

Chalcogen Derivatives of Iron Carbonyls. X. Reaction Mechanism of the CO Substitution on $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ ($\text{X} = \text{S}, \text{Se}$) with Ligands

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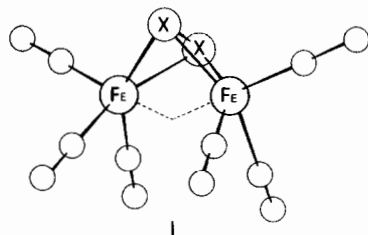
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The reaction of the title complexes with phosphine-like ligands proceeds by two competing paths, one, first order in [complex] and [L], the other first order in [complex] and second order in [L]. The mechanism can be explained by a rate-determining formation of an intermediate $\text{Fe}_2(\text{CO})_6\text{L}(\mu\text{X})_2$, which can lose CO or react further with another L prior to decomposition. The effect of both X and L on the rate of the two paths is discussed. The values of the rate constants show a large discriminating ability of the substrate versus the ligand, and this is tentatively explained by a facile coordination of the ligand on the complex via a low-energy empty M.O.

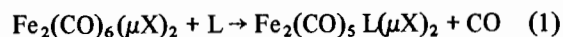
Introduction

Although the complexes $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ ($\text{X} = \text{S}, \text{Se}$) (I) are well known and have been obtained in large yields in a variety of ways [1, 2], few data have been reported till now on their chemistry. Instead, extensive investigations of the CO substitution



reaction have been carried out on the structurally related organochalcogen complexes ($\text{X} = \text{SR}, \text{SeR}, \text{TeR}$) [1, 3], whose main structural difference is the absence of the chalcogen–chalcogen bond. Several reports on the latter compounds deal with the CO substitution by tertiary phosphines, phosphites, arsines and stibines or ditertiary phosphines and

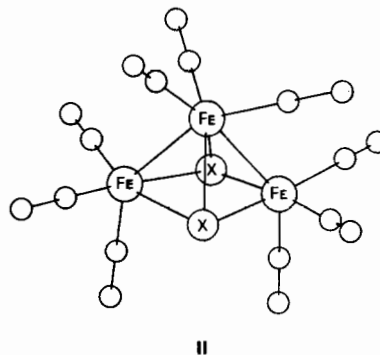
arsines [4]. These reactions generally afford a large range of products, depending on the reaction conditions and on the ligand employed. Mono-, bi- or tri-substituted derivatives of the parent dimer have been obtained with monodentate ligands, together with other derivatives in which the diphosphine behaves as either a chelating or a bridging ligand. In any case, the result of the reaction (eqn. 1) is the substitution of one or more COs by an equivalent amount of phosphine-like ligands; the internal core formed by the two iron atoms bonded by the two bridging X ligands is always retained:



The kinetic analysis, unless complicated by the presence of the so-called *syn-anti* isomerization, concerning the position of the groups R bonded to the chalcogen atoms, follows a second-order law, which is first-order in each reagent [5].

The two complexes $\text{Fe}_2(\text{CO})_6\text{S}_2$ and $\text{Fe}_2(\text{CO})_6\text{Se}_2$ show a quite different chemistry when reacting with phosphines, since an important path of the reaction is not a simple CO substitution, but a change in the Fe_2X_2 core.

In a typical reaction, the substituted derivatives of the parent compound, $\text{Fe}_2(\text{CO})_5\text{L}(\mu\text{X})_2$ and $\text{Fe}_2(\text{CO})_4\text{L}_2(\mu\text{X})_2$, have been isolated, together with the more complex polynuclear clusters $\text{Fe}_3(\text{CO})_{9-n}\text{L}_n(\mu_3\text{X})_2$ ($n = 0, 1, 2$) (II: $n = 0$): their yields depend



