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Chalcogen Derivatives of Iron Carbonyls. V. Kinetics and Mechanism of CO Exchange and of Substitution Reactions of $Fe_3(CO)_9XY$ Complexes (X and Y = S, Se, Te with X ≠ Y)[1]

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$Fe_3(CO)_9XY$ complexes undergo carbonyl substitution with triphenylarsine and triphenylphosphite to give the mono- and di-substituted derivatives, $Fe_3(CO)_8LXY$ and $Fe_3(CO)_7L_2XY$. The preparation and spectra of these compounds are reported. The substitution reactions and the CO exchange reaction proceed according to the two term rate law: rate = k_1[complex] + k_2[complex][ligand], in which the relative values of k_1 and k_2 depend on the nature of X, Y, and L. The results are in agreement with the reactivity of the $Fe_3(CO)_9X_2$ complexes.

Introduction

Several kinetic studies have been made of the CO exchange and of substitution reactions with ligands on metal carbonyls and their derivatives.[2] It has been found that the more common kinetic process is a dissociative mechanism although there are some examples in which a bimolecular associative mechanism is predominant. In a previous work[3] we have reported that in some chalcogen derivatives of iron carbonyls, $Fe_3(CO)_9X_2$, the kinetic mechanism strictly depends on the nature of the chalcogen atom X: the lower is the electronegativity of the X atoms, the greater is the probability of an S_N2 reaction with respect to an S_N1 reaction.

Recently we have prepared the new complexes $Fe_3(CO)_9XY$, in which X and Y are different chalcogen atoms.[1] In order to examine thoroughly the influence of the chalcogen atoms on the substrate reactivity we have investigated the reaction of these complexes with various ligands. The purpose of this paper is to present the results of this study.

Experimental Section

Compounds and Solvents. The solvents used were purified by distillation and carefully dried. $Fe(CO)_5$ (Fluka AG) was reagent grade and was used without further purification. $As(C_6H_5)_3$ (Aldrich) was recrystallized from n-heptane, $P(OC_6H_5)_3$ (Fluka AG) was distilled at reduced pressure. N_2, argon and CO were dried on $CaCl_2$ and silicagel columns before the use: ^{14}CO, purchased from Amersham Radiochemical Centre at high specific activity, was diluted with inactive CO.

The complexes $Fe_3(CO)_9SSe$, $Fe_3(CO)_9STe$, and $Fe_3(CO)_9SeTe$ were prepared by reacting at 0°C $Fe(CO)_5$ in alkaline methanol solution with one equimolar mixture of sodium sulfite and selenite, sodium sulfite and tellurite, sodium selenite and tellurite respectively. After acidification, the precipitate was collected, carefully dried and extracted with petroleum ether. The solution was subtimed to the thin-layer cromatography and finally the complex was crystallized from n-heptane. More detailed data on these preparations were previously reported.[1]

Preparation of the Substitution Products. All the preparations of these compounds were carried out using anhydrous solvents and under nitrogen with the careful exclusion of oxigen. However, owing to their stability on air they were chromatographed and isolated with no further precautions. Yields for the monosubstituted derivatives were about 50%, for the disubstituted derivatives about 20%. The separation from the unreacted starting complex and the excess of the ligand was generally accomplished by means of the thin-layer chromatography (TLC) with silicagel type G according to Stahl as adsorbent and various solvents, or solvent mixtures, as developers (the compounds moved always in the order: starting complex, monosubstituted, disubstituted). Repeated TLC separation and crystallisation were often necessary to remove the residual traces of the ligand. The large excess of the ligand was used to increasing the yield of the products.

$Fe_3(CO)_8As(C_6H_5)_3SSe$ A reaction mixture containing 1.40 g of $Fe_3(CO)_9SSe$ (2.6 mmoles) and 9.2 g of $As(C_6H_5)_3$(30 mmoles) in 100 ml of n-heptane was allowed to stand at 60° for 2 days. The derivative $Fe_3(CO)_8As(C_6H_5)_3SSe$ was separed from the unreacted $Fe_3(CO)_9SSe$ by means of TLC and recrystallized from n-heptane.

$Fe_3(CO)_8As(C_6H_5)_3SeTe$. From a similar experiment to that described above $Fe_3(CO)_8As(C_5H_5)_3SeTe$

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was obtained in black crystals from 1.32 g. of $Fe_3(CO)_9SeTe$ (2.1 mmoles) and 7.65 g. of $As(C_6H_5)_3$ (25 mmoles). The reaction was carried out in n-heptane solution at 60° for 10 hr.

