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CHALCOGEN DERIVATIVES OF IRON CARBONYLS
I. SUBSTITUTED DERIVATIVES OF $Fe_3(CO)_9X_2$ COMPLEXES (X=S, Se, Te) WITH LIGANDS

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SUMMARY

Series of mono- and disubstituted derivatives of $Fe_3(CO)_9X_2$ complexes (X = S, Se, Te) with ligands are prepared. Different reactions are found with the Te compound, which also gives additional derivatives. An explanation is proposed, referred to the difference in electron attracting power of the chalcogen atoms. Also the preparations, the properties and the main infrared absorption frequencies of the new compounds are reported.

INTRODUCTION

Derivatives of iron carbonyls containing chalcogen atoms are principally found in two forms: binuclear, of the type $Fe_2(CO)_6X_2R_2$ (where X=S, or Se and R is an alkylic or arylic group); trinuclear, of the type $Fe_3(CO)_9X_2$ (where X=S, Se, Te). Both types of compounds were found by Hieber *et al.*[1] when they reacted iron carbonyl anions ($Fe(CO)_4''$, $Fe_2(CO)_8''$, $Fe_3(CO)_{11}''$) with organic disulphides and diselenides or alkaline sulphites, selenites, and tellurites, respectively.

King[2] has prepared $Fe_3(CO)_9S_2$ itself by means of the reaction of triirondodecacarbonyl with cyclohexene sulphide. It has also been found that, in these binuclear derivatives, some ligands may substitute one or, in more drastic conditions, even two CO groups[3].

We therefore decided to investigate reactions of the trinuclear derivatives $Fe_3(CO)_9X_2$ with some phosphine and arsine type ligands. The object of our research was to evaluate the effect that chalcogen atoms have on CO–metal bonds, the present work thus being a continuation of similar studies on $Co_2(CO)_6C_2RR'$ type complexes and the effect of the R and R′ groups on the CO–metal bond[4].

DERIVATIVES OF $Fe_3(CO)_9S_2$ AND $Fe_3(CO)_9Se_2$

These two complexes react with ligands in the following way:

$$Fe_3(CO)_9X_2+L \rightleftarrows Fe_3(CO)_8LX_2+CO \quad (1)$$
$$Fe_3(CO)_8LX_2+L \rightleftarrows Fe_3(CO)_7L_2X_2+CO \quad (2)$$

At not too high temperatures and low ligand concentrations, reaction (1) predomi-

TABLE 1

ANALYTICAL DATA

Compound	Physic form	M.p. (°C)	Carbon		Hydrogen		Iron		Mol. weight	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Fe_3(CO)_8As(C_6H_5)_3S_2$	brown crystals	dec. >120	41.1	40.98	2.03	1.98	21.6	21.99	755	762
$Fe_3(CO)_7[As(C_6H_5)_3]_2S_2$	green brown crystals	dec. >180	49.5	49.65	2.98	2.91	16.3	16.11		1040
$Fe_3(CO)_8As(C_6H_5)_3Se_2$	black crystals	dec. >140	36.7	36.49	1.81	1.77	19.2	19.58		856
$Fe_3(CO)_9As(C_6H_5)_3Te_2$	brown crystals	dec. >115	33.2	33.05	1.64	1.54	17.1	17.08	955	981
$Fe_3(CO)_8As(C_6H_5)_3Te_2$	black crystals	dec. >160	32.4	32.77	1.64	1.59	17.8	17.58	940	953
$Fe_3(CO)_7[As(C_6H_5)_3]_2Te_2$	green brown crystals	dec. >180	41.5	41.95	2.54	2.46	13.4	13.61		1231
$Fe_3(CO)_8P(OC_6H_5)_3S_2$	deep red liquid	—	40.5	40.76	1.94	1.97	21.9	21.87	785	766
$Fe_3(CO)_7[P(OC_6H_5)_3]_2S_2$	deep red liquid	—	49.3	49.27	3.00	2.88	16.1	15.98	1030	1048
$Fe_3(CO)_8P(OC_6H_5)_3Se_2$	deep red liquid	—	36.1	36.32	1.69	1.76	19.7	19.49	869	860
$Fe_3(CO)_7[P(OC_6H_5)_3]_2Se_2$	deep red liquid	—	45.4	45.22	2.75	2.65	14.3	14.67	1120	1142
$Fe_3(CO)_9P(OC_6H_5)_3Te_2$	deep red crystals	128	33.1	32.92	1.59	1.53	17.2	17.01	962	985
$Fe_3(CO)_8P(OC_6H_5)_3Te_2$	black crystals	99	32.8	32.63	1.62	1.58	17.5	17.50	944	957
$Fe_3(CO)_7[P(OC_6H_5)_3]_2Te_2$	red amorphous solid	130–131	41.6	41.67	2.61	2.44	13.4	13.52		1239
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3S_2$	brown amorphous solid	92–93	36.6	36.50	4.14	4.14	25.6	25.46	671	658
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2S_2$	brown amorphous solid	89	44.9	44.73	6.72	6.54	20.7	20.13		832
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3Se_2$	red brown liquid	—	31.9	31.95	3.72	3.62	22.3	22.28	734	752
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2Se_2$	dark brown liquid	—	39.9	40.20	5.31	5.08	18.2	18.09		926
$Fe_3(CO)_9P(n\text{-}C_4H_9)_3Te_2$	brown amorphous solid	109	28.6	28.75	3.04	3.10	19.2	19.10	910	877
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3Te_2$	dark brown liquid	—	28.3	28.29	3.32	3.20	19.8	19.73	830	849
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2Te_2$	brown liquid	—	36.6	36.38	5.18	5.32	16.7	16.34		1023
$Fe_3(CO)_{10}Te_2$	black crystals	dec. >100	17.1	17.09	—	—	24.0	23.84	690	703

