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Chalcogen Derivatives of Iron Carbonyls. II. Carbon Monoxide Isotopic Exchange and Substitution Reactions with Ligands in $Fe_3(CO)_9X_2(X=S, Se, Te)$ Complexes*

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Kinetic results on the CO isotopic exchange and substitution reactions with ligands in $Fe_3(CO)_9X_2$ (X= S, Se, Te) complexes are reported. The reaction rates follow an S_N1 and/or S_N2 mechanism depending upon the electronegativity of X and the nucleophilicity of L. The values of k_1 are in agreement with the ν_{C-O} and are referred to a dissociation mechanism. An explanation in terms of electron distribution within the complex is proposed.

Introduction

The effect exercised on the CO-metal bond by substituents introduced into the complex molecule forms an interesting branch of the study of metal carbonyls, though the literature contains few examples of studies in this field. Wojcicki and Basolo[1] studied the effect of a halogen (Y) in $Mn(CO)_5Y$ complexes by means of CO exchange; Angelici and Basolo also studied CO substitution reactions with ligands[2] and the effect of L on $Mn(CO)_4LY$ substitute derivatives.[3] Studies of analogous Re complexes[4] and of $[M(CO)_4Y]_2$ dimers of both metals[5,6] have also been reported. The influence of the R group in CO-ligand substitution reactions was evaluated in a series of acyl[7] and allyl[8] derivatives of cobalt tetracarbonyl $RCo(CO)_4$ by Heck. The object of our investigations has been a series of acetylene derivatives of dicobalt octacarbonyls of the $Co_2(CO)_6C_2RR'$ type. We have already reported the interesting relationships between the nature of the R and R′ substituent groups and rates of CO exchange and CO substitution reactions[10] in these complexes.

Our more recent studies have been directed to chalcogen derivatives of ironcarbonyls with formula $Fe_3(CO)_9X_2$, and differences, due to the nature of the chalcogen atom, in their reactions with ligands have been shown.[11] The present study, therefore, investigates the kinetic behaviour of these complexes in exchange and carbonyl group substitution reactions.

Experimental Section

Compounds and Solvents. Methods described in the literature[12] were used in the preparation and purification of the $Fe_3(CO)_9X_2$ complexes; thin-layer chromatography, IR spectrophotometry and elementary analysis were used in purity control. Triphenylarsine was supplied by Alfa Inorganics and crystallized from petroleum ether; triphenylphosphite and tributylphosphine were obtained from the Fluka A.G. and K.&K. Laboratories respectively and were distilled at reduced pressure before use. For solvent, we used n-heptane, dried on sodium and distilled.

^{14}CO was supplied by the Amersham Radiochemical Centre and was diluted with high-purity inactive CO which had been previously dried on calcium chloride and silica gel columns. Argon and helium were subjected to the same treatment.

CO Isotopic Exchange Reactions. A previously described method[9] was used for the study of isotopic exchange reactions; some of these are very slow and it is preferable to exchange inactive CO with the previously labelled complex. During the reaction the compound stability was checked by means of thin-layer chromatography and IR spectra analysis. No decomposition was noted except in the case of the vials used at $t=\infty$ (values $<5\%$ in all cases). All experiments were carried out in the absence of light.

The solubility of CO in n-heptane at the vial filling temperature (25°) has already been reported;[13] determinations were made by us at other temperatures.

The equation of McKay[14] was followed in all the studied reactions and the linearity of $\ln(1-F)$ *versus* time was good. The exchange fraction F is given by A_o-A_t/A_o-A_∞, where A_o, A_t, and A_∞ are specific solution activities at $t=0$, $t=t$, and $t=\infty$ respectively. The value A_∞ corresponds to the exchange of

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(2) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

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(6) F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, *6*, 154 (1967).

(7) R. F. Heck, *J. Am. Chem. Soc.*, *85*, 651 (1963).

(8) R. F. Heck, *J. Am. Chem. Soc.*, *85*, 655 (1963).

