Reaction of Di-μ-phenylthio-bis(tricarbonyliron)(*Fe–Fe*) with Triphenylphosphine: a Detailed Kinetic and Mechanistic Study

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Di-μ-phenylthio-bis(tricarbonyliron)(*Fe–Fe*) undergoes a two-step CO substitution reaction with triphenylphosphine in decalin. The substitution does not go to completion in the presence of carbon monoxide and the kinetics of the forward and reverse reaction for each step have been studied. The unsubstituted complex undergoes direct attack by PPh_3 either on the predominant *anti*-form or on the very reactive *syn*-form which is produced in the rate-determining *anti–syn*-isomerisation. The monosubstituted complex, which is also present mainly in the *anti*-form in equilibrium with a reactive *syn*-form, reacts with carbon monoxide through an S_N2 mechanism, but a CO-dissociative mechanism is involved in its reaction with the bulkier PPh_3. The bis(phosphine) complex so obtained is unable to undergo S_N2 displacement even by carbon monoxide and must previously lose one molecule of phosphine. Relative rate constants for bimolecular attack on the co-ordinatively unsaturated intermediate by carbon monoxide and triphenylphosphine have been obtained. Equilibrium and activation parameters for these reactions are reported.

DI-μ-PHENYLTHIO-BIS(TRICARBONYLIRON)(*Fe–Fe*), (I), is a metal–metal bonded carbonyl with two organosulphur bridges. An *X*-ray study of its *anti*-form shows that the two Fe atoms are at the centre of two octahedrons, which share a face defined by the sulphur atoms and the bent iron–iron bond. The Fe–S–Fe bridge angles are *ca.* 67° and the Fe–Fe bond distance is 2·516 Å.[1] These values are consistent with those found in the *anti*-di-μ-ethylthio- and μ-(*cis*-stilbene-α,β-dithiolato-*SS′*:*S′S*)-analogues.[2,3] *syn–anti*-Isomerism is possible for these complexes as a consequence of different relative positions of the organic radicals at the sulphur atoms, and for the methyl-, ethyl-, and benzyl-thio-derivatives both isomers have been isolated by chromatography and characterised by their n.m.r. and i.r. spectra. Despite careful efforts, no spectroscopic evidence has been obtained for different forms of the phenylthio-derivative.[4] This complex is also known to undergo substitution of one or two CO groups by triphenylphosphine, giving derivatives substituted *trans* to the metal–metal bond.[5]

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[1] W. Henslee and R. E. Davis, *Cryst. Struct. Comm.*, 1972, **1**, 403.

[2] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 328.

[3] H. P. Weber and R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 182.

[4] L. Maresca, F. Greggio, G. Sbrignadello, and G. Bor, *Inorg. Chim. Acta*, 1971, **5**, 667 and refs. therein.

[5] J. A. de Beer and R. J. Haines, *J. Organometallic Chem.*, 1972, **36**, 297 and refs. therein.

In contrast to the amount of information on the preparation of phosphine-substituted di-μ-mercapto-hexacarbonyldi-iron complexes,[5] few data on the mechanistic aspects of these reactions are available.[4] In principle, the routes to substitution could offer examples of co-ordinatively unsaturated 'open-bridged' intermediates, which are of interest in catalysis. This paper reports a detailed mechanistic study of the reactions shown in equations (1) and (2) in decalin as solvent. While this

$$[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3] + PPh_3 \rightleftharpoons [(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + CO \quad (1)$$

$$[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + PPh_3 \rightleftharpoons [(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + CO \quad (2)$$

work was in progress a paper appeared concerning the mechanism of carbon monoxide substitution of a series of bis(tricarbonylmercaptoiron) complexes with phosphorus- and arsenic-containing ligands.[6] That study was carried out by following carbon-monoxide evolution, and was limited to the forward reaction and to cases where the first substitution was rate determining. The results are, where comparable, consistent.

EXPERIMENTAL

The complexes $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3]$, (I), and $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$, (II), were prepared by the published method.[4] Their i.r. spectra in decalin showed peaks respectively at 2 075m—s, 2 038vs, 2 006s, and 1 984w, and 2 051s, 1 989vs, 1 973w, and 1 942w cm^{-1} (*cf.* in n-hexane 2 075m—s, 2 039vs, 2 007s, 1 998s, 1 991(sh), 1 986w and 2 052s, 1 991s, 1 975w, and 1 944w cm^{-1}).[4] The complex $[(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$, (III), was prepared by reaction under argon of (I) (0·412 g, 0·825 mmol) with PPh_3 (0·499 g, 1·9 mmol) in carefully deoxygenated decalin (25 cm^3). After 2 h at 130 °C the solution was cooled and dark red crystals which precipitated were filtered off, washed with n-hexane, and recrystallised from methylene chloride–methanol, yield $\geqslant$50%. I.r. spectrum in decalin: 1 996s, 1 955s, and 1 935m—s cm^{-1} (*cf.* in CH_2Cl_2: 1 992s, 1 947m, and 1 928s cm^{-1}).[5] Triphenylphosphine (Fluka) was recrystallised from methylene chloride–methanol. Decalin (R.P.E. C.Erba) was used as received. Argon and carbon monoxide were high-purity SIO products. Certified Ar–CO mixtures were provided by S.I.A.D., relative errors in their analysed contents being always less than 0·5%.