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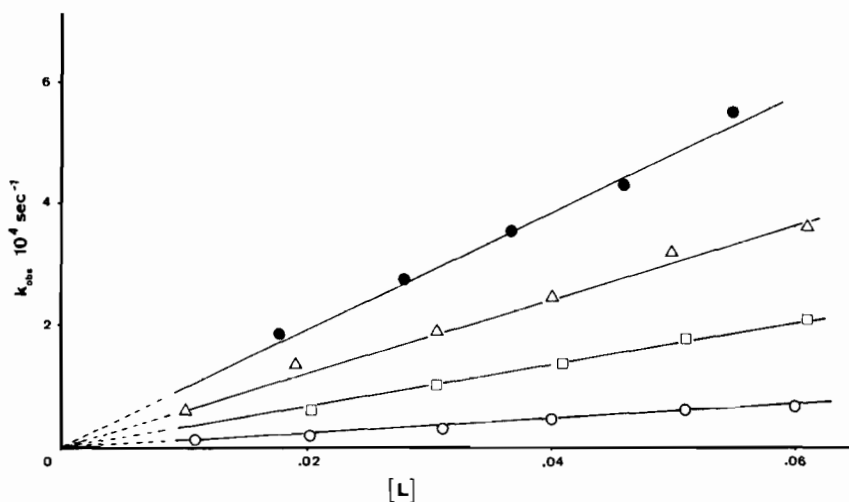
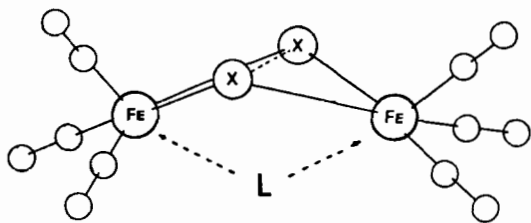


Fig. 1. Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ with L: plots of k_{obs} vs. [L]. Open circles, X = S, L = $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$; squares, X = S, L = $\text{P}(\text{C}_6\text{H}_5)_3$; triangles, X = S, L = $\text{P}(\text{OC}_6\text{H}_5)_3$ at 30 °C; closed circles, X = Se, L = $\text{P}(\text{OC}_2\text{H}_5)_3$.

on the nature of the ligand and of the X atoms and on the reaction conditions. The proposed mechanism implies that the initial step of the reaction leads to the formation of an unstable $\text{Fe}_2(\text{CO})_6\text{L}(\mu\text{X})_2$ 'adduct', which has been isolated only when L = $\text{P}(\text{C}_6\text{H}_5)_3$: spectroscopic and reactivity data suggest structure (III) [2].



III

The loss of CO from (III) is the obvious way to obtain the $\text{Fe}_2(\text{CO})_5\text{L}(\mu\text{X})_2$ derivative. On the other hand, the formation of the tri-iron complexes is explained by the coordination of another parent molecule on the adduct, via the X atoms, and subsequent rearrangements. Thus the structural difference with the analogous complexes $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ (X = SR, SeR, TeR), *i.e.* the absence of the R groups, allows the direct participation of the chalcogen atoms to the reaction mechanism.

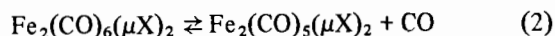
Then the kinetic study of this reaction, in its most general conditions, is expected to be complicated enough to prevent a reliable interpretation of the data, unless some experimental simplifications are introduced. As the major complication from the kinetic point of view comes from the reaction of the

intermediate with the starting complex, this path can be neglected by using large concentrations of the ligand: the absence of any tri-iron products in these experimental conditions [2] is a test of the correctness of this simplification.

The results of a systematic study of the kinetic behaviour of $\text{Fe}_2(\text{CO})_6\text{S}_2$ and of $\text{Fe}_2(\text{CO})_6\text{Se}_2$ with ligands are reported herein.