(9) G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, *6*, 1225 (1967).

(10) G. Cetini, O. Gambino, P. L. Stanghellini, and R. Rossetti, Accad. Naz. del XL, vol. 18, Serie IV (1967).

(11) *J. Organometall. Chem.* in press.

(12) W. Hieber and J. Gruber, *Z. anorg. allg. Chem.*, *296*, 91 (1958).

(13) J. C. Gjaldbeck, *Acta Chem. Scand.*, *7*, 623 (1952).

(14) H. A. C. McKay, *Nature*, *142*, 997 (1938).

all 9 CO's, these being equivalent for all three complexes, and was determined experimentally in some cases and theoretically in others; good agreement between experimental and theoretical values was found on every occasion.

The least squares method was used to find the half-life for exchange ($t_{1/2}$) from the plot of ln(1–F) *vs.* time. From $t_{1/2}$, the exchange rate R and the specific rate constant k are estimated from

$$R = \frac{0.693}{t_{1/2}} \cdot \frac{n[Fe_3(CO)_9X_2][CO_t]}{n[Fe_3(CO)_9X_2]+[CO_t]} \qquad (1)$$

$$R = k[Fe_3(CO)_9X_2]^a[CO_d]^b \qquad (2)$$

where n is the number of exchangeable CO's, $[Fe_3(CO)_9X_2]$ is the molar concentration of the complex in solution, $[CO_d]$ and $[CO_t]$ are the molar concentrations of dissolved and total CO (solution+gas) (the total concentration being calculated as though all the CO was in solution) and a and b are the orders of the reaction, referred to the complex and the CO respectively.

Substitution Reactions. These reactions were investigated by measuring the decrease of the IR band of $Fe_3(CO)_9X_2$ complexes at the highest frequency in the CO stretching region. For this purpose, we used a Mod. IR 12 double beam spectrophotometer with NaCl optics (Beckmann). The following technique was employed. The required volume of complex and ligand in n-heptane solution was introduced[15] into glass vials fitted with a bubbling tube and a rubber cap, as already reported.[16] Air was expelled by slow bubbling of helium for about 10′ and the vial was then flame-sealed and placed in a constant temperature (±0.1°C) thermostat bath. A sample of the solution was syringed out via the rubber cap at intervals and examined by the IR technique.

Reactions with L do not go to completion unless a great excess of ligand is used (if the concentration of L is 1÷2 times that of the complex, reaction is about 50% complete). Equilibrium conditions could not be ascertained due to the uncertainty of CO concentration determinations. We therefore preferred pseudo first-order conditions and used a great excess of ligand (20 fold or more) in every case. On the other hand, vial volume was so great with respect to that of the solution that very little partial CO pressure was developed and the degree of inverse reaction was negligible.

The experimental data give satisfactory linear plots of $\ln(A_t-A_\infty)$ *vs.* time; the value for k_{obsd} was obtained from the best inclination of this line by the least squares method. In these calculations, A_t and A_∞ are the absorbancies at t=t and t=∞ respectively, the latter being taken as O for the reasons already given.

The reactions were followed for periods of about two half-lives. There were no signs of decomposition and the only products observed were the monosubstitute derivative (in the case of S and Se) and the «adduct» (in the case of Te). Analysis was carried out by means of thin-layer chromatography (absorbent: Kieselgel G according to Stahl; developer: 1:1 petroleum ether and CS_2). The separated products were indentified by comparing their IR spectra with those of derivatives prepared as already reported.[11]

The reaction of $Fe_3(CO)_9Te_2$ with triphenylarsine can only be followed for a short time, since it is very fast and is accompanied by interference between the «adduct» and the complex IR bands; this interference is only negligible at the start of the reaction when the bands of the «adduct» are of low intensity. Since in this brief period $A_t \simeq A_o$, the kinetic equation