Procedures.—Solutions of PPh_3 were prepared by weight. After careful deoxygenation by freeze–pump–thaw cycles, these solutions were transferred under the appropriate gas to the reaction vessel containing known amounts of the solid complex. These transfers were made through stainless-steel tubing inserted through Suba-seal rubber stoppers by applying a suitable pressure of gas. A small modification of this procedure was adopted for the sparingly soluble complex (III). Carefully deoxygenated suspensions of the complex in decalin were heated under carbon monoxide at 70 °C with vigorous shaking until some dissolution of the complex occurred, after which the solid was filtered off. In all cases the vessels, wrapped in aluminium foil, were immersed in an oil-bath thermostatted within ±0·1 °C and aliquot portions were removed periodically, through stainless-steel tubing, by an applied pressure of gas. For reactions below *ca.* 70 °C, samples were ejected directly into an i.r. cell and spectra scanned immediately in the C–O stretching region. For reactions at higher temperature samples were collected in small phials, cooled in ice, and their i.r. or visible–u.v. spectra monitored with Perkin-Elmer 457 and Optica CF4R spectrophotometers respectively. The pressure into the reaction vessel was controlled with a manometer and concentrations, at the various temperatures, of carbon monoxide were calculated as previously stated.[7]

RESULTS

The reaction proceeds in two distinct stages, the first being characterised by growth of the i.r. bands of $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$, (II), and the second by decay of these bands and growth of those characteristic of $[(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$, (III). Rather different temperatures are required for the two substitutions, 30—70 °C for the first and 90—130 °C for the second. This fact, together with favourable equilibrium positions, allowed a kinetic study of the forward and reverse reaction for both substitutions to be carried out.

The first stage in the presence of CO gave an equilibrium mixture of complexes (I) and (II), whereas under Ar quantitative formation of (II) was observed. The reaction was monitored by following the variation of absorbance of the bands at 2 038 and/or 2 051 cm^{-1}. Under psuedo-first-order conditions, plots of log $|A_t - A_\infty|$ against time were linear over three half-lives. The observed rate constants, $k_{obs.}$, determined in this way, represent, under Ar, the rate of the forward reaction ($= k_{f(Ar)}$), whereas under CO, at equilibrium where $A_\infty = A_e$, the sum of the forward and reverse reaction ($= k_{f(CO)} + k_r$).[8] In the latter case the two terms can be separated by introducing the spectrophotometrically determined concentration ratio, at equilibrium, of complexes (I) and (II); consistent results were obtained by starting from (I) or (II). The CO dependence of the reverse reaction was studied also by following the disappearance of complex (II) at various partial CO pressures without PPh_3 added. Equilibrium was reached in these cases despite the low final PPh_3 concentration ($< 3 \times 10^{-4}$M).* The reaction was considered to be of the type $A \underset{k'}{\overset{k}{\rightleftharpoons}} B + C$ for which $k(= k_r$ in this case) can be determined by using equation (3) where A_0 = initial absorbance.[8] Good linearity was obtained in each case.

$$\ln\frac{A_0^2 - A_eA_t}{(A_t - A_e)A_0} = \left(\frac{A_0 + A_e}{A_0 - A_e}\right)kt \qquad (3)$$

All rate data for this first stage, together with the equilibrium constants, are collected in Table 1. Values of the equilibrium constant at various temperatures (Table 1) were calculated from two experiments where the change in

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* 1M = 1 mol dm^{-3}, 1 atm = 101 325 Pa, 1 cal = 4·184 J.

[6] P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, 1973, **12**, 2526.

[7] M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1974, 1350.

[8] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, Tokio, 1961, p. 186.

equilibrium concentrations with temperature for the same solution was observed, and are consistent with the observations under kinetic conditions.

The reaction under an atmosphere of argon followed the rate equation $k_{f(Ar)} = \{a/(1 + c/[PPh_3])\} + b[PPh_3]$. One atmosphere CO pressure did not affect the rate of the forward reaction and $k_{obs.}$ values under CO, at 40 °C, were always greater, at the same PPh_3 concentrations, than corresponding values under Ar. This difference, at constant 1 atm CO pressure, decreased with increasing $[PPh_3]$, and was not negligible with $[PPh_3] = 0{\cdot}561$M, as shown by the presence of some complex (I) at equilibrium. The reverse reaction followed the rate equation $k_r = \{d[CO]/(1 + f[PPh_3])\} + g[CO]$.