$Fe_3(CO)_8As(C_6H_5)_3STe$ and $Fe_3(CO)_7[As(C_6H_5)_3]_2STe$. $Fe_3(CO)_9STe$ (3.2 g. 5.5 mmoles) and $As(C_6H_5)_3$ (18.4 g. 60 mmoles) was allowed to react in n-heptane solution at 60° for 50 hr. The solution was chromatographed on TLC (eluent: petroleum ether with 5% ethyl ether) and two greenish-brown bands were separed and collected. After crystallisation they gave pure brown microcrystalline powder of $Fe_3(CO)_8As(C_6H_5)_3STe$ and $Fe_3(CO)_7[As(C_6H_5)_3]_2STe$, respectively.

$Fe_3(CO)_8P(OC_6H_5)_3SSe$ and $Fe_3(CO)_7[P(OC_6H_5)_3]SSe$. $Fe_3(CO)_9SSe$ (2.3 g. 4.3 mmoles) and $P(OC_6H_5)_3$) (11 ml ~ 41 mmoles) were refluxed for 15 hr in 400 ml of petroleum ether. The separation of the reaction mixture by means of TLC (eluent: petroleum ether with 5% of ethyl ether) gave two sharp red–brown bands. After the solvent evaporation at reduced pressure we obtained from the first $Fe_3(CO)_8P(OC_6H_5)_3SSe$ as a red–brown air sensitive viscous liquid, and from the second an amorphous red–brown solid, which was identified as $Fe_3(CO)_7[P(OC_6H_5)_3]_2SSe$.

$Fe_3(CO)_8P(OC_6H_5)_3STe$ and $Fe_3(CO)_7[P(OC_6H_5)_3]_2STe$. 1.97 g. of $Fe_3(CO)_9STe$ (3.4 mmoles) dissolved in n-heptane were reacted with 11 ml of $P(OC_6H_5)_3$ (~ 41 mmoles) for 2 days at 60°. Chromatographic separation showed, besides the starting complex, two red–brown bands, which, after further purification, gave $Fe_3(CO)_8P(OC_6H_5)_3STe$ and $Fe_3(CO)_7[P(OC_6H_5)_3]_2STe$ both as red–brown viscous liquids.

$Fe_3(CO)_8P(OC_6H_5)_3SeTe$ and $Fe_3(CO)_7[P(OC_6H_5)_3]_2SeTe$. A reaction mixture containing g. 1.65 of $Fe_3(CO)_9SeTe$ (2.6 mmoles) and 8.0 ml of $P(OC_6H_5)_3$ (~ 30 mmoles) in 300 ml of petroleum ether was allowed to stand at 40°. The initial formation of a red–orange complex was detected by TLC, but this compound (a "1:1 adduct"? see Ref. 4) was too unstable to be isolated and identified. After 20 hr two compounds were separated by TLC and collected after the solvent evaporation: the mono– and di–substituted derivatives, as a red–brown liquid and an amorphous brown solid, respectively.

Colors, melting points and analytical data are given in Table I. The molecular weights were determined in benzene solution, using a Hewlett–Packard Mod. 302 Mechrolab osmometer; the melting points, by means of a Leitz Mod. 350 heating plate. The elemental analyses were performed by a Mod. 185 C, H and N analyser (F and M Scientific Co). and by a Perkin–Elmer Mod. 303 atomic absorption spectrophotometer with DCR1.

The carbonyl stretching frequencies are given in Table II. The spectra were recorded in CCl_4 solution, using a Beckman IR 12 double beam infrared spectrophotometer, with KBr optics.

Kinetic studies. All the reactions were carried out in n–heptane solution and in absence of the light.

The rate of the substitution reactions were determined by following the disappearance of the highest frequency CO stretching absorption of the substrate: the infrared spectra were compared with that of a reference solution containing no metal complex. There is no interference between the absorption band of the starting complex and those of the monosubstituted products because of the difference of the frequency values (more than 10 cm^{-1}).

The reactions were carried out in a nitrogen filled ampoules, similar to that already illustrated[5], kept in a constant temperature baths (± 0.1 C°). Samples of the solution were periodically withdrawn with a syringe thorough the rubber cap and transferred to a 0.8 mm KBr cell. Good linear plots were obtained from the data by plotting $\ln(A/A_o)$ *vs.* time, where A is the absorbance at the time t and A_o the absorbance

Table I. Analytical data.