Table I.[a] Rates of ^{14}CO exchange with $Fe_3(CO)_9X_2$ complexes in n-heptane

Complex	Compl. conc. m*M*	CO_d m*M*	CO_t mmoles	t°	$R\times10^9$	$k_1\times10^5$ sec^{-1}	$k_2\times10^3$ M^{-1} sec^{-1}
$Fe_3(CO)_9S_2$	1.564	7.5	0.987	50.0	6.33	0.405	0.539
	0.810	2.9	0.425	60.0	14.8	1.83	6.3
	1.564	6.0	0.972		27.7	1.77	3.0
	0.810	2.0	0.425	70.0	63.4	7.83	39
	1.577	4.0	0.861		133	8.45	21
$Fe_3(CO)_9Se_2$	0.787	2.9	0.419	60.0	2.89	0.367	1.27
	1.497	5.7	0.812		5.70	0.381	0.67
	0.787	2.0	0.419	70.0	11.6	1.48	7.4
	1.497	4.0	0.808		23.7	1.58	3.96
	0.792	1.5	0.429	77.4	37.0	4.68	31
	1.513	2.7	0.775		67.5	4.46	16.5
$Fe_3(CO)_9Te_2$	0.483	8.5	0.953	40.0	4.88	1.01	1.19
	1.474	8.8	0.907		15.0	1.02	1.16
	0.234	0.74	0.0833	50.0	0.831	0.355	4.80
	0.280	3.65	0.394		4.47	1.60	4.37
	0.490	7.4	0.944		15.0	3.05	4.11
	1.496	7.5	0.895		47.3	3.16	4.22
	0.280	2.9	0.394	60.0	8.96	3.20	11.0
	0.991	0.61	0.0848		6.93	0.699	11.5
	1.464	5.9	0.888		97.9	6.69	11.3

[a] For the meaning of R, CO_d, and CO_t, see Experimental Section.

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(15) If the reaction is too fast at room temperature, the ligand, or the prethermostated solution of the ligand in n-heptane, is introduced via the cap after the vial hase been placed in the thermostat.

(16) G. Cetini, O. Gambino, R. Rossetti, and E. Sappa, *J. Organometall. Chem.*, *8*, 149 (1967).

can be generally reduced to the form

$$\frac{A_o - A_t}{A_o} = k_{obsd}t$$

where A_o is the absorbance at $t=0$.

Results

Table I sets out the isotopic exchange rates for $Fe_3(CO)_9X_2$ complexes. The specific first (k_1) and second (k_2) order rate constants were calculated from equation (2) representing b as equal to 0 and 1 respectively. In the case of complexes with S and Se, it can readily be seen that k_2 values vary considerably in function of variations in CO concentration, whereas k_1 values are virtually constant; this is evidence of a first order rate of exchange. The position is reversed in the case of $Fe_3(CO)_9Te_2$ and it becomes obvious that exchange kinetics clearly depends on CO concentration.

The substitution reactions of the S and Se complexes are given by the equation:

$$Fe_3CO)_9X_2 + L \rightleftharpoons Fe_3(CO)_8LX_2 + CO$$

whereas $Fe_3(CO)_9Te_2$ acquires a molecule of the ligand:

$$Fe_3(CO)_9Te_2 + L \rightleftharpoons Fe_3(CO)_9LTe_2$$

Table II sets out the k_{obsd} values for these reactions in relation to the nature and concentration of the ligand. It will be noted that a simple first order law applies to the reaction of the S complex with $As(C_6H_5)_3$ and $P(OC_6H_5)_3$:

$$\text{rate} = k_1[\text{complex}]$$

whereas, in the case of tributylphosphine, there is a second order rate:

$$\text{rate} = k_2[\text{complex}][\text{ligand}]$$

For the Se complex, the rate of reaction with $As(C_6H_5)_3$ is once again independent of ligand concentration, whereas, in the case of $P(OC_6H_5)_3$, the reaction follows a two-term kinetic law of the type:

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{ligand}]$$

In the case of tributylphosphine, the reaction is so fast that the methods employed were inadequate for determination purposes and no values could be obtained: dependence of reaction rate on ligand concentration was noted, however. The Te complex could only be kinetically studied with $As(C_6H_5)_3$ since reactions with other ligand were too fast. A second order rate was observed and similar behaviour was qualitatively assessed in the case of $P(OC_6H_5)_3$ and $P(nC_4H_9)_3$.