The second stage under Ar gives the product (III), whereas in the presence of CO an equilibrium mixture of complexes (I)—(III) can be observed. The study of this stage was complicated by some decomposition of both complexes (II) and (III). Complex (II), for example, under Ar and in the absence of PPh_3, decomposed, at the high temperatures employed, giving some (I) as a result of substitution of a PPh_3 by the carbon monoxide previously released. Complex (III) is unstable also in the presence of PPh_3, both under argon and under 1 atm carbon monoxide, and slowly decomposes to give unknown products. The second stage was monitored by following the decreasing intensity of the band at 2 051 cm^{-1}. Plots of log $|A_t - A_\infty|$ against time, for runs under argon, were linear only with $[PPh_3] > 0{\cdot}1$M; at lower $[PPh_3]$ an initial rapid reaction was observed followed by a curve in the plots, the gradient decreasing as the reaction proceeded. Evaluation of the rate of approach to equilibrium was possible only for $[PPh_3]/[CO] \geqslant 2 \times 10^1$, because

TABLE 1

Rate and equilibrium data for the reaction $[(OC)_3\overline{Fe(\mu\text{-}SPh)_2Fe}(CO)_3] + PPh_3 \rightleftharpoons [(OC)_3\overline{Fe(\mu\text{-}SPh)_2Fe}(CO)_2(PPh_3)] + CO$ in decalin. [Complex] [a] = 2×10^{-4}—5×10^{-4}M

θ_c/°C	$10^3[PPh_3]$/M	P_{CO}/atm	$10^3[CO]$/M	$10^5k_{f(Ar)}$/s^{-1}	$10^5(k_{f(CO)} + k_r)$/s^{-1}	$[B]_e/[A]_e$	$10^5k_{f(CO)}$/s^{-1}	10^5k_r/s^{-1}	K
30·0	3·81	0·00	0·00	3·72					
	6·60	0·00	0·00	5·30					
	14·2	0·00	0·00	8·13					
	35·3	0·00	0·00	12·5					
	65·5	0·00	0·00	15·2					
	140	0·00	0·00	17·2					
	231	0·00	0·00	19·5					
	278	0·00	0·00	20·6					
	416	0·00	0·00	23·2					
	566	0·00	0·00	26·6					
40·0	0·29 [b]	0·55	3·2					5·50 [c]	
	0·34 [b]	1·10	6·4					9·50 [c]	
	7·86	0·00	0·00	15·4					
	7·86	1·10	6·4		21·4	2·0	14·3	7·13	
	20·2	0·00	0·00	28·0					
	20·2	1·10	6·4		34·0	5·0	28·3	5·67	
	49·1	0·00	0·00	39·8					
	49·1	1·10	6·4		45·0	10·0	40·9	4·09	
	88·5	0·00	0·00	50·0					1·65 [d]
	88·5	1·10	6·4		55·0	18·6	52·2	2·81	
	138	0·00	0·00	52·5					
	216	0·00	0·00	58·1					
	315	0·00	0·00	64·0					
	432	0·00	0·00	71·0					
	561	0·00	0·00	81·0					
	561	1·10	6·4		87·2	*ca.* 100	86·3	*ca.* 0·90	
50·0	0·23 [b]	0·55	3·2					9·87 [c]	
	0·69 [b]	1·10	6·3					20·8 [c]	
	7·40	1·10	6·3		45·2	1·7	28·5	16·7	
	7·95	0·00	0·00	33·0					
	8·05	1·10	6·3		44·0 [c]	2·4	31·1	12·9	
	19·5	0·00	0·00	66·6					1·65 [d]
	48·7	0·00	0·00	106					
	136	0·00	0·00	156					
	214	0·00	0·00	172					
	312	0·00	0·00	192					
	429	0·00	0·00	216					
	555	0·00	0·00	243					
60·0	0·39 [b]	1·10	6·2					37·2 [c]	1·51 [d]
70·0	0·13 [b]	0·053	0·29					3·54 [c]	
	0·24 [b]	0·106	0·59					5·90 [c]	
	0·26 [b]	0·276	1·54					15·7 [c]	
	0·24 [b]	0·55	3·1					35·0 [c]	1·40 [d]
	0·58 [b]	1·10	6·1					63·0 [c]	

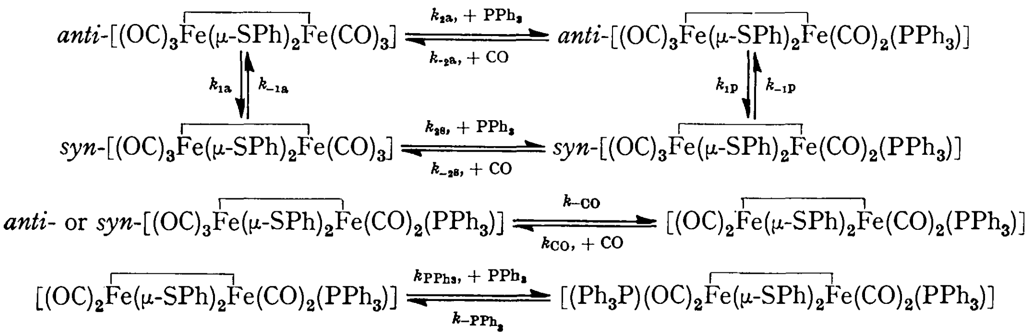
[a] $[(OC)_3\overline{Fe(\mu\text{-}SPh)_2Fe}(CO)_3]$ (= A), $[(OC)_3\overline{Fe(\mu\text{-}SPh)_2Fe}(CO)_2(PPh_3)]$ (= B). [b] Approximate final concentration. [c] Starting from B; all other runs started from A. [d] See text: $\Delta H^\ominus = -5$ kJ mol^{-1} (-1 kcal mol^{-1}), $\Delta S^\ominus = -12$ J K^{-1} mol^{-1} (-3 cal K^{-1} mol^{-1}).