Results

The CO exchange reaction on $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ does not give any reliable kinetic results. The complex dissolved in n-heptane under a ^{14}C O atmosphere has not gained any radioactivity after long time and its concentration remains practically constant, as checked by the IR spectrum. Decomposition of the complex can sometimes occur in a rapid and complete way, producing a solid residue, formed by FeX, X or Fe powder, whereas the solution contains no more $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$, but traces (less than 5%) of $\text{Fe}_3(\text{CO})_9\text{X}_2$ complex. The rapidity of the decomposition probably suggests that the solid products can catalyse the reaction and prevent reliable rate measurements. The CO pressure has an inhibiting effect on the decomposition: $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ complexes are stable for several days at 80 °C under 1 atmosphere of CO and decompose in a few hours when the pressure is 0.5 atm or lower. This indicates that the CO dissociation has an extremely low rate and that the equilibrium (2) is shifted to the left:



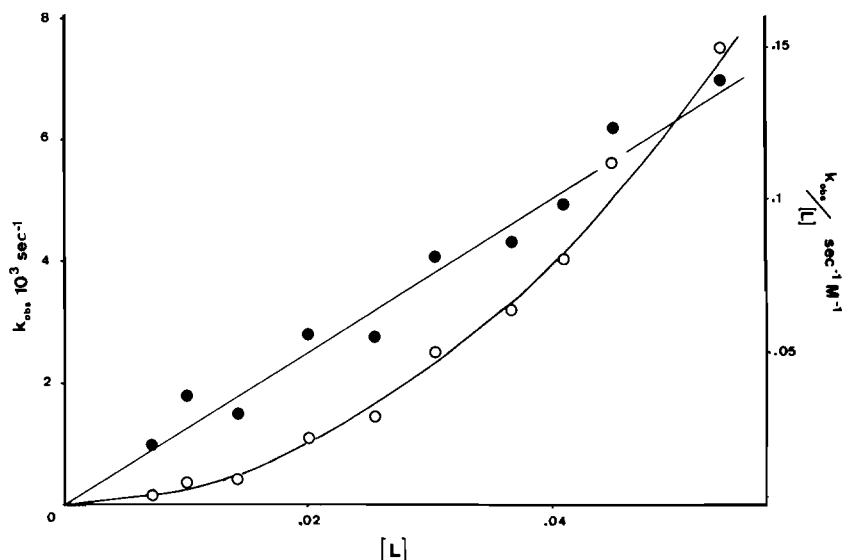


Fig. 2. Reaction of $\text{Fe}_2(\text{CO})_6\text{Se}_2$ with $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ at 30°C . Open circles, plots of k_{obs} vs. $[\text{L}]$; closed circles, plots of $k_{\text{obs}}/[\text{L}]$ vs. $[\text{L}]$.

The formation of $\text{Fe}_3(\text{CO})_9\text{X}_2$ can be explained by reaction of $\text{Fe}_2(\text{CO})_5(\mu\text{X})_2$ or other unstable intermediates with $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$, in a way similar to that already reported [2].

The reactions of $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ ($\text{X} = \text{S}, \text{Se}$) with L ($\text{L} = \text{As}(\text{C}_6\text{H}_5)_3, \text{P}(\text{OC}_6\text{H}_5)_3, \text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5, \text{P}(\text{C}_6\text{H}_5)_3$) and of $\text{Fe}_2(\text{CO})_6\text{Se}_2$ with $\text{P}(\text{OC}_2\text{H}_5)_3$ follow a second order kinetic equation, depending both on the substrate and on the ligand concentration. The rate expression is:

$$\text{rate} = k_{\text{obs}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2] = k_{\text{II}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2][\text{L}] \quad (3)$$

or:

$$k_{\text{obs}} = k_{\text{II}}[\text{L}]$$

as clearly shown by Fig. 1, in which the dependence of k_{obs} on $[\text{L}]$ is illustrated. Every straight line has zero intercept, indicating that a first order reaction makes no contribution to the rate, as expected by comparing the rate of the ligand substitution with that of the probable first-order decomposition.

The other reactions show a more complicated kinetic behaviour, indicating a higher order dependence of the rate on the ligand concentration. The results can be rationalised if $k_{\text{obs}}/[\text{L}]$ vs. $[\text{L}]$ is reported, as illustrated in Figs. 2 and 3.

