS

The reaction of [$FeCo_2(CO)_9S$] with phosphorus donor ligands gives a mixture of the CO-substituted products, but the trisubstituted derivative can be obtained only with very basic ligands such as PBu^n_3. In contrast to the isocyanide derivative,[15] [$FeCo_2(CO)_6(PBu^n_3)_3S$] exists in only one isomeric form without CO bridging.

The rate measurements were performed under pseudo-first-order conditions, *i.e.* with the ligand concentration in excess. Values of the rate constants so obtained, $k_{obs.}$, are in Table 2. The dependence of the reaction rate on the ligand concentration is expressed in the most general case by equation (4). Values of k_1 and k_2 were calculated from the

$$\text{Rate} = k_{obs.}[\text{complex}] = (k_1 + k_2[\text{L}])[\text{complex}] \quad (4)$$

intercept and gradient of the straight lines obtained by plotting $k_{obs.}$ against [L]. Reaction (1) gave reliable

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[13] H. A. C. McKay, *Nature*, 1938, **142**, 997.

[14] G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, 1967, **6**, 1225.

[15] J. Newman and A. R. Manning, *J.C.S. Dalton*, 1974, 2549.

TABLE 2

Pseudo-first-order rate constants for the reaction $[FeCo_2(CO)_{9-x}L_xS] + L$ ($x = 0$—2) in n-heptane

Complex	Ligand	$\frac{\theta_c}{°C}$	$\frac{10^3[\text{Ligand}]}{\text{mol dm}^{-3}}$	$\frac{10^4\, k_{obs.}}{s^{-1}}$
$[FeCo_2(CO)_9S]$	CO	50.0	2.3	0.51
			3.4	0.76
			5.4	0.84
			7.5	1.17
		60.0	1.85	1.93
			2.7	2.3
			4.3	2.6
			6.0	3.4
		70.0	1.3	7.0
			2.0	7.7
			3.1	8.3
			4.3	10.1
	$AsPh_3$	40.0	20.4	0.074
			30.1	0.072
			40.7	0.084
			50.4	0.079
			60.0	0.086
			81.0	0.092
			100	0.102
			120	0.114
	PPh_3	23.0	20.2	3.0
			30.3	3.9
			40.6	5.6
			50.2	7.4
			60.6	8.5
		30.0	20.0	3.8
			30.3	6.1
			40.6	8.4
			50.3	10.3
	$P(OPh)_3$	13.5	18.4	7.7
			30.0	13.2
			35.7	15.0
			41.3	17.0
			46.9	19.3
			52.6	21.3
		21.5	13.1	9.7
			18.8	15.2
			24.4	16.1
			30.0	20.9
			37.5	26.9
	$P(OEt)_3$	30.0	10.1	1 539
			20.1	3 350
			29.9	6 400
			40.3	7 500
			49.5	8 800
			59.8	10 800
	PEt_2Ph	25.0	0.99	219
			1.41	300
			1.98	440
			2.54	570
		40.0	4.98	1 760
			10.0	3 400
			14.7	5 200
			20.4	6 900
			35.1	11 200
	PBu^n_3	30.0	2.14	2 060
			4.50	4 800
			7.07	7 800
			10.1	9 900
		40.0	2.59	1 900
			5.06	3 700
			7.63	3 950
			10.2	6 800
			12.7	9 100

TABLE 2 (*Continued*)

Complex	Ligand	θ_c °C	10^3[Ligand] mol dm^{-3}	10^4 $k_{obs.}$ s^{-1}
[$FeCo_2(CO)_8(PBu^n_3)S$]	PBu^n_3	29.4	42.9	47
			71.4	86
			100	125
			129	154
			157	196
			214	264
		40.1	42.9	85
			57.1	109
			71.4	138
			85.7	157
			114	216
			143	269
			178	314
			214	420
[$FeCo_2(CO)_7(PBu^n_3)_2S$]	PBu^n_3	50.2	40.2	0.53
			67.0	0.51
			94	0.58
			134	0.62
			201	0.61
		70.1	67.0	5.2
			134	4.9
			201	6.0
			280	5.5
			350	5.4

TABLE 3

Rate constants and activation parameters * for the reactions [$FeCo_2(CO)_{9-x}L_xS$] + L (x = 0—2) in n-heptane