only in this case is formation of complex (I) negligible. The quantity A_e was determined by graphic extrapolation and data treated as for the first stage. The rate of the reverse reaction in the absence of added PPh_3, which gave for $[CO] \geqslant 2 \times 10^{-3}$M the product (I) without visible accumulation of (II), was monitored by following the decreasing intensity of the peak at 414 nm. Plots of log $|A_t - A_\infty|$ against time were linear over three half-lives and were consistent with semiquantitative data obtained from the low-absorbing peak of the product at 2 038 cm^{-1}.

All rate data and equilibrium constants are collected in Table 2. Comparison of the data obtained for the forward reaction under Ar and under CO, together with the behaviour under Ar at low $[PPh_3]$, suggests a rate equation of the type $k_f = g[PPh_3]/([PPh_3] + h[CO])$. Finally the rate of the reverse reaction, *i.e.* substitution of PPh_3 by CO in the complex (III), is expressed by the rate law $k_r = i[CO]/([CO] + l[PPh_3])$.

DISCUSSION

The kinetic data are consistent with the reaction scheme shown below (where the subscripts *a* and *s* refer to the *anti*- and *syn*-forms respectively) in the assumption that both the complexes (I) and (II) are present at equilibrium mainly in the *anti*-forms and that the *syn*-species can be treated as reactive intermediates. This assumption is in accord with previous observations[4,6] on the reactivity of these complexes and with the isolation of the *anti*-isomer of complex (I).[1] The second CO substitution takes place at higher temperatures and does not interfere in the study of the first.



The rate equation of approach to equilibrium for the first substitution is given by (4) [subscript *p* referring to mono(phosphine) substitution], where the terms in braces represent respectively the rate of the forward and the reverse reactions.

$$k_{obs.} = k_f + k_r = \left\{\frac{k_{1a}}{1 + (k_{-1a}/k_{2s}[PPh_3]) + (k_{-1a}k_{-2s}[CO]/k_{2s}k_{-1p}[PPh_3])} + k_{2a}[PPh_3]\right\} + \left\{\frac{k_{1p}k_{-2s}[CO]/k_{-1p}}{1 + (k_{-2s}[CO]/k_{-1p}) + (k_{2s}[PPh_3]/k_{-1a})} + k_{-2a}[CO]\right\} \quad (4)$$

It can be easily seen that in the absence of appreciable amounts of carbon monoxide (4) reduces to the form found experimentally under Ar. Furthermore, in this case equation (4) can be rearranged to give (5), so that linear plots of $1/(k_{f(Ar)} - k_{2a}[PPh_3])$

$$1/(k_{f(Ar)} - k_{2a}[PPh_3]) = (1/k_{1a}) + (k_{-1a}/k_{1a}k_{2s}[PPh_3]) \quad (5)$$

against $1/[PPh_3]$ should be obtained and values of k_{1a} and k_{-1a}/k_{2s} be derived therefrom. Good linear plots were indeed obtained. Values of k_{1a} and k_{2a} are given in Table 3 together with the corresponding activation parameters. The values of k_{1a} and k_{2a} were obtained by linear least-squares analysis of the dependence of $k_{f(Ar)}$ on $[PPh_3]$ for $[PPh_3] \geqslant 1{\cdot}36$M, each value of $k_{f(Ar)}$ being assumed to have the same percentage standard deviation at a given temperature Values of k_{1a} and k_{-1a}/k_{2s} were also obtained by making use of equation (5). Values of $1/(k_{f(Ar)} - k_{2a}[PPh_3])$ were weighted in accordance with standard deviations calculated from those already found for $k_{f(Ar)}$ and k_{2a} (Table 3). All listed uncertainties are standard deviations that have been corrected for the number of degrees of freedom, so that estimates of the 95% confidence limits can be obtained by doubling the uncertainties. The agreement between the two sets of values for k_{1a} is good, as is that for their activation parameters (Tables 3 and 4). Rate equation (4) is also consistent with the observation that there is no appreciable CO effect on the rate of the forward reaction if it is assumed that $k_{-1a}/k_{2s}[PPh_3] \gg k_{-1a}k_{-2s}[CO]/k_{2s}k_{-1p}[PPh_3]$, *i.e.* $k_{-2s}[CO] \ll k_{-1p}$. The validity of this assumption is confirmed by the observed rate law for the reverse reaction and it simply means that, at the low CO concentration employed, the *syn*-mono(phosphine) complex undergoes substitution at a rate much lower than its rate of *syn*–*anti*-isomerisation. The kinetic parameters k_{1a}, k_{2a}, and k_{-1a}/k_{2s} obtained also justify *a posteriori* the kinetic treatment of the reverse reaction in the absence of PPh_3 added. In fact, with the low PPh_3 concentration reached during the reaction, k_r is almost constant and k_f is well approximated by $[PPh_3]k_1k_{2s}/k_{-1a}$.