Compound	Isolated as	M.P.	Elemental analysis [a] C	 H	 Fe	Mol. Weight [a]
$Fe_3(CO)_8As(C_6H_5)_3SSe$	greenish-brown cryst.	dec.	38.4 (38.61)	1.95 (1.87)	21.0 (20.71)	822 (808.8)
$Fe_3(CO)_8As(C_6H_5)_3STe$	brown microcrystals	140°	36.2 (36.42)	1.70 (1.76)	19.1 (19.54)	840 (857.5)
$Fe_3(CO)_7[As(C_6H_5)_3]_2STe$	brown microcrystals	160° dec.	45.8 (45.48)	2.80 (2.66)	14.4 (14.75)	1050 (1135.7)
$Fe_3(CO)_8As(C_6H_5)_3SeTe$	black crystals	dec.	34.5 (34.53)	1.77 (1.67)	18.3 (18.52)	889 (904.4)
$Fe_3(CO)_8P(OC_6H_5)_3SSe$	red brown liquid	—	38.6 (38.41)	1.95 (1.86)	21.1 (20.61)	844 (812.9)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2SSe$	amorph. red brown solid	dec.	48.1 (47.16)	2.84 (2.76)	15.4 (15.30)	— (1095.2)
$Fe_3(CO)_8P(OC_5H_5)_3STe$	red brown liquid	—	33.0 (32.25)	1.58 (1.75)	19.0 (19.44)	822 (861.6)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2STe$	red brown liquid	—	45.8 (45.15)	2.78 (2.64)	14.9 (14.65)	— (1143.9)
$Fe_3(CO)_8P(OC_6H_5)_3SeTe$	red brown liquid	—	34.1 (34.37)	1.92 (1.66)	18.3 (18.44)	875 (908.5)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2SeTe$	amorph. brown solid	45°	43.3 (43.37)	2.64 (2.54)	14.2 (14.07)	— (1190.8)

[a] in parenthesis the calculated values.

Table II. Carbonyl stretching frequencies (CCl_4 solution).

Compound	IR (cm^{-1}) [a]
$Fe_3(CO)_8As(C_6H_5)_3SSe$	2079 (w) 2070 (s) 2040 (m) 2030 (s) ~2009 (s) ~2005 (s) 1977 (m sh) ~1959 (w sh)
$Fe_3(CO)_8As(C_6H_5)_3STe$	2065 (s) 2027 (s) 2005 (s br) 1975 (m sh) 1950 (w sh)
$Fe_3(CO)_7[As(C_6H_5)_3]_2STe$	2049 (w) 2036 (m) 2031 (m) 1998 (s) 1990 (s) 1974 (m) 1943 (m)
$Fe_3(CO)_8As(C_6H_5)_3SeTe$	2077 (w) 2067 (s) 2038 (m) 2027 (s) 2005 (s br) ~1977 (m sh) ~1955 (w sh)
$Fe_3(CO)_8P(OC_6H_5)_3SSe$	2074 (s) 2049 (m) 2035 (vs) 2022 (m) 2010 (s) ~1990 (m sh)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2SSe$	2058 (m) 2051 (s) 2020 (vs) 1999 (s) 1991 (s)
$Fe_3(CO)_8P(OC_6H_5)_3STe$	2069 (s) 2044 (m) 2032 (vs) 2017 (m) 2003 (s) ~1989 (m sh)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2STe$	2052 (m sh) 2047 (s) 2010 (vs) ~1996 (s br) ~1985 (s br)
$Fe_3(CO)_8P(OC_6H_5)_3SeTe$	2065 (s) 2041 (m) 2027 (vs) 2013 (m) 2001 (s) ~1985 (m sh)
$Fe_3(CO)_7[P(OC_6H_5)_3]_2SeTe$	2048 (m sh) 2043 (s) 2008 (vs) ~1998 (s br) ~ 1982 (s br)

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

at the beginning of the reaction. All the kinetic studies were carried out under pseudo–first–order conditions, using at least a tenfold excess of the ligand: so all reactions proceeded to completion. Plots of $\ln(A/A_o)$ *vs.* time yielded pseudo–first–order rate constants k_{obsd}: its standard deviation was about 5%.