Complex	Ligand	θ_c °C	10^4 k_1 s^{-1}	10^2 k_2 dm^3 mol^{-1} s^{-1}	$\Delta H_1^\ddagger$ kcal mol^{-1}	$\Delta S_1^\ddagger$ cal K^{-1} mol^{-1}	$\Delta H_2^\ddagger$ kcal mol^{-1}	$\Delta S_2^\ddagger$ cal K^{-1} mol^{-1}
[$FeCo_2(CO)_9S$]	CO	50.0	0.29 ± 0.04	1.15 ± 0.29	32 ± 4	19 ± 7	23.0 ± 1.5	3.4 ± 2.9
		60.0	1.34 ± 0.24	3.3 ± 0.6				
		70.0	5.6 ± 0.6	9.8 ± 2.2				
	$AsPh_3$	40.0	0.063 ± 0.008	0.004 0 ± 0.000 4				
	PPh_3	23.0		1.44 ± 0.11			9.9 ± 2.4	−34 ± 6
		30.0		2.17 ± 0.05				
	$P(OPh)_3$	13.5		3.93 ± 0.16			10.5 ± 3.1	−28 ± 8
		21.5		6.7 ± 0.8				
	$P(OEt)_3$	30.0		1 840 ± 150				
	PEt_2Ph	25.0		2 320 ± 100			3.1 ± 0.8	−42 ± 2
		40.0		3 130 ± 120				
	PBu^n_3	30.0		9 900 ± 1 200			−8 ± 5	−75 ± 11
		40.0		6 900 ± 1 200				
[$FeCo_2(CO)_8(PBu^n_3)S$]	PBu^n_3	29.4		12.6 ± 0.3			6.3 ± 0.9	−42 ± 2
		40.1		18.7 ± 0.7				
[$FeCo_2(CO)_7(PBu^n_3)_2S$]	PBu^n_3	50.2	0.57 ± 0.05		24.2 ± 1.4	−3.4 ± 3.1		
		70.1	5.4 ± 0.4					

* 1 cal = 4.184 J.

values of both k_1 and k_2 when L = CO and $AsPh_3$; in the other cases only k_2 was obtained, k_1 being much less than the standard deviation of k_2[L]. Reactions (2) and (3) were followed with L = PBu^n_3 and values of k_2 and k_1, respectively, were obtained. All these values are collected in Table 3, together with the relevant activation parameters; the errors are standard deviations.

DISCUSSION

Equation (4) gives a good fit to the kinetic data for [$FeCo_2(CO)_9S$], clearly indicating that two competing paths are involved, a first-order path independent of the ligand concentration and a second-order path linearly dependent on [L]. The first-order path contributes to a small extent to the overall mechanism and, in general, reliable measurements cannot be obtained, except with poor nucleophiles such as CO or $AsPh_3$. The values of k_1 are similar, so a common mechanism can be proposed which implies a CO dissociation. Even if other mechanisms are possible for metal–metal bonded carbonyls, in the absence of any evidence for them the following seems the most reliable:

$$\begin{aligned} [FeCo_2(CO)_9S] &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FeCo_2(CO)_8S] + CO \\ [FeCo_2(CO)_8S] + L &\xrightarrow{k_3} [FeCo_2(CO)_8(L)S] \end{aligned} \quad (5)$$

The rate equation for the dissociative path is given by (6) which for reactions in the absence of free carbon

$$k_{obs.} = \frac{k_1 k_3[L]}{k_{-1}[CO] + k_3[L]} \quad (6)$$

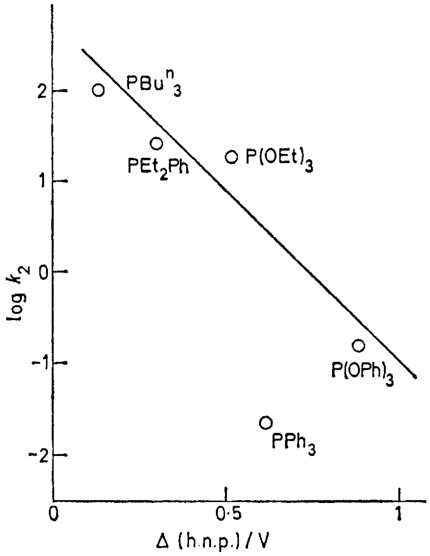
monoxide transforms into $k_{obs.} = k_1$, the ligand-independent term of the general rate expression (4). The values of the activation parameters agree with those of similar reactions,[2] indicating that bond breaking is important in the formation of the active intermediate.

The similarity of the i.r. spectra of $[FeCo_2(CO)_8(AsPh_3)S]$ and of other monosubstituted derivatives suggests that they have similar structures,[1,10] *i.e.* the CO dissociation occurs only at the cobalt atom. So it may be that in the intermolecular ^{14}CO exchange process each labelled CO molecule co-ordinates at Co after the Co–CO dissociation: the very fast intramolecular CO scrambling [1] accounts for the kinetic equivalence of all the nine CO groups.