All k_r values obtained in this way were divided by the CO concentration and the results pooled, assuming the same percentage error in each one, to give the activation parameters (Table 3). Uncertainties listed have the meaning previously described. In order to separate the terms due to both paths, that inhibited and that not inhibited by PPh_3, one may use the data at 40 °C related

TABLE 2

Rate and equilibrium data for the reaction $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + PPh_3 \rightleftharpoons [(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + CO$ in decalin. [Complex] = 2×10^{-4}—5×10^{-4} [a] or *ca.* 2×10^{-5}M [b]

θ_c/°C	$10^3[PPh_3]$/M	P_{CO}/atm	$10^3[CO]$/M	$10^4 k_{f(Ar)}$/s^{-1}	$10^4(k_{f(CO)} + k_r)$/s^{-1}	$[B]_e/[A]_e$	$10^4 k_{f(CO)}$/s^{-1}	$10^4 k_r$/s^{-1}	$10^2 K$
90·0	0·02 [c]	1·10	5·8					1·00 [d]	
	0·02 [c]	1·10	5·8					1·05 [d]	
100·0	0·02 [c]	1·10	5·6					3·60 [d]	
	0·02 [c]	1·46	7·5					3·82 [d]	
110·0	0·02 [c]	1·10	5·4					12·0 [d]	
	0·02 [c]	1·10	5·4					13·2 [d]	
	92·3	0·00	0·00	1·11 [e]					
	92·3	1·10	5·4		2·06	0·63	0·80	1·26	3·69 [f]
	323	0·00	0·00	1·26					
	323	1·10	5·4		1·48	2·46	1·05	0·43	4·11 [f]
	526	0·00	0·00	1·25					
	526	1·10	5·4		1·33	5·15	1·11	0·22	5·29 [f]
120·0	95·0	1·10	5·1		7·53	0·82	3·39	4·14	4·40 [f]
	320	0·00	0·00	4·44					
	320	1·10	5·1		5·57	2·83	4·12	1·45	4·51 [f]
	521	0·00	0·00	4·44					
	521	1·10	5·1		4·81	5·52	4·07	0·74	5·40 [f]
130·0	91·5	0·00	0·00	12·0 [e]					
	91·5	1·10	4·8		23·0	0·62	8·8	14·2	3·25 [f]
	317	0·00	0·00	13·3					
	317	1·10	4·8		14·8	2·60	10·7	4·1	3·94 [f]
	516	0·00	0·00	13·4					
	516	1·10	4·8		16·5	5·70	14·0	2·5	5·30 [f]

[a] Starting complex = $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$ (=A). [b] Starting complex = $[(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$ (=B). [c] Approximate final concentration. [d] Starting from B; all other runs started from A. [e] Low value not used in computation of kinetic parameters. [f] $\Delta H^\ominus \simeq -4$ kJ mol^{-1} (*ca.* -1 kcal mol^{-1}), $\Delta S^\ominus \simeq -30$ J K^{-1} mol^{-1} (-8 cal K^{-1} mol^{-1}).

TABLE 3

Kinetic parameters [a] obtained from the rate equations $k_{f(Ar)} = k_{1a} + k_{2a}[PPh_3]$ [b] and $k_r = \{(k_{-2s}k_{1p}/k_{-1p}) + k_{-2a}\}[CO]$ for the reaction $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3] + PPh_3 \rightleftharpoons [(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + CO$

θ_c/°C	$10^4 k_{1a}/s^{-1}$	$10^4 k_{2a}$/l mol^{-1} s^{-1}	$\sigma(k_{f(Ar)})$/%	$10^2\{(k_{-2s}k_{1p}/k_{-1p}) + k_{-2a}\}$/ l mol^{-1} s^{-1}
30·0	1·43 ± 0·04	2·18 ± 0·12	1·7	
40·0	4·35 ± 0·10	6·55 ± 0·31	1·6	1·58 [c]
50·0	12·8 ± 0·1	20·7 ± 0·2	0·4	3·18 [c]
60·0				6·00 [c]
70·0				10·7 [c]

$\Delta H_{1a}^\ddagger = 86{\cdot}7 \pm 1{\cdot}0$ kJ mol^{-1} ($20{\cdot}7 \pm 0{\cdot}3$ kcal mol^{-1})
$\Delta S_{1a}^\ddagger = -32 \pm 3$ J K^{-1} mol^{-1} (-8 ± 1 cal K^{-1} mol^{-1})
$\Delta H_{2a}^\ddagger = 90{\cdot}1 \pm 1{\cdot}9$ kJ mol^{-1} ($21{\cdot}6 \pm 0{\cdot}5$ kcal mol^{-1})
$\Delta S_{2a}^\ddagger = -18 \pm 6$ J K^{-1} mol^{-1} (-4 ± 2 cal K^{-1} mol^{-1})
$\Delta H_{\{(-2s1p/-1p)+(-2a)\}}^\ddagger = 53{\cdot}9 \pm 2{\cdot}0$ kJ mol^{-1} ($12{\cdot}9 \pm 0{\cdot}5$ kcal mol^{-1})
$\Delta S_{\{(-2s1p/-1p)+(-2a)\}}^\ddagger = -107 \pm 6$ J K^{-1} mol^{-1} (-26 ± 2 cal K^{-1} mol^{-1})
$\sigma(k_r)/\% = 9{\cdot}0$

[a] Uncertainties are standard deviations (see text). [b] For $[PPh_3] \geqslant 1{\cdot}36$M. [c] $k_{-2s}k_{1p}/k_{-1p} \geqslant$ *ca.* $10\,k_{-2a}$.