When $\text{X} = \text{Se}$ and $\text{L} = \text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ and $\text{P}(\text{nC}_4\text{H}_9)_3$, straight lines passing through zero are obtained, which suggests a second order dependence of the rate on $[\text{L}]$, according to the expression:

$$\frac{k_{\text{obs}}}{[\text{L}]} = k_{\text{III}}[\text{L}] \quad (4)$$

or:

$$\text{rate} = k_{\text{obs}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2] = k_{\text{III}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2][\text{L}]^2$$

The reactions of the S complex with the same ligands show that the lines $k_{\text{obs}}/[\text{L}]$ vs. $[\text{L}]$ have not negligible intercept value, thus indicating that the third order kinetic mechanism operates together with a second order one. The reaction rate can be represented by:

$$\text{rate} = k_{\text{obs}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2] = k_{\text{II}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2][\text{L}] + k_{\text{III}}[\text{Fe}_2(\text{CO})_6(\mu\text{X})_2][\text{L}]^2 \quad (5)$$

or:

$$k_{\text{obs}} = k_{\text{II}}[\text{L}] + k_{\text{III}}[\text{L}]^2$$

When $\text{L} = \text{P}(\text{nC}_4\text{H}_9)_3$, the increase of the temperature has an opposite effect on the value of the rate constants and, correspondingly, k_{II} increases and k_{III} decreases. Accordingly, it is not surprising that the k_{II} term is negligible with respect to the k_{III} term at 30°C , whereas at 40°C its contribution to the overall rate can be clearly determined.

The values of the observed rate constant and those of the specific rate constants, obtained from the

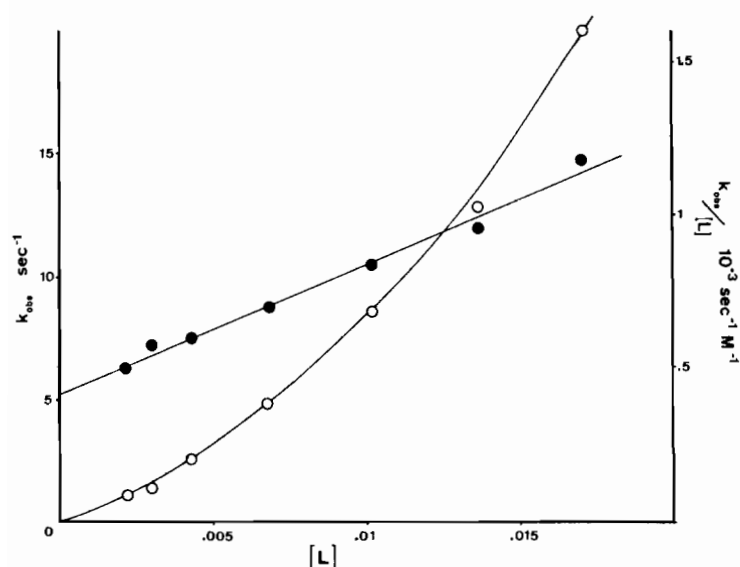


Fig. 3. Reaction of $\text{Fe}_2(\text{CO})_6\text{S}_2$ with $\text{P}(\text{nC}_4\text{H}_9)_3$ at 40°C . Open circles, plots of k_{obs} vs. $[\text{L}]$; closed circles, plots of $k_{\text{obs}}/[\text{L}]$ vs. $[\text{L}]$.

TABLE I. Values of the Observed Rate Constant for the Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ with Ligands in n-Heptane.