The values of the second-order rate constant k_2 are very high compared with other binuclear or cluster metal carbonyls.[2-9] More surprisingly, these values are two or three orders of magnitude greater than those found for mononuclear complexes having lower co-ordination numbers, such as $[Co(CO)_3NO]$ [16] and $[Fe(CO)_2(NO)_2]$.[17] This suggests a strong co-ordinating ability or Lewis acidity for this kind of cluster structure and also a large bond-making effect in the transition state. The low values of the activation enthalpy and the largely negative values of the activation entropy support this. These values do not exclude the possibility of a rapid pre-association mechanism. In this case we would expect that $k_{obs.}$ levels off at very high [L] values, but, unfortunately, reliable measurements could not be obtained under these conditions.

Cobb *et al.*[18] suggested that a rough measure of bond making is the discriminating ability of the electrophile towards the entering ligands, and used for this purpose the gradients of plots of $-\log k_2$ against Δ(h.n.p.).* Low values of the gradient are found for six-co-ordinate metal complexes {0.7 V^{-1} for octahedral $[Cr(CO)_6]$, 2.5 and 2.92 V^{-1} for quasi-octahedral $[Ru_3(CO)_{12}]$ and $[Co_2(CO)_6(C_2Ph_2)]$ respectively}, higher values for trigonal-bipyramidal $[Mn(CO)_5(NO)]$ (3.7 V^{-1}) and for tetrahedral $[Co(CO)_3(NO)]$ (4.8 V^{-1}) and $[Fe(CO)_2(NO)_2]$ (6.0 V^{-1}); clearly indicating that the discrimination among the ligands depends primarily on steric effects, *i.e.* on the ligand geometry around the metal. The Figure shows plots of $\log k_2$ against Δ(h.n.p.) for $[FeCo_2(CO)_9S]$: the linearity is good, excluding the triphenylphosphine value. This behaviour is common in complexes showing pronounced bond making [2] and it is ascribed to the steric hindrance of PPh_3, as demonstrated by the great cone angle on the P atom.[19] The gradient, ignoring the PPh_3 point, is 3.8 V^{-1}, closer to the values for four- and five-co-ordinate complexes than to those for pseudo-octahedral structures. By using $\log k_2$ for $[Co(CO)_3(NO)]$, taken as a standard complex, instead of Δ(h.n.p.), a straight line is also obtained, with a gradient of 0.86 and an intercept of 3.2. Including the points for L = $AsPh_3$ and PPh_3, the gradient becomes 1.4 and the intercept 4.0.

If we assume that the discrimination behaviour of the ligands is primarily due both to their steric bulk and their flexibility in electronic distribution, two points can be made about the behaviour of $[FeCo_2(CO)_9S]$. First, the steric hindrance of the co-ordination site to the approaching nucleophile is not so great as the octahedral symmetry around the metal atoms [20] would suggest. The complex $[FeCo_2(CO)_9S]$ resembles tetrahedral $[Co(CO)_3(NO)]$, even though the approach of bulky ligands such as PPh_3 and $AsPh_3$ is slightly more difficult in this case, as suggested by the increased value of the gradient of the plot of $\log k_2\{[FeCo_2(CO)_9S]\}$ against $\log k_2\{[Co(CO)_3(NO)]\}$, when these ligands are considered. Secondly, the electrophilicity of $[FeCo_2(CO)_9S]$ is surprisingly high. The value of the intercept indicates that despite the fact that the co-ordination site on $[FeCo_2(CO)_9S]$ is more encumbered its reactivity is at least a thousand times that of $[Co(CO)_3(NO)]$.



A plot of $\log k_2$ at 30.0 °C against the half-neutralization potential of phosphorus ligands. Values of k_2 not reported in Table 3 were calculated by extrapolation

A qualitative description of the bonding in triangular $[M_3(CO)_9X]$ and $[M_2M'(CO)_9X]$ clusters (M = Co, M' = Fe, X = S, Se, or Te) in terms of the LCAO–MO model has been proposed by Strouse and Dahl [21] to explain e.s.r. and structural data. The bonding picture suggests, in particular, that the lowest empty ($M_2M'X$ clusters) or half-filled (M_3X clusters) molecular orbital is antibonding with respect to the metal–metal framework and that it is comprised primarily of the in-plane trimetal antibonding combination of d_{xy} atomic orbitals. The kinetic behaviour of $[FeCo_2(CO)_9S]$ could suggest that co-ordination of the ligands to the trimetallic framework occurs on the other side of the sulphur atom, *via* the lowest empty molecular orbital. This would

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* Δ(h.n.p.) is the half-neutralization potential for titration of the phosphorus ligand by perchloric acid in nitromethane (C. A. Streuli, *Analyt. Chem.*, 1960, **32**, 985).