nate. Increases in temperature and ligand concentration shift (2) considerably to the right and reaction mixtures with mono- and disubstituted derivatives are obtained. If the reaction is halted fairly quickly, only monosubstituted derivatives will be obtained and much longer reaction periods will be required if satisfactory disubstituted yields are desired. In some instances, it was found preferable to carry out reactions (2) directly on separately prepared $Fe_3(CO)_8LX_2$. When some ligands (especially $P(n\text{-}C_4H_9)_3$) were used, traces of other compounds were observed; these were probably trisubstituted derivatives but the quantities were too small to permit definite isolation and identification. Nor could their yield be increased by the adoption of more drastic reaction conditions, since these led to almost total demolition of the derivatives obtained.

In general, the sulphur compound proved more reactive than that containing selenium; the reactivity of the ligands employed varied in the order $P(n\text{-}C_4H_9)_3 > P(OC_6H_5)_3 > As(C_6H_5)_3$, *i.e.* in order of decreasing basicity. This corresponds with what has been reported for substitutions on binuclear chalcogen complexes of the type $Fe_2(CO)_6X_2R_2$[3].

The derivatives obtained were deeply coloured substances, red-brown in the case of substitutions with $P(n\text{-}C_4H_9)_3$ and $P(OC_6H_5)_3$, and green-brown in the case of $As(C_6H_5)_3$. The latter are only slightly soluble in aliphatic hydrocarbons and can thus be readily crystallised by such solvents; they are, however, soluble in CS_2, CCl_4, benzene, etc. The remaining derivatives were extremely difficult to crystallise because of their very ready solubility in all organic solvents; at room temperature, some are very viscous liquids and mix with the main organic solvents in all proportions. The analytical data and leading characteristics of these compounds are set out in Table 1.

The solid derivatives were stable in an inert atmosphere and decomposed very slowly in air, whereas the liquids were more easily altered. Phenyl derivatives were more stable than alkyl derivatives, although no substantial difference was observed between those of sulphur and of selenium. Solutions of these compounds decompose slowly in air, with the formation of amorphous brown precipitates, and can be kept for a long time under an inert gas. Both (1) and (2) shift leftwards in the presence of CO gas, with the formation of monosubstitutes or of the starting products. Light seemed to have no significant influence on the changes observed in these compounds or in their solutions.

$Fe_3(CO)_9Te_2$ DERIVATIVES

This complex behaves differently from S and Se-analogues. Its first reaction with a ligand is of the type:

$$Fe_3(CO)_9Te_2 + L \rightleftarrows Fe_3(CO)_9LTe_2 \qquad (3)$$

that is to say, a ligand molecule is adducted. Next, the "adduct" thus formed may loose a CO molecule according to the reaction:

$$Fe_3(CO)_9LTe_2 \rightleftarrows Fe_3(CO)_8LTe_2 + CO \qquad (4)$$

or, again, the adducted ligand molecule may be lost and the starting compound reformed. In general, these reactions occur simultaneously, the nature of the ligand determining which of the two will prevail. If L is triphenylarsine, there will be an almost complete return to the starting product. At the opposite extreme, with $P(n\text{-}C_4H_9)_3$ the "adduct" transforms according to (3) and (4) in about equimolecular quantities.