Complex	Ligand	t °C	[Ligand]	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$
$\text{Fe}_2(\text{CO})_6\text{S}_2$	$\text{As}(\text{C}_6\text{H}_5)_3$	70.0	0.0201	0.0067
			0.0300	0.0087
			0.0407	0.0109
			0.0504	0.0132
			0.0749	0.0193
			0.099	0.026
			0.149	0.041
	0.199	0.054		
	$\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$	30.0	0.0108	0.107
			0.0206	0.188
			0.0311	0.31
			0.0404	0.44
			0.0512	0.57
	$\text{P}(\text{C}_6\text{H}_5)_3$	30.0	0.060	0.65
0.0207			0.61	
0.0305			1.00	
0.0411			1.37	
0.0511			1.74	
$\text{P}(\text{OC}_6\text{H}_5)_3$	30.0	0.0610	2.08	
		0.0099	0.57	
		0.0191	1.36	
		0.0305	1.88	
		0.0401	2.45	
		0.0496	3.2	
		0.061	3.6	
$\text{P}(\text{OC}_6\text{H}_5)_3$	40.0	0.0210	2.65	
		0.0305	5.0	
		0.0401	6.3	

(continued on facing page)

TABLE I. (continued)

Complex	Ligand	t °C	[Ligand]	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$
			0.0496	7.2
			0.061	8.7
			0.080	12.1
	P(C ₂ H ₅) ₂ C ₆ H ₅	30.0	0.0023	2,800
			0.0032	3,800
			0.0045	6,400
			0.0074	13,100
			0.0102	16,600
			0.0136	29,400
			0.0170	40,000
		40.0	0.0021	175
			0.0040	360
			0.0058	570
			0.0077	830
			0.0092	1,070
			0.0100	1,220
			0.0106	1,210
	P(nC ₄ H ₉) ₃	30.0	0.0021	5,400
			0.0032	11,900
			0.0045	24,100
			0.0071	53,000
			0.0101	104,000
			0.0141	228,000
			0.0174	376,000
		40.0	0.0021	10,600
			0.0030	17,300
			0.0043	25,800
			0.0069	48,000
			0.0103	86,000
			0.0137	132,000
			0.0171	201,000
Fe ₂ (CO) ₆ Se ₂	As(C ₆ H ₅) ₃	70.0	0.100	0.00177
			0.150	0.00188
			0.200	0.00250
			0.250	0.00344
	P(OCH ₂) ₃ CC ₂ H ₅	60.0	0.022	0.64
			0.028	0.75
			0.041	1.16
			0.051	1.34
			0.061	1.52
	P(C ₆ H ₅) ₃	60.0	0.020	0.284
			0.030	0.45
			0.040	0.65
			0.050	0.78
			0.060	0.93
	P(OC ₆ H ₅) ₃	60.0	0.093	0.40
			0.147	0.65
			0.250	0.85
			0.347	1.15

(continued overleaf)

TABLE I. (continued)

Complex	Ligand	t °C	[Ligand]	k _{obs} × 10 ⁴ sec ⁻¹
			0.41	1.42
			0.53	1.75
			0.64	2.31
		70.0	0.024	0.29
			0.031	0.35
			0.041	0.43
			0.050	0.53
			0.061	0.64
	P(OC ₂ H ₅) ₃	30.0	0.018	1.87
			0.028	2.78
			0.037	3.55
			0.047	4.3
			0.055	5.5
	P(C ₂ H ₅) ₂ C ₆ H ₅	30.0	0.007	1.40
			0.010	3.64
			0.014	4.2
			0.020	11.2
			0.026	14.3
			0.031	25.1
			0.037	31.8
			0.041	40
			0.045	56
			0.054	75
		40.0	0.019	9.3
			0.028	18.5
			0.038	49
			0.047	61
			0.057	110
			0.079	226
			0.100	313
			0.121	443
			0.136	560
	P(nC ₄ H ₉) ₃	30.0	0.0029	9.0
			0.0043	15.1
			0.0057	31.3
			0.0071	48
			0.0086	69
			0.0100	86
			0.0114	124
			0.0129	151
		40.0	0.0029	11.2
			0.0043	35
			0.0057	47
			0.0071	73
			0.0086	116
			0.0100	148
			0.0114	186
			0.0129	229
			0.0143	269

TABLE II. Specific Rate Constants for the Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ with Ligands in n-Heptane.