[16] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

[17] D. E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2531.

[18] M. A. Cobb, B. Hungate, and A. Poë, *J.C.S. Dalton*, 1976, 2226.

[19] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[20] D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6027.

[21] C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6032.

account for the steric accessibility of the co-ordination site and its great co-ordination ability: the antibonding molecular orbital is probably not greatly destabilized since $[Co_3(CO)_9S]$ and $[Co_3(CO)_9Se]$, in which this orbital is half-filled, are quite stable complexes.[21,22] The Dahl bonding model is referred to an M_3X cluster of idealized C_{3v} symmetry and does not account for the effect of different metal atoms. So it cannot explain why the substitution occurs preferentially at the cobalt atoms, unless the lowest empty molecular orbital is more concentrated on the Co_2 part of the cluster, but at present this is only speculation.

Another possible mechanism is attack of the ligand *via* the S atom, which can act like a Lewis acid by means of appropriate empty orbitals, as previously suggested for $[Fe_3(CO)_9XY]$ complexes.[9] This may account for the ligand being bonded to the more accessible equatorial position in substituted $[FeCo_2(CO)_8(L)S]$ complexes,[1] and for the steric accessibility of the co-ordination site: direct ligand attack at a single metal atom seems unlikely.

The reactions of $[FeCo_2(CO)_9S]$ offer another example of heteronuclear metal carbonyls in which CO substitution occurs preferentially or exclusively at one metal atom, as at Re in $[(OC)_5MnRe(CO)_5]$,[23] at Co in $[(OC)_4CoMn(CO)_5]$,[24] and at three cobalt atoms in $[FeCo_3H(CO)_{12}]$.[25] In all the known examples, as with $[FeCo_2(CO)_9S]$, the ligand preferentially replaces carbonyl groups at metals which have more protons and which are correspondingly more electrophilic. This effect is confirmed by the high-field ^{13}C chemical shift of the cobalt-bonded with respect to the iron-bonded carbonyls.[1]

The kinetic data for the subsequent reactions are well explained in terms of equation (4). The second substitution [equation (2)], as the first one, shows a high value of k_2, which renders negligible the contribution of the ligand-independent path, whereas in the third substitution [equation (3)] the effect is reversed and the contribution of the k_2 path to the overall reaction rate is very small. So the order of ligand attack on the substrate decreases as follows: k_2[reaction (1)] $\gg$ k_2[reaction (2)] $\gg$ k_2[reaction (3)]; the same trend is exhibited by the activation parameters, $\Delta H_2^‡$ and $\Delta S_2^‡$ being much higher for the second stage than for the first. These facts suggest that the bond making in the transition state becomes less pronounced, for the successive substitutions, because of both the steric and electronic effects of the ligand already present in the complex. The basicity of PBu_3 probably plays the most important role, as the increased electron density on the cluster can result in a decrease in the electrophilicity of the co-ordination site.

The very small value of k_2 for the third substitution indicates the great difficulty of the Fe atom in acting as a co-ordination centre and suggests that the ease of CO substitution on the different metal atoms depends more strongly on their electrophilicity than on the M–CO dissociation energy. In fact, the ligand-independent path for the third stage (probably Fe–CO dissociation) shows a specific rate constant and activation enthalpy very close to those of the first stage (probably Co–CO dissociation).

In general, for binuclear carbonyls, substitution on the second metal is greatly or scarcely affected by the ligand bound to the first metal, according to whether the mechanism is bi- or uni-molecular, respectively.[26] The same effect is shown by $[FeCo_2(CO)_9S]$, unlike $[Ir_4(CO)_{12}]$:[7] the chemistry of the metal carbonyl clusters and the importance of the interactions between the metal atoms clearly requires further study.

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[22] L. Marko, G. Bor, and E. Klumpp, *Chem. and Ind.*, 1961, 1491; L. Marko, G. Bor, E. Klumpp, B. Marko, and G. Almasy, *Chem. Ber.*, 1963, **96**, 955; S. A. Khattab, L. Marko, G. Bor, and B. Marko, *J. Organometallic Chem.*, 1964, **1**, 373.

[23] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **61**, 315.

[24] G. Sbrignadello, G. Bor, and L. Maresca, *J. Organometallic Chem.*, 1972, **46**, 345.

[25] C. G. Cooke and M. J. Mays, *J.C.S. Dalton*, 1975, 455.

[26] H. Waversik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113; M. Basato and A. Poë, *J.C.S. Dalton*, 1974, 456; M. Basato, J. P. Fawcett, and A. Poë, *ibid.*, p. 1350; M. Basato, *ibid.*, 1976, 1679.