Table III gives values for k_1 and k_2 relating to the kinetics of exchange and substitution; k_1 values are expressed as means of k_{obsd} and k_2 values are obtained

Table II. Pseudo first-order rate constants for reactions of $Fe_3(CO)_9X_2$ with ligands in n-heptane

Complex [a]	Ligand	Ligand Conc. *M*	t°	$k_{obsd} \times 10^5 sec^{-1}$
$Fe_3(CO)_9S_2$	$As(C_6H_5)_3$	0.0303	53.5°	0.637
		0.0403		0.617
		0.0509		0.637
		0.0599		0.651
		0.0180	60.0°	1.60
		0.0252		1.58
		0.0332		1.63
		0.0393		1.57
		0.0419		1.74
		0.0521		1.75
		0.0603		1.61
		0.0301	66.7°	5.04
		0.0404		4.83
		0.0510		4.71
		0.0602		4.81
	$P(OC_6H_5)_3$	0.0300	53.3°	0.619
		0.0398		0.608
		0.0503		0.637
		0.0300	60.0°	1.62
		0.0404		1.70
		0.0498		1.67
		0.0601		1.68
		0.0300	66.7°	4.96
		0.0398		5.02
		0.0503		4.86
		0.0601		4.85
	$P(nC_4H_9)_3$	0.0308	25.0°	1.86
		0.0417		3.34
		0.0517		3.64
		0.0617		5.11
		0.0308	32.0°	4.3
		0.0417		6.2
		0.0517		8.1
		0.0617		10.8
		0.0098	40.4°	1.50
		0.0147		3.2
		0.0302		9.1
		0.0416		13.7
		0.0517		20.0
		0.0617		22.7
$Fe_3(CO)_9Se_2$	$As(C_6H_5)_3$	0.0203	60.0°	0.394
		0.0314		0.337
		0.0413		0.400
		0.0516		0.380
		0.0601		0.355
		0.0353	70.0°	1.76
		0.0405		1.78
		0.0488		1.76
		0.0510		1.68
		0.0558		1.67
		0.0602		1.67
		0.0301	77.2°	4.71
		0.0402		5.02
		0.0508		4.48
		0.0599		4.56
	$P(OC_6H_5)_3$	0.0300	53.4°	0.967
		0.0404		1.26
		0.0498		1.57
		0.0601		1.78
		0.0300	60.0°	1.64
		0.0398		2.10
		0.0503		2.49
		0.0601		2.93
		0.0300	70.0°	3.97
		0.0404		4.58
		0.0498		5.37
		0.0601		6.00
$Fe_3(CO)_9Te_2$	$As(C_6H_5)_3$	0.0106	32.0°	2.1
		0.0160		3.1
		0.0201		3.5
		0.0225		4.4
		0.0261		5.5
		0.0302		5.6

[a] The complex concentrations are always 0.780 m*M*.

Table III. Specific reaction rates of CO isotopic exchange and substitution with ligands in $Fe_3(CO)_9X_2$ complexes in n-heptane