TABLE 4

Kinetic parameters [a] obtained from the rate equation $1/(k_{f(Ar)} - k_{2a}[PPh_3]) = (1/k_{1a}) + (k_{-1a}/k_{1a}k_{2s}[PPh_3])$ [b]

θ_c/°C	$10^4 k_{1a}/s^{-1}$	$10^2(k_{-1a}/k_{2s})$/mol l^{-1}
30·0	1·56 ± 0·02	1·29 ± 0·04
40·0	4·99 ± 0·07	1·79 ± 0·07
50·0	15·2 ± 0·1	2·87 ± 0·03

$\Delta H_{1a}^\ddagger = 90 \pm 1$ kJ mol^{-1} ($21{\cdot}5 \pm 0{\cdot}2$ kcal mol^{-1})
$\Delta S_{1a}^\ddagger = -20 \pm 2$ J K^{-1} mol^{-1} (-5 ± 1 cal K^{-1} mol^{-1})
$\Delta H_{-1a}^\ddagger - \Delta H_{2s}^\ddagger = 33 \pm 2$ kJ mol^{-1} ($8{\cdot}0 \pm 0{\cdot}3$ kcal mol^{-1})
$\Delta S_{-1a}^\ddagger - \Delta S_{2s}^\ddagger = 74 \pm 4$ J K^{-1} mol^{-1} (18 ± 1 cal K^{-1} mol^{-1})

[a] Uncertainties are standard deviations (see text); the standard deviations take into account the covariance of the parameters $1/k_{1a}$ and $k_{-1a}/k_{1a}k_{2s}$ obtained from least-squares analysis according to equation (5). [b] Values of k_{2a} from Table 3.

to the $[PPh_3]$ dependence of k_r. Plots of $1/(k_r - k_{-2a}[CO])$ against $[PPh_3]$ should be linear with intercept $k_{-1p}/k_{1p}k_{-2s}[CO]$ and gradient $k_{-1p}k_{2s}/k_{1p}k_{-2s}k_{-1a}[CO]$, from which the value of k_{2s}/k_{-1a} can be derived. The best consistency with the value of k_{2s}/k_{-1a} already determined with accuracy in the study of the forward reaction under Ar was obtained by assuming $k_{-2a}[CO] = k_r$ for the run with $[PPh_3] = 0{\cdot}561$M. In fact at this high PPh_3 concentration only the uninhibited path is likely to be important. Good linearity was obtained for the data at 40·0 °C, using $k_{-2a}[CO] \simeq 0{\cdot}90 \times 10^{-5}$ s^{-1}, from which a value of $1{\cdot}85 \times 10^{-2}$ mol l^{-1} can be determined for k_{-1a}/k_{2s} compared with the value of $1{\cdot}50 \times 10^{-2}$ mol l^{-1}

already found. Greater values for k_{-1a}/k_{2s} and marked curvature in plots were observed with decreasing estimated values for $k_{-2a}[CO]$. An upper limit of *ca.* $10^{-1}k_{-2s}k_{1p}/k_{-1p}$ can be defined for k_{-2a} at 40·0 °C. Such a relation is approximately valid also at the higher temperatures studied, as can be inferred from the kinetic and thermodynamic data listed in Tables 1, 3, and 4.

The rate equation of approach to equilibrium for the second CO substitution is given by (6). The agreement

$$k_{obs.} = k_f + k_r = \frac{k_{-CO}[PPh_3]}{[PPh_3] + (k_{CO}[CO]/k_{PPh_3})} + \frac{k_{-PPh_3}[CO]}{[CO] + (k_{PPh_3}[PPh_3]/k_{CO})} \quad (6)$$

with the experimental rate laws is evident. Kinetic parameters were derived assuming the same percentage standard deviation for each observed rate constant and are collected in Table 5. Values of the competition parameter k_{PPh_3}/k_{CO} for bimolecular attack by triphenylphosphine and carbon monoxide on the unsaturated intermediate were calculated from equation (7). Good

$$1/k_r = \{1 + (k_{PPh_3}[PPh_3]/k_{CO}[CO])\}/k_{-PPh_3} \quad (7)$$

linear plots were obtained for the dependence of $1/k_r$ on $[PPh_3]$. The values derived for k_{PPh_3}/k_{CO} (Table 5) are also consistent with the small CO effect on the rate of the forward reaction at the high PPh_3 concentration employed.