Complex	Ligand	t °C	$10^2 k_{\text{II}} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-2} k_{\text{III}} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
$\text{Fe}_2(\text{CO})_6\text{S}_2$	$\text{As}(\text{C}_6\text{H}_5)_3$	70.0	0.00269 ± 0.00006	
	$\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$	30.0	0.115 ± 0.005	
	$\text{P}(\text{C}_6\text{H}_5)_3$	30.0	0.363 ± 0.006	
	$\text{P}(\text{OC}_6\text{H}_5)_3$	30.0	0.60 ± 0.04	
		40.0	1.50 ± 0.11	
	$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	30.0	$1,040 \pm 110$	7.8 ± 1.0
		40.0	750 ± 35	4.2 ± 0.5
	$\text{P}(\text{nC}_4\text{H}_9)_3$	30.0		$1,210 \pm 74$
		40.0	$41,800 \pm 2,400$	420 ± 24
	$\text{Fe}_2(\text{CO})_6\text{Se}_2$	$\text{As}(\text{C}_6\text{H}_5)_3$	70.0	0.00011 ± 0.00003
$\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$		60.0	0.024 ± 0.001	
$\text{P}(\text{C}_6\text{H}_5)_3$		60.0	0.163 ± 0.008	
$\text{P}(\text{OC}_6\text{H}_5)_3$		60.0	0.034 ± 0.002	
		70.0	0.095 ± 0.004	
$\text{P}(\text{OC}_2\text{H}_5)_3$		30.0	0.96 ± 0.06	
$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$		30.0		0.025 ± 0.002
		40.0		0.031 ± 0.002
$\text{P}(\text{nC}_4\text{H}_9)_3$		30.0		0.89 ± 0.05
		40.0		1.31 ± 0.10

TABLE III. Values of the Activation Parameters.

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Complex	Ligand	$\Delta H_{\text{II}}^\ddagger$ (kJ mol ⁻¹)	$\Delta H_{\text{III}}^\ddagger$ (kJ mol ⁻¹)	$\Delta S_{\text{II}}^\ddagger$ (J K ⁻¹ mol ⁻¹)	$\Delta S_{\text{III}}^\ddagger$ (J K ⁻¹ mol ⁻¹)
$\text{Fe}_2(\text{CO})_6\text{S}_2$	$\text{P}(\text{OC}_6\text{H}_5)_3$	70 ± 9		55 ± 21	
	$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$	-28 ± 11	-51 ± 16	-318 ± 25	-360 ± 37
	$\text{P}(\text{nC}_4\text{H}_9)_3$		-86 ± 8		-428 ± 18
$\text{Fe}_2(\text{CO})_6\text{Se}_2$	$\text{P}(\text{OC}_6\text{H}_5)_3$	96 ± 8		-24 ± 18	
	$\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$		15 ± 8		-188 ± 20
	$\text{P}(\text{nC}_4\text{H}_9)_3$		28 ± 9		-116 ± 21

eqns. (3), (4) and (5) by a least-squares procedure, are reported in Tables I and II, respectively. Table III collects the values of the activation parameters. The error is the standard deviation.

Discussion

The most relevant feature of the reaction of $\text{Fe}_2(\text{CO})_6\text{S}_2$ and $\text{Fe}_2(\text{CO})_6\text{Se}_2$ with phosphine-like ligands arises from the complicated pattern of the

general mechanism and, in this light, the difference from the behaviour of the similar $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ (X = SR, SeR, TeR) complexes is straightforward.

The analysis of the kinetic data leads firstly to point out the absence of the first-order mechanism, which means that the CO dissociation is very unlikely and the Fe-CO bond is kinetically very strong. This is not unexpected, as $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ complexes react preferentially via an $\text{S}_{\text{N}}2$ mechanism, and when the direct ligand coordination is sterically forbidden, the dissociation of CO requires

high temperatures and great activation enthalpy values [6].