Complex	Ligand	t°	$k_1 \times 10^5$ sec^{-1}	$k_2 \times 10^3$ M^{-1} sec^{-1}
$Fe_3(CO)_9S_2$	CO	50.0	0.405±0.028	—
		60.0	1.80 ±0.04	—
		70.0	8.14 ±0.48	—
	$As(C_6H_5)_3$	53.5	0.636±0.014	—
		60.0	1.64 ±0.03	—
		66.7	4.84 ±0.13	—
	$P(OC_6H_5)_3$	53.3	0.621±0.020	—
		60.0	1.67 ±0.09	—
		66.7	4.92 ±0.08	—
	$P(nC_4H_9)_3$	25.0	—	1.00 ±0.11
		32.0	—	2.08 ±0.16
		40.4	—	4.22 ±0.18
$Fe_3(CO)_9Se_2$	CO	60.0	0.372±0.031	—
		70.0	1.53 ±0.07	—
		77.4	4.57 ±0.12	—
	$As(C_6H_5)_3$	60.0	0.373±0.011	—
		70.0	1.72 ±0.05	—
		77.2	4.69 ±0.19	—
	$P(OC_6H_5)_3$	53.4	0.16 ±0.08	0.275±0.017
		60.0	0.39 ±0.05	0.422±0.012
		70.0	1.9 ±0.15	0.689±0.033
$Fe_3(CO)_9Te_2$	CO	40.0	—	1.17 ±0.05
		50.0	—	4.14 ±0.16
		60.0	—	11.3 ±0.1
	$As(C_6H_5)_3$	32.0	—	1.9 ±0.1

Table IV. Activation parameters for CO isotopic exchange and substitution reactions with ligands in $Fe_3(CO)_9X_2$ complexes in n-heptane

Complex	Ligand	ΔH_1 kcal/mole	ΔH_2 kcal/mole	ΔS_1 e.u.	ΔS_2 e.u.
$Fe_3(CO)_9S_2$	CO	32.4±0.7	—	17.0±1.4	—
	$As(C_6H_5)_3$	33.2±1.5	—	19.1±2.6	—
	$P(OC_6H_5)_3$	33.3±1.4		19.4±2.4	—
	$P(nC_4H_9)_3$	—	16.9±0.9	—	−15.7±1.9
$Fe_3(CO)_9Se_2$	CO	32.6±0.6	—	14.4±1.0	—
	$As(C_6H_5)_3$	33.6±0.5	—	17.2±0.9	—
	$P(OC_6H_5)_3$	32 ±2	14 ±3.4	11.6±0.8	−39.5±1.4
$Fe_3(CO)_9Te_2$	CO		22.9±1.1		1.0±2.1

from the slope of the straight line given by the plot of k_{obsd} *vs.* [L]. For the reaction of $Fe_3(CO)_9Se_2$ with $P(OC_6H_5)_3$, k_1 represents the intercept and k_2 the slope of the line k_{obsd} *vs.* [L].

Table IV gives the activation enthalpy and entropy values determined from the data of Table III; the limits of error (as in Table III) are the standard deviation.

Discussion

Analysis of the data focusses attention on two kinetic phenomena in the reactions we examined: an S_N1 mechanism, probably linked to dissociation within the complex, and an S_N2 mechanism, which also involves the ligand directly. Both may be simultaneously present in all our reactions, but one or the other almost invariably prevails and experimental evaluation is thus impossible; except in the case of the Se complex and the phosphite, however, solely S_N1 or S_N2 reactions were obtained. Note should be taken, in any event, of the important kinetic variation associated with differences in the chalcogen atom bonded to the complex and the ligand employed. In the case of the S complex, CO exchange and arsine and phosphite substitution reactions display an S_N1 mechanism, whereas a second order phenomenon is observed in tributylphosphine substitutions. The behaviour of the Se complex is identical in isotopic exchange and arsine substitution reactions; with the phosphite, however, S_N2 reactions prevail and this is even more true in the case of tributylphosphine. S_N1 type reactions are not found with the tellurium complex, and only the S_N2 mechanism is clearly evident, even in the exchange reaction. The chances of S_N2 type kinetics therefore increase in the direction $CO < As(C_6H_5)_3 < P(OC_6H_5)_3 < P(nC_4H_9)_3$, whereas, for the same ligand, the pattern is S<Se<Te; the probability of occurrence of the dissociative mechanism S_N1 varies in the opposite order.