The method used to investigate the rate of CO isotopic exchange with $Fe_3(CO)_9XY$ was similar to that described earlier[6]. We preferred to exchange the inactive gaseous CO with previously labelled complexes because of the slowness of the reaction rates. All the exchange reactions investigated were found to follow the Mc Kay equation[7] and give satisfactory linear plots of $\ln(1 - F)$ *vs.* time, were F is the exchange fraction. From these plots the half–lives for exchange were determined and used to estimate the values of k_{obsd}: the mathematical treatment of the data are previously reported[3]. The experimental infinite–time activities were in good agreement with the calculated values based on the exchange of all the CO molecules in the compounds.

The solubility of CO in n–heptane at room temperature was known[8]; at other temperatures were determined by us and already reported[9]. The complexes are stable in solution during the exchange studies: the IR spectra of the solution compared with that of a freshly prepared solution at same concentration show no decomposition at all.

Results and Discussion

The derivative complexes are deeply coloured substances, air–sensitive as liquids or in solution, stable as solids. They are insoluble in water, soluble in organic solvents, especially ethyl ether, benzene, CS_2. The data of Table II shown the absence of carbonyl bands in the 1700-1850 cm^{-1} region of the IR spectrum, which indicates the absence of carbonyl bridging groups. It is of interest that the shift of the CO stretching bands are to lower energy or smaller wave numbers as one go from $Fe_3(CO)_8LXY$ to $Fe_3(CO)_7L_2XY$. This is in accord with L being a better σ donor and poorer π acceptor than CO[10]. The triphenylarsine which is poorer π bonder than triphenylphosphite shows generally larger shifts to lower energy than the phosphite. A similar trend is noted by changing the chalcogen atoms from S, to Se, to Te, i.e. by lowering their electronegativities. All these effects put more electron density on the metal atoms, which is then delocalized into the antibonding orbitals of the CO groups. This lowers the $C{\equiv}O$ bond order and, in consequence, the values of the CO stretching frequencies. The same effect was previously noted about derivatives of the $Fe_3(CO)_9X_2$ complexes[4].

The $Fe_3(CO)_8LXY$ and the $Fe_3(CO)_7L_2XY$ complexes should present more than one isomeric form. On the basis of the proposed kinetic mechanism (see later) is probable that in the monosubstituted complexes L is coordinated on an Fe atom adjacent to the chalcogen atoms and in the disubstitude complexes the two L molecules are coordinated on the two different Fe atoms, because of their steric hindrance. However, it can not be excluded that two or more isomers are present as a result of the ligand exchange between the iron atoms in the complex, so that it is impossible to drawn a definite conclusion about this problem.

The complexes $Fe_3(CO)_9XY$ react with such ligands as $As(C_6H_5)_3$ and $P(OC_6H_5)_3$ according to the equation:

$$Fe_3(CO)_9XY + L \rightleftarrows Fe_3(CO)_8LXY + CO \qquad (1)$$

Afterwords, a second substitution takes place:

$$Fe(CO)_8LXY + L \rightleftarrows Fe_3(CO)_7L_2XY + CO$$

Further substitution can occur, perhaps, but probably, in so drastic reaction conditions to cause the almost total demolition of the complexes. Pseudo–first–order rate constant (k_{obsd}) for reaction 1 as obtained at various ligand concentrations, together with those for the CO isotopic exchange reactions, are reported in Table III. The data easily show that the rates of the reactions between $Fe_3(CO)_9SSe$ and $Fe_3(CO)_9STe$ with CO or $As(C_6H_5)_3$ obey a first–order rate law:

$$\text{rate} = k_1[\text{complex}] \qquad (2)$$

whereas the rates of the reactions of both complexes with $P(OC_6H_5)_3$ follow the two–term rate law:

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{ligand}] \qquad (3)$$

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Table III. Pseudo-first-order rate constants for reactions of the $Fe_3(CO)_9XY$ complexes in n-heptane.