The most common reaction mechanism is a second-order one, first order in the concentration of both complex and ligand, which means that the rate determining step is most probably a direct coordination of the ligand on the substrate, giving the intermediate $\text{Fe}_2(\text{CO})_6\text{L}(\mu\text{X})_2$. This is expected to be very unstable and in effect evidence of a 1:1 'adduct' has been obtained only when $\text{X} = \text{S}$ and $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ [2]. Triphenylphosphine probably represents in this case a compromise among the ligands, as the less basic ligands give rise to a too weak ligand-complex interaction to stabilise the adduct and the strong nucleophiles can easily react further (*vide infra*). According to the stability of the intermediate, a contemporaneous or subsequent loss of carbon monoxide can occur, giving rise to the monosubstituted derivative $\text{Fe}_2(\text{CO})_5\text{L}(\mu\text{X})_2$. Actually, the ligands which react by such mechanism lead to stable well-characterised monosubstituted complexes.

To explain the structure of the adduct we proposed [2] that the substrate can coordinate by means of the L.U.M.O., which is the antibonding counterpart of the H.O.M.O., closely corresponding to the classical Fe-Fe bent bond [7]. The kinetic evidence suggests that the ligand attack occurs on the metal atoms via the metal-like orbitals, because the sulfur compound reacts much faster than the selenium compound, that being explained by the greater electron attracting power of the S atoms, which enhances the positivisation of the Fe's (and their coordinating ability *versus* the ligand). For instance, the reactivity of the S-complex with $\text{P}(\text{OC}_6\text{H}_5)_3$ is about 6,000 times greater than that of the Se-complex, and, accordingly, the activation enthalpy is about 26 kJ mol^{-1} less.

The other series of iron-chalcogen carbonyls, the trinuclear $\text{Fe}_3(\text{CO})_9\text{X}_2$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) complexes, whose reactivity is in the order $\text{Te} > \text{Se} > \text{S}$, shows the formation of an adduct, via the coordination of the ligand on the chalcogen atoms [8]. The structure of the $\text{Fe}_3(\text{CO})_9\text{X}_2$ complexes (II) [9] is strictly related to that of the binuclear ones [10] and can be regarded as arising from the insertion of a $\text{Fe}(\text{CO})_3$ fragment into the Fe-Fe bond of $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$, so that the quasi-tetrahedral Fe_2X_2 core is distorted to a quasi-planar framework, which forms the base of the square pyramidal cluster Fe_3X_2 . Keeping in mind this structural relationship, which is not purely formal, as (II) derivatives can be easily obtained from the reaction of (I) with L [2], it is noteworthy that the ligand attack occurs in both series on the same side, probably via analogous M.O.s, which in (I) is substantially a metal orbital and in (II) could have prevailing chalcogen character.

The comparison between the rate constants of the various ligands suggests some qualitative observa-

tions. The effect of the ligands is mainly electronic, e.g. the k_{II} values agree quite well with Tolman's electronic parameter [11]. On the other hand, steric inhibition effect is shown by $\text{P}(\text{C}_6\text{H}_5)_3$, which reacts more slowly than expected on the basis of its nucleophilicity: this effect is more evident on $\text{Fe}_2(\text{CO})_6\text{S}_2$, which has probably shorter Fe-Fe and Fe-X distances than $\text{Fe}_2(\text{CO})_6\text{Se}_2$, as is shown by the basal framework of the corresponding $\text{Fe}_3(\text{CO})_9\text{X}_2$ [9]. The ratio between the reaction rates with different ligands on the same complex is quite large. $\text{P}(\text{C}_6\text{H}_5)_3$ reacts at least a thousand times faster than $\text{As}(\text{C}_6\text{H}_5)_3$ on both substrates and $k_{\text{II}}(\text{P}(\text{OC}_2\text{H}_5)_3)$ on the Se-complex is $\gg 40 k_{\text{II}}(\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5)$. This suggests a high discriminating ability of the substrates *versus* the ligands and a large bond making effect in the transition state. The same effect is shown by the comparison of the rate constants of both complexes with the same ligand. The ratio $k_{\text{II}}(\text{S})/k_{\text{II}}(\text{Se})$ is about 25 for $\text{As}(\text{C}_6\text{H}_5)_3$, greater than 1,000 for $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$, nearly 6,000 for $\text{P}(\text{OC}_6\text{H}_5)_3$ [12].