The structure of the examined complexes has already been reported [17].

The cluster Fe_3X_2 has a distorted tetragonal pyramid arrangement, in which each X atom is linked to all 3 iron atoms; the influence of the two X atoms is, however, equally shared over the metal atoms. Given its electronic affinity, X may exert an electron-attract-

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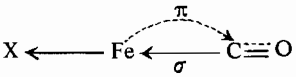
(17) L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, *2*, 1067 (1963); C. H. Wei and L. F. Dahl, *Inorg. Chem.*, *4*, 493 (1965).

ing power on Fe leading to an increased negative charge on X and the consequent increased positive charge on Fe. From this follows the reduced Fe→C π-back-donation and, in consequence, a decrease in the Fe–C and a corresponding increase in the C–O bond order. The following schema illustrates this phenomenon:



It is obvious that this phenomenon will be more pronounced the greater the electron-attracting power of X, with accompanying increases in the weakness of the Fe–CO and in the strength of the C–O bonds. The electronegativity value of X may be taken as the measure of this electron-attracting power and the literature indicates that it varies in the order S > Se > Te:[18] CO stretching frequencies vary in the same order and this is in agreement with the hypothesis already advanced. As can be seen in Figure 1, the linearity of these variations shows that the phenomenon is essentially due to an inductive effect of X on the sequence X–Fe–C–O.

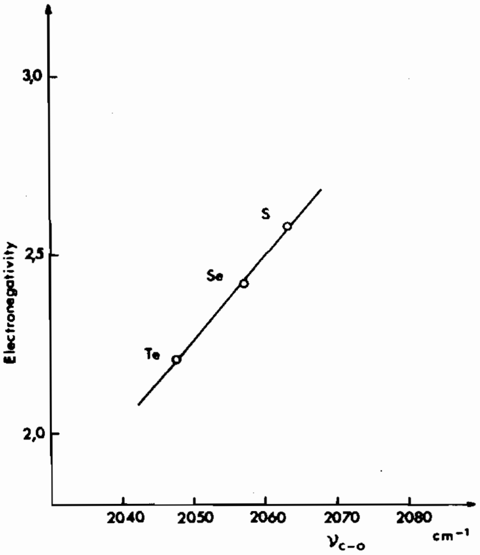


Figure 1. Chalcogen electronegativities *vs.* ν_{CO} in the $Fe_3(CO)_9X_2$ complexes. The values of the electronegativity are those from: H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 55, 745 (1955) (see ref. 18); the ν_{CO} are the highest CO stretching frequencies of each compound (the other frequencies follow, however, a similar relationship).

We may therefore suggest that the S_N1 mechanism requires the rupture of the Fe–CO bond as the rate determining step. From what has already been said, a specific rate constant k_1, varying in the order S > Se > Te, would in fact be expected. The observed data are in full agreement with this hypothesis, at least with respect to the first two elements; in the case of Te, we may assume that the S_N1 reaction rate is extremely low and therefore not experimentally observable in the presence of an S_N2 rate. Further evidence is supplied by the independence of the k_1 values with respect to the nature of the ligand (both for S and for Se), and the activation parameters; these give typically dissociative enthalpy and entropy values.

The second order mechanism may be explained on the hypothesis that ligand (or CO) attack on the complex is the rate-determining step. This would lead to the formation of an activated complex of the type $[Fe_3(CO)_9X_2L]^*$, followed by rapid re-arrangement and the expulsion of one CO:

$$\begin{gathered} Fe_3(CO)_9X_2 + L \overset{k_2}{\rightleftarrows} (Fe_3(CO)_9X_2L)^* \\ (Fe_3(CO)_9X_2L)^* \longrightarrow Fe_3(CO)_8LX_2 + CO \end{gathered} \tag{1a}$$