When an excess of ligand is used and experimental conditions are rendered more drastic, the subsequent reaction (analogous to (2)) will be observed and a disubstitute will be formed. For the reasons already explained, the trisubstituted derivatives cannot be isolated.

When L = CO, (3) will also occur, although high CO pressures (70–80 atm) are required; at low pressures, $Fe_3(CO)_9Te_2$ remains unchanged. The reaction was therefore carried out in an autoclave at room temperature (or slightly above, *i.e.* 30–35°) on solutions of $Fe_3(CO)_9Te_2$ in petroleum ether. After some hours, $Fe_3(CO)_{10}Te_2$ was obtained; this is very slightly soluble in petroleum ether and crystallizes readily into small black, metal-like crystals. With the ligands, (3) occurs very rapidly (almost instantaneously with tributylphosphine), and the various adducts are given with virtually quantitative yields.

Very long reaction times, however, are needed to obtain the monosubstitutes and very drastic reaction conditions are required for good disubstitute yields. The reactivity of the ligands is the same as that already mentioned (CO, however, being the least reactive of all), while $Fe_3(CO)_9Te_2$ reacts more rapidly than the equivalent sulphur and selenium compounds.

The characteristics of the mono- and disubstituted Te derivatives (physical state, colour, stability, solubility, etc.) are very similar to those described for the S and the Se complexes, and are also set out in Table 1. The "adducts", however, are solid substances, of a red-brown or black colour. Some of them are obtained as crystals from saturated hydrocarbons, in which they are poorly soluble. They are, on the other hand, readily soluble in CCl_4, $CHCl_3$, CS_2, ethers, etc. where they produce intense red-orange solutions. Even in the solid state, they are unstable both in air and under an inert gas; in solution they change very rapidly according to (3) or (4).

INFRARED SPECTRA

The main IR frequency values for the prepared compounds are given in Table 2. In the region between 1900 and 2100 cm^{-1}, CCl_4 was used since this solvent is optically transparent in this region, has good resolution characteristics and readily dissolves all the derivatives examined. Spectra for $Fe_3(CO)_9X_2$ complexes have already been reported[1a]. They present three strong bands between 2000 and 2100 cm^{-1}, with frequency variations in the order S > Se > Te. In the same way, a shift towards lower frequency values on passing from S to Te complexes can be observed for all the derivatives. In addition, in compounds with the same number of ligand molecules, the position of ν(C–O) depends on the nature of the ligand itself. Absorption frequencies for the carbonyl groups vary in the direction $P(OC_6H_5)_3 > As(C_6H_5)_3 > P(n\text{-}C_4H_9)_3$, *i.e.* in the direction of variation of the π-accepting ability of the ligands[5], and the phenomenon can be referred to these characteristics. The same reason can be used to explain the shift towards low frequencies observed on passing from the monosubstituted to their respective disubstituted derivatives. Monosubstitute IR

TABLE 2

IR FREQUENCIES[a]