Other $\text{Fe}_2(\text{CO})_6(\mu\text{X})_2$ complexes, in which X_2 are S-bridged or N-bridged groups, show a much lesser discriminating ability *versus* the ligands. $\text{Fe}_2(\text{CO})_6\text{S}_2\text{-C}_6\text{H}_3\text{CH}_3$ is reported to react with $\text{P}(\text{C}_6\text{H}_5)_3$ about 8 times faster than with $\text{As}(\text{C}_6\text{H}_5)_3$ and with $\text{P}(\text{OCH}_3)_3$ not more than 20 times faster than with $\text{P}(\text{OC}_6\text{H}_5)_3$ [5]. On the other hand, the strongly electron withdrawing N-groups do not increase, to a great extent, the reactivity of the complex, as shown by the comparison between the k_{II} of $\text{Fe}_2(\text{CO})_6\text{N}_2\text{C}_{12}\text{H}_8$ and of $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$ which is 1 for $\text{As}(\text{C}_6\text{H}_5)_3$, 20 for $\text{P}(\text{C}_6\text{H}_5)_3$ and about 100 for $\text{P}(\text{OC}_6\text{H}_5)_3$ [13]. All these complexes are reported to react by a mechanism implying coordination of the ligand directly on a Fe atom.

It appears that, when the ligand coordination to a substrate occurs on a unique metal atom [5, 13], probably via an empty non-bonding or anti-bonding atomic orbital, the second order constant has medium-low values and spans a range not exceeding 10^3 . In other cases k_{II} can have very high values and the range is 10^8 or more. Examples of the latter behaviour are $\text{Fe}_2(\text{CO})_6\text{S}_2$ and $\text{Fe}_2(\text{CO})_6\text{Se}_2$ complexes and the previously reported $\text{Co}_2\text{FeS}(\text{CO})_9$ [14]. To explain the difference, we propose that in the latter cases the substrate can coordinate the ligand by means of an empty antibonding M.O., substantially metal in character. The delocalization of this orbital and its quite low energy could facilitate the attack of the ligand.

Strongly nucleophilic ligands, such as $\text{P}(\text{nC}_4\text{H}_9)_3$ and $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, show a second order dependence of the reaction rate on the ligand concentration. Among the mechanisms that might be considered, the most probable one can be an attack of the ligand on the intermediate, before it loses a molecule of

reaction mixture by TLC and characterised by infrared spectroscopy and elemental analysis; full details have been previously reported [2].

Kinetic Measurements

The reaction rates are very different and require different measurement techniques. The most part of them are slow enough to be followed by point-to-point measurement of the I.R. absorption of the highest CO stretching band of the parent complex (at 2083 cm^{-1} for $\text{Fe}_2(\text{CO})_6\text{S}_2$ and at 2077 cm^{-1} for $\text{Fe}_2(\text{CO})_6\text{Se}_2$). Fast reactions required continuous measurement of the absorbance of the solution at fixed wavelength in the visible region by common UV-visible spectroscopy or, in some cases, by a stopped-flow technique. 380 nm was in this case a suitable value, because the absorbance of the ligand is zero and that of the parent complex much greater than that of the reaction products. Details on the experimental techniques and on the treatment of the data are fully reported in a previous paper [14].

Apparatus

The following apparatus was used: IR Beckman 12 grating spectrophotometer; UV-visible Unicam SP 1700 spectrophotometer with Techne C 100 Circulator; Durrum-Gibson stopped-flow spectrophotometer.

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