Compound	Ligand	t° C	Compl. conc. m*M*	Lig. conc. m*M*	$k_{obsd} . 10^{-5}$ sec^{-1}
$Fe_3(CO)_9SSe$	CO	60.0	0.435	6.24	0.787
			0.786	4.56	0.830
			1.030	3.40	0.868
			1.370	1.68	0.850
		65.0	0.435	5.30	1.75
			0.786	3.90	1.68
			1.030	2.90	1.99
			1.370	1.43	1.78
		70.0	0.463	4.48	3.68
			0.825	3.23	3.73
			0.961	2.47	3.56
			1.365	1.14	3.85
	$As(C_6H_5)_3$	60.0	0.787	10.1	0.889
				20.3	0.857
				30.2	0.808
				40.1	0.856
				50.2	0.848
	$P(OC_6H_5)_3$	60.0	0.778	10.1	0.631
				20.0	0.710
				30.0	0.827
				40.0	0.880
				50.0	0.922
$Fe_3(CO)_9STe$	CO	60.0	0.433	6.10	0.789
			0.790	4.65	0.708
			1.036	3.41	0.695
			1.081	1.64	0.714
		65.0	0.432	5.39	1.62
			0.725	4.00	1.69
			1.028	2.89	1.56
			1.310	1.36	1.65
		70.0	0.432	4.52	3.13
			0.725	3.33	3.14
			1.028	2.41	2.98
			1.315	1.14	3.41
	$As(C_6H_5)_3$	60.0	0.774	10.2	0.767
				15.0	0.783
				20.3	0.733
				30.0	0.784
				40.5	0.774
				45.2	0.753
	$P(OC_6H_5)_3$	60.0	0.780	10.0	1.27
				20.0	1.47
				30.1	2.13
				40.1	2.36
				50.1	2.94
$Fe_3(CO)_9SeTe$	CO	60.0	0.433	6.31	0.715
			0.747	4.58	0.624
			1.003	3.30	0.491
			1.338	1.67	0.430
		65.0	0.413	5.26	1.31
			0.735	4.00	1.11
			1.026	2.86	1.02
			1.230	1.37	0.804
		70.0	0.413	4.41	2.25
			0.735	3.35	2.02
			1.026	2.36	1.86
			1.230	1.15	1.61
	$As(C_6H_5)_3$	60.0	0.781	10.0	0.554
				20.0	0.760
				30.0	0.950
				40.0	1.18
				50.0	1.34
	$P(OC_6H_5)_3$	32.0	0.780	10.3	0.726
				20.0	1.71
				30.0	2.19
				40.0	2.63
				50.0	3.55

$Fe_3(CO_9SeTe$ reacts with CO and $As(C_6H_5)_3$ according to eq. (3) and with $P(OC_6H_5)_3$ according to a second–order rate law:

$$\text{rate}=k_2[\text{complex}][\text{ligand}] \qquad (4)$$

Table IV shows the values of k_1 and k_2. The first–and second–order rate constants were determined from linear plots of k_{obsd} *vs.* the concentration of the ligand. The first–order rate constants were deter-

Table IV. Specific rate constants of CO isotopic exchange and substitution with ligands of $Fe_3(CO)_9XY$ complexes in n-heptane.

Complex	Ligand	t°C	$k_1 \cdot 10^5$ sec^{-1}	$k_2 \cdot 10^3$ M^{-1} sec^{-1}
$Fe_3(CO)_9SSe$	CO	60.0	0.834 ± 0.035	—
		65.0	1.80 ± 0.13	—
		70.0	3.71 ± 0.12	—
	$As(C_6H_5)_3$	60.0	0.852 ± 0.029	—
	$P(OC_6H_5)_3$	60.0	0.57 ± 0.03	0.075 ± 0.010
$Fe_3(CO)_9STe$	CO	60.0	0.726 ± 0.042	—
		65.0	1.63 ± 0.05	—
		70.0	3.16 ± 0.18	—
	$As(C_6H_5)_3$	60.0	0.77 ± 0.02	—
	$P(OC_6H_5)_3$	60.0	0.77 ± 0.17	0.42 ± 0.05
$Fe_3(CO)_9SeTe$	CO	60.0	0.31 ± 0.05	0.65 ± 0.11
		65.0	0.64 ± 0.05	1.26 ± 0.14
		70.0	1.39 ± 0.03	1.93 ± 0.10
	$As(C_6H_5)_3$	60.0	0.36 ± 0.02	0.20 ± 0.07
	$P(OC_6H_5)_3$	32.0	—	0.66 ± 0.07

Table V. Order of the reactions of the $Fe_3(CO)_9X_2$[a] and $Fe_3(CO)_9XY$ complexes.

Complex	Ligand CO	$As(C_6H_5)_3$	$P(OC_6H_5)_3$	$P(nC_4H_9)_3$
$Fe_3(CO)_9S_2$	I	I	I	II
$Fe_3(CO)_9SSe$	I	I	I+II	
$Fe_3(CO)_9STe$	I	I	I+II	
$Fe_3(CO)_9Se_2$	I	I	I+II	
$Fe_3(CO)_9SeTe$	I+II	I+II	II	
$Fe_3(CO)_9Te_2$	II	II	II	II

[a] from Ref. 3.

mined from the zero ligand concentration intercept of the best line, the second–order rate constants from its slope. In the case of the first–order reactions (eq. 2), the values of k_1 were determined as mean of the k_{obsd} values. The error is always the standard deviation.