TABLE 5

Kinetic parameters[a] obtained from the rate equations $k_{f(Ar)} = k_{-CO}$ and $1/k_r = \{1 + (k_{PPh_3}[PPh_3]/k_{CO}[CO])\}/k_{-PPh_3}$[b] for the reaction $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + PPh_3 \rightleftharpoons [(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)] + CO$

θ_c/°C	$10^4k_{-CO}/s^{-1}$	$10^4k_{-PPh_3}/s^{-1}$	k_{PPh_3}/k_{CO}
90·0		1·02	
100·0		3·71	
110·0	1·26	12·6	0·52 ± 0·05[c,d]
120·0	4·44		0·43 ± 0·04[d,e]
130·0	13·4		0·39 ± 0·04[d,e]

$\Delta H_{-CO}^{\ddagger} = 148 \pm 3$ kJ mol^{-1} (35·5 ± 0·7 kcal mol^{-1})
$\Delta S_{-CO}^{\ddagger} = 66 \pm 7$ J K^{-1} mol^{-1} (16 ± 2 cal K^{-1} mol^{-1}) $\sigma(k_{f(Ar)}) = 4{\cdot}4\%$
$\Delta H_{-PPh_3}^{\ddagger} = 142 \pm 4$ kJ mol^{-1} (33·9 ± 0·9 kcal mol^{-1})
$\Delta S_{-PPh_3}^{\ddagger} = 68 \pm 10$ J K^{-1} mol^{-1} (16 ± 3 cal K^{-1} mol^{-1}) $\sigma(k_r) = 6{\cdot}4\%$
$\Delta H_{PPh_3}^{\ddagger} - \Delta H_{CO}^{\ddagger} = -19 \pm 9$ kJ mol^{-1} (−4 ± 2 kcal mol^{-1})
$\Delta S_{PPh_3}^{\ddagger} - \Delta S_{CO}^{\ddagger} = -54 \pm 22$ J K^{-1} mol^{-1} (−13 ± 6 cal K^{-1} mol^{-1})

[a] Uncertainties are standard deviations (see text). [b] Assuming $k_{-PPh_3} = k_r$ for runs using $[(Ph_3P)(OC)_2Fe(\mu\text{-}SPh)_2Fe(CO)_2(PPh_3)]$ as the starting complex, which gives a *ca.* 2 × 10^{-5}M final PPh_3 concentration. [c] Determined using the listed k_{-PPh_3} value. [d] Assuming $\sigma(k_r) = 10\%$ for equilibrium reactions. [e] Determined using an extrapolated k_{-PPh_3} value.

The present results are in good quantitative agreement with those obtained by Ellgen *et al.*[6] for a one-temperature study of the first CO substitution by PPh_3 in complex (I). In fact one can extrapolate values of 2·39 × 10^{-4} s^{-1} for k_{1a} and 4·10 × 10^{-4} l mol^{-1} s^{-1} for k_{2a} at 35 °C in decalin, compared with the reported values of 2·4 × 10^{-4} s^{-1} and 4·9 × 10^{-4} l mol^{-1} s^{-1} in toluene at the same temperature. The present interpretation of the results also agrees with S_N2 attack on the *anti*- and *syn*-forms of complex (I). The good linearity observed in the rate plots suggests that the reactive *syn*-species is present at equilibrium, *i.e.* at the beginning of the reaction, in very small concentration compared to the *anti*-form. If one assumes a ratio $[anti] : [syn] \geqslant 20 : 1$, it means also that $k_{-1a} \geqslant 20k_{1a}$ and by introducing this inequality in the obtained competition parameters k_{-1a}/k_{2s} a lower limit of 2·23 × 10^{-1} l mol^{-1} s^{-1} can be estimated, for example, at 30 °C for k_{2s}. The *syn*-isomer thus reacts more than 100 times faster than the *anti*-isomer compared with factors of 40 and 20 found for the corresponding benzyl- and methyl-thio-derivatives, respectively.[6] Furthermore the extrapolated value of $k_{2s} \geqslant 2{\cdot}6 \times 10^{-1}$ l mol^{-1} s^{-1} at 35 °C for the phenylthio- as compared to the value of 2·3 × 10^{-2} l mol^{-1} s^{-1} for the benzylthio-derivative suggests that for the *syn*-form some inductive effects should be effective.

The activation parameters obtained for bimolecular attack on the *anti*-form of the phenylthio-derivative by PPh_3 can be compared with corresponding data for iron carbonyl complexes containing sulphur bridging atoms bonded together by the rigid organic groups 3,4-tolyl and 1,2-ethyl. In the present case the higher activation enthalpy (20·7 compared with 12·5 kcal mol^{-1} for substitution with PPh_3 in the 3,4-tolyl derivative) and much less negative activation entropy (−8 compared with −31 cal K^{-1} mol^{-1}) indicate much less order requirements and less pronounced bond making in the activated complex. This different behaviour is not easily attributable to steric effects in view of the very similar structure of $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3]$ and $[(OC)_3Fe(\mu\text{-}S_2Ph_2C_2)Fe(CO)_3]$, the latter being characterised by the sulphur atoms being bonded through the *cis*-stilbene moiety. But some specific role of small structural differences cannot be ruled out, considering, for example, the different reactivity of the structurally very similar *anti*- and *syn*-forms.