This mechanism is more probable in the case of the less electronegative Te than in that of S or Se and coordination of the entering ligand with an iron atom is unlikely. One would, in fact, expected that coordination would more readily occur in the case of the S complex, since the higher electron-attracting power of this element, as already explained, leads to greater increase of the positive charge on the metal atoms and makes them more suitable for the coordination of nucleophilic ligands. It is, however, more likely that, as suggested by us with respect to the structure of the $Fe_3(CO)_9LTe_2$ «adducts», coordination takes place on the chalcogen atom since this can function as a weak Lewis acid by means of the empty d orbitals in its outermost valency shell (5d for Te, 4d for Se, and 3d for S). The literature reports examples of nucleophilic coordinations of Te halides[19] and Se oxyhalides[20]; strongly nucleophilic reagent attacks on the sulphur atom of the sulphonic group have also been suggested.[21] This interpretation is in agreement with the experimental data since these indicate increasing S_N2 reaction facility in the order S < Se < Te. It is probable that an increase in the negative charge of the chalcogen atom destabilises the d orbitals and renders their interaction with the fully occupied orbitals of the ligand coordinating atom less likely.

The phenomenon can also be explained in terms of the «softness» or «hardness» of the chalcogen atom: Te, being softer, has a greater tendency to coordinate the soft bases used in our experiments than the relatively harder Se and S.

It is also clear that, as has been shown experimentally, coordination occurs more readily with increase in ligand basicity. With ligands whose basic properties are very small (*e.g.* CO and $As(C_6H_5)_3$), coordination is very unlikely and a dissociative mechanism is involved; increases in basicity (phosphite) increase the chances of coordination and, with strongly basic ligands (tributylphosphine), coordination prevails over dissociation. From the data, we suppose that $As(C_6H_5)_3$ is less basic than $P(OC_6H_5)_3$. This is not an arbitrary hypothesis, even if $As(C_6H_5)_3$ has lower

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[18] See, for example. A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, *5*, 264 (1958) and references therein.

[19] See ref. 11 and references therein.

[20] A. W. Cordes and T. V. Hughes, *Inorg. Chem.*, 3, 1640 (1964).

[21] J. F. Bunnett and J. Y. Bassett, *J. Am. Chem. Soc.*, *81*, 2104 (1959); F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Am. Chem. Soc.*, 73, 5004 (1951).

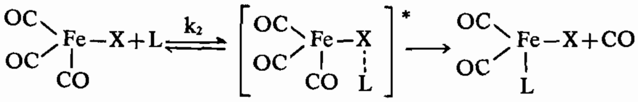
π-bonding ability and, in consequence, must have a higher σ-bonding ability than $P(OC_6H_5)_3$ (it is known that the qualitative order of various ligands in their ability to function as π-acceptors is about the reverse of the order as σ-donors[22]). Actually, arsines are often «poorer» reagents than phosphines or phosphites; this is possibly due to the nature of the substrate metal which, if it is of the b[23] or soft[24] class, forms complexes whose stability varies with the donor ligand atom in the order $N \ll P > As > Sb$. A similar interpretation has been given by Thorsteinson and Basolo.[25] These authors reported a kinetic behaviour of substitution reactions on $Co(CO)_3NO$, with various ligands, that had many features in common with that observed by us.

It may be noted, lastly, that the scheme (Ia) for the S_N2 mechanism is not valid for reactions with the Te complex; here, the mechanism can be indicated by the more complicated scheme:

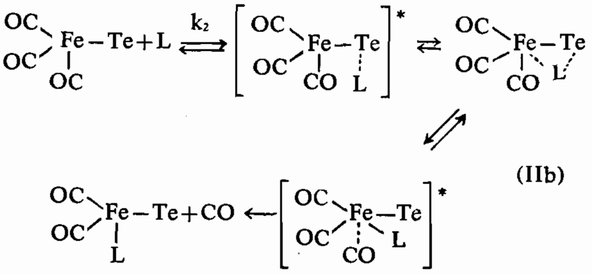
$$\begin{aligned}
&Fe_3(CO)_9Te_2 + L \overset{k_2}{\rightleftharpoons} (Fe_3(CO)_9Te_2 \ldots L)^* \\
&(Fe_3(CO)_9Te_2 \ldots L)^* \rightleftharpoons Fe_3(CO)_9LTe_2 \\
&Fe_3(CO)_9LTe_2 \rightleftharpoons (CO \ldots Fe_3(CO)_8LTe_2)^* \\
&(CO \ldots Fe_3(CO)_8LTe_2)^* \rightarrow Fe_3(CO)_8LTe_2 + CO
\end{aligned} \tag{Ib}$$

which implies the presence of an addition product («adduct») that, in this case, displays a certain degree of stability.

From the structural point of view, (Ia) and (Ib) can be set out in the following way (for the sake of simplicity, only the part of the molecule involved in the phenomenon is dealt with):



(IIa)



(IIb)

(II a) relates to reactions with S and Se and needs no further explanation. (IIb), on the other hand, is concerned with reactions involving the Te complex. These presuppose labile coordination of L to one Te atom (or both atoms), followed by internal rearrangement of the activated complex and the displacement of L on to an adjacent (basal) Fe atom; this would thus be seven-coordinated like the apical Fe atom (the ligand may, however, be in a bridge position between Fe and Te). As reaction progresses, labilisation of a Fe–CO bond takes place in the «adduct» molecule (unstable on account of steric hindrance of the ligand), followed by final rearrangement and the formation of the monosubstituted derivative.

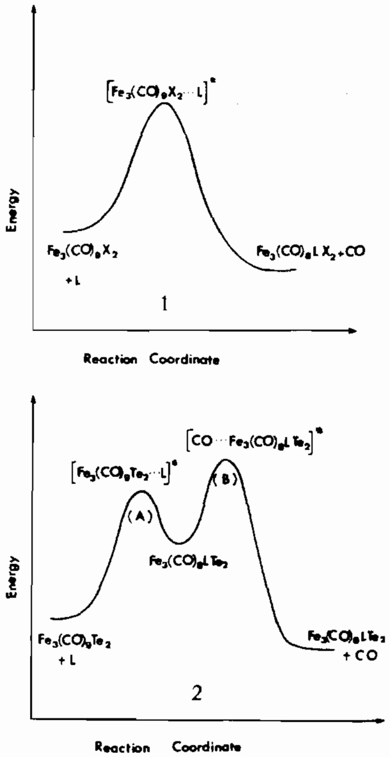


Figure 2. Reaction profile (arbitrary scale) for S_N2 mechanism in the substitution reactions. (1) With S and Se complexes. (2) With Te complex, which involves an unstable «adduct» intermediate.

The two processes can be represented by means of the reaction profiles plotted in Figure 2. Profile 1 refers to S_N2 type reactions for S and Se complexes; profile 2 refers to $Fe_3(CO)_9Te_2$ reactions. The two peaks (A and B) correspond to the two activated complexes and the valley represents the «adduct». The height of the two maxima with respect to the position of the «adduct» is not known and naturally varies from ligand to ligand. On the basis of existing knowledge concerning transformation reactions by which the «adduct» is converted to the start complex or to the monosubstitute,[11] we may conclude that B is certainly higher than A when $As(C_6H_5)_3$ and $P(OC_6H_5)_3$ are the ligands; with tributylphosphine, the two peaks should be of about equal height.

We may also point out, easily, that the (IIa) and (IIb) mechanisms are substantially the same, apart from some non detectable intermediate stages in the former. It follows, therefore, that profile 1 of Figure 2 can be treated as a variant of profile 2; the height of B is much less than that of A and can be ignored for practical purposes.

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[22] W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, *2*, 723 (1963).

[23] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), *12*, 265 (1958).

[24] R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 3533 (1963).

[25] E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, *88*, 3929 (1966).