The linear trend of k_{obsd} vs. [L] suggests a kinetic mechanism, generally represented by eq. (3), involving a competitive first and second order processes with relative weight variable, according to the type of complex and of ligand. The orders of the reactions are summarized in Table V, including those for the $Fe_3(CO)_9X_2$ reactions. It can be noted that the rate of the reactions involving poor reagents generally shows no dependence on the reagent concentrations: i.e. the second order term of eq. (3) becomes inoperative and poor reagents show only first order kinetics. Whereas, with the better reagents the second order term is of over-riding importance and the first order term is too small in comparison to be obtained experimentally.

More interesting is the behaviour of the complexes by changing the chalcogen atoms. As their electronegativities decrease from S (2.58), to Se (2.42), to Te (2.21), decreases also the probability of the first-order process and increases the probability of the second-order process. The relative values of k_1 for the CO exchange reaction are for example: 10 for $Fe_3(CO)_9S_2$; 4.6 for $Fe_3(CO)_9SSe$; 4.0 for $Fe_3(CO)_9STe$; 2.0 for $Fe_3(CO)_9Se_2$; 1.7 for $Fe_3(CO)_9SeTe$ and zero for $Fe_3(CO)_9Te_2$, whereas those of k_2 for the same reaction are 10 for $Fe_3(CO)_9Te_2$; 0.57 for $Fe_3(CO)_9SeTe$ and zero for the other ones.

The probable reaction scheme for the first- and second-order terms of eq. (3) are the following:

$$Fe_3(CO)_9XY \overset{k_1}{\rightleftarrows} Fe_3(CO)_8XY^* + CO$$

$$Fe_3(CO)_8XY^* + L \xrightarrow{\text{fast}} Fe_3(CO)_8LXY \qquad \text{I}$$

$$Fe_3(CO)_9XY + L \overset{k_2}{\rightleftarrows} Fe_3(CO)_9LXY^*$$

$$Fe_3(CO)_9LXY \xrightarrow{\text{fast}} Fe_3(CO)_8LXY + CO \qquad \text{II}$$

The first-order term for the reaction (1) and for the CO exchange reaction is consistent with a mechanism involving rate-determining dissociation of a CO group. The values of the activation enthalpy and entropy (Table VI) support a dissociative mechanism. In this case one could take the relative rates given before as a rough measure of the Fe–CO bond strenght. This is in agreement with the rise in frequency of the highest energy carbonyl stretching band which varies in the order $Te_2 < SeTe < Se_2 \leqslant STe < SSe < S_2$.[1]

Table VI. Activation parameters for CO isotopic exchange reaction of the $Fe_3(CO)_9XY$ complexes in n-heptane.

Complex		ΔH*, Kcal/mole	ΔS*, e.u.
$Fe_3(CO)_9SSe$		33.1 ± 0.7	18 ± 1
$Fe_3(CO)_9STe$		32.7 ± 3.2	16 ± 5
$Fe_3(CO)_9SeTe$	1st ord.	33.4 ± 2.1	17 ± 4
	2nd ord.	24.2 ± 5.8	−1 ± 10

The second-order term is represented by a mechanism involving a direct coordination of the ligand on the complex as the rate-determining step. The activation parameters for the CO exchange reaction of $Fe_3(CO_9SeTe$ are in the experimentally observed limits for nucleophilic substitution on complexes.[2]

The present results confirm the previous hypothesis about the ligand coordination on the chalcogen atoms rather than on the metal atoms. The increasing electronegativity of the chalcogen atoms increases the positive charge on the iron atom and should favour the nucleophilic attack of the ligand, whereas the experimental data show the opposite effect. It seems reasonable to interpret this in terms of ligand coordination on the chalcogen atoms: the lower is the electronegativity of the X and Y atoms, the greater is the probability of a nucleophilic coordination on these. It is in accord with the «hardness» and the «softness» of the Lewis acids and bases.[11] The greater «softness» of the Te atoms may facilitate attack of the « shoft » bases as $P(OC_6H_5)_3$ or $As(C_6H_5)_3$, than the relatively « harder » Se and especially S atoms could do.

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(11) R.G. Pearson, *J. Am. Chem. Soc.*, *85*, 3533 (1963).