The activation parameters for the *anti*–*syn*-conversion are consistent with a mechanism in which bond breaking occurs to some extent. In fact, a much higher activation enthalpy is expected for conversions involving planar transition states.[9] This *syn*–*anti*-isomerisation can be compared with the pyramidal inversion in sulphoxides, which goes mainly through a planar transition state with $\Delta H^{\ddagger} = 36$—43 kcal mol^{-1} and $\Delta S^{\ddagger} \simeq 0$ cal K^{-1} mol^{-1}.[10] The values found are close to those reported for a series of *cis*- and *trans*-$[(R_2S)_2PtCl_2]$ complexes[11] and a similar mechanism is thought to be operating. For the inversion at sulphur in these complexes a mechanism was proposed in which the sulphur retains a distorted tetrahedral con-

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figuration and the platinum atom forms a σ-bond alternately with the two sulphur lone pairs. The same behaviour was postulated in the *anti–syn*-isomerisation of $[(cp)(OC)Fe(\mu\text{-}SPh)_2Fe(CO)(cp)]$ (cp = η-cyclopentadienyl) despite the different activation parameters, $\Delta H^\ddagger = 30{\cdot}68$—$31{\cdot}84$ kcal mol^{-1} and $\Delta S^\ddagger = 24{\cdot}6$—$21{\cdot}5$ cal K^{-1} mol^{-1}, with a large positive entropy which would suggest a much more extended bond breaking.[12]

Complex (II) undergoes PPh_3 substitution by carbon monoxide with S_N2 displacement. The *syn*-form is, also in this case, much more reactive than the *anti*-form, and from arguments similar to those previously outlined it can be seen that at 40 °C k_{-2s} should be greater than $3{\cdot}16 \times 10^{-1}$ l mol^{-1} s^{-1} and at least 200 times greater than k_{-2a}. It should be noted that the rate at which carbon monoxide attacks the complex (II) is close to the rate of attack of PPh_3 on (I). Very few data are available on S_N2 substitution by carbon monoxide, being mainly related to CO exchange.[13–15] The scarcity of data is probably a consequence of unfavourable equilibrium positions at the low CO pressure available in kinetic studies. This low CO concentration together with experimental difficulties could well explain why carbon monoxide is suggested to exchange mainly by a S_N1 mechanism.[14–15] Interpretation of the activation parameters must be extremely careful, considering the equilibrium involved, and it can only be pointed out that they fall in the range characteristic of bimolecular attack on an unhindered complex with a high degree of bond making.[15]

Complex (II) is unable to undergo CO substitution by PPh_3 *via* direct attack on the metal. The rate law and activation parameters are consistent with a CO-dissociative process and the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are very close to those found for dissociative substitution reactions of $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ (L = PBu^n_3 or CO)[16] and $[L(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$ (L = PPh_3 or CO).[7] Similar behaviour has been noted in the reaction of $[(OC)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ with tributylphosphine, where substitution with one phosphine makes attack of the second molecule of phosphine much more difficult.[16] This different behaviour between first and second substitution seems to be mainly due to steric effects, it being usually accepted that carbon monoxide is not a better nucleophile than triphenylphosphine. On the other hand it has been observed that with the less bulky tributylphosphine bis(mercaptoiron) derivatives undergo second substitution at a rate approximately equal to that of the first.[6] The importance of steric effects in bimolecular substitution of metal carbonyls is well established, for example, in the substitution of PPh_3 into the complexes $Ru_3(CO)_{12}$,[17] $Mo(CO)_6$ and $W(CO)_6$,[18] and of tricyclohexylphosphine into $[Co(CO)_3(NO)]$ and $[(cp)Rh(CO)_2]$.[19]

Complex (III) is unable to undergo direct attack also by carbon monoxide. The activation parameters, together with the nature of the retardation of the rate by PPh_3, are in good agreement with a reversible PPh_3-dissociative mechanism. Values of *ca.* 28 kcal mol^{-1} and *ca.* 7 cal K^{-1} mol^{-1} have been reported for phosphine dissociation in *trans*-tricarbonyl(halogeno)bis(triphenylphosphine)manganese complexes.[20]

The ratio of the rate constants for bimolecular attack by carbon monoxide and triphenylphosphine on the co-ordinatively unsaturated intermediate involved shows that CO attacks the vacant site somewhat more readily than does PPh_3. Similar values have been obtained for k_{CO}/k_{PBu_3} in the dissociative substitution reactions of $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ (L = CO or PBu_3) and for k_{CO}/k_{PPh_3} with $[(OC)_3Co(\mu\text{-}CO)(\mu\text{-}GePh_2)Co(CO)_3]$ and $[(Ph_3P)(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$.[7,16] The ratio markedly changes in favour of the phosphine for S_N2 attack on the less hindered $[Mo(CO)_4(PPh_3)]$ and $Ni(CO)_3$ complexes.[21,22]

I thank Mr. A. Ravazzolo for accurate technical assistance.

[4/1551 *Received, 26th July,* 1974]

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