Compound	IR frequencies in CO stretching region (cm^{-1})[b]	Other frequencies (cm^{-1})[c]
$Fe_3(CO)_8As(C_6H_5)_3S_2$	2074 s, 2046 m, 2033.5 vs, ~2012 vs, ~2009 vs, 1975 m(br), 1960 m(sh).	737 m, 691 m
$Fe_3(CO)_7[As(C_6H_5)_3]_2S_2$	2057 m, 2045 s, 2007 vs, 1998 vs, 1987 m, 1964 m, 1952 m	736 m, 690 m
$Fe_3(CO)_8As(C_6H_5)_3Se_2$	2067 s, 2039 m, 2028 vs, ~2009 vs, ~2006 vs, 1969 m, 1954 m(sh)	737 m, 693 m
$Fe_3(CO)_9As(C_6H_5)_3Te_2$	2067 m, 2042 (vs), 2016.5 vs, 1982 s, 1968.5 m, 1956 w	737 m, 693 m
$Fe_3(CO)_8As(C_6H_5)_3Te_2$	2068 w, 2057 s, 2027 m, 2018 vs, 1995 vs(br), 1944 m(br)	736 m, 694 m
$Fe_3(CO)_7[As(C_6H_5)_3]_2Te_2$	2048 m, 2043 m, 2029 s, 2017 s, 1986 vs(br), 1937 m(br)	736 m, 691 m
$Fe_3(CO)_8P(OC_6H_5)_3S_2$	2078 s, 2053 s, 2038 vs, 2026 m, 2014 s, 1991 m(br)	1215 m, 1191 s, 1162 m
$Fe_3(CO)_7[P(OC_6H_5)_3]_2S_2$	2062 m, 2055 s, 2025 vs, 2004 s, 1992 m(sh)	1216 m, 1193 s, 1187 m(sh), 1163 m
$Fe_3(CO)_8P(OC_6H_5)_3Se_2$	2070.5 s, 2047 m, 2032 vs, 2019 m, 2005 s, 1987 m(br)	1215 m, 1192 s, 1182 m(sh), 1164 m
$Fe_3(CO)_7[P(OC_6H_5)_3]_2Se_2$	2055 m, 2049 s, 2016 vs(br), 2001 s(br), ~1986 m(br)	1217 m, 1194 s, 1185 m(sh), 1163 m
$Fe_3(CO)_9P(OC_6H_5)_3Te_2$	2078 w, 2046 vs, 2026 vs, 2006 m, 1983.5 s, ~1972 m, ~1957 w	1213 m, 1187 s, 1180 m(sh), 1163 m
$Fe_3(CO)_8P(OC_6H_5)_3Te_2$	2060 s, 2037 m(sh), 2025 vs, 2007 m, 1998 s, 1981 m(br)	1218 m, 1194 s, 1182 m, 1163 m
$Fe_3(CO)_7[P(OC_6H_5)_3]_2Te_2$	2055 m, 2034 s, 2010 vs, 1976 s, 1963 m(br)	1213 m, 1191 s, 1163 m
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3S_2$	2072 s, 2045.5 m, 2029 vs, 2011 vs, 1994 m, 1968 m(br)	2965 s, 2937 s, 2880 m, 2869 m
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2S_2$	2037.5 s, 1984 vs(br), 1975 s(sh), 1961 m(br), 1941 m(br)	2966 vs, 2937 s(br), ~2915 m(sh), 2877 m, 2868 m
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3Se_2$	2066 s, 2039 m, 2024.5 vs, 2005 vs, 1986 m(br), ~1973 m(br), 1962 m(br)	2963 s, 2938 s, 2880 m, 2862 m(br)
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2Se_2$	2047 m, 2032 s, 1992 vs, 1978 s(br), 1963 m(br), ~1940 m(br), ~1920 m(br)	2964 vs, 2938 s, 2910 m, 2873 m, 2863 m
$Fe_3(CO)_9P(n\text{-}C_4H_9)_3Te_2$	2064 m, 2038 vs, 2014 vs, 1995 m(br), 1981.5 s, 1962 m, 1954 w(br)	2965 s, 2938 s, 2879 w, 2869 m(sh)
$Fe_3(CO)_8P(n\text{-}C_4H_9)_3Te_2$	2056 s, 2029 m, 2016 vs, 1995 vs, ~1980 m(sh), 1950 m	2964 s, 2938 s, ~2908 m(sh), 2878 m, 2869 m(br)
$Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2Te_2$	2025 s, 1983 vs(br), 1973 s(sh), 1959 m(sh), 1931 m(br), ~1920 m(br)	2964 s, 2937 s, 2906 m, 2877 m, 2866 m
$Fe_3(CO)_{10}Te_2$	2104 m, 2053 s, 2046 s, 2036 m, 2016 s, 1991 s, 1979 m, 1965 m(br)	
$Fe_3(CO)_9S_2$	2063 vs, 2045 vs, 2024.5 s	
$Fe_3(CO)_9Se_2$	2057 vs, 2037 vs, 2016.5 s	
$Fe_3(CO)_9Te_2$	2047.5 vs, 2027 vs, 2006.5 s	

[a] vs = very strong; s = strong; m = medium; w = weak; (sh) = shoulder; (br) = broad. [b] In CCl_4. [c] In CS_2 in 600–1300 cm^{-1} region; in CCl_4 in 2800–3000 cm^{-1} region.

spectra are very similar to each other irrespective of the chalcogen atom or the ligand molecule involved, and the same can be said of the disubstitutes and the adducts. Table 2 sets out some characteristic frequencies of the ligand bound to the complex: in the 600–800 cm^{-1} region for $As(C_6H_5)_3$ (C–H bending of the benzene ring out of the plane) in CS_2 solution; in the 1100–1250 cm^{-1} region for $P(OC_6H_5)_3$ (P–O stretching) in CS_2; in the 2800–3000 cm^{-1} region for $P(n\text{-}C_4H_9)_3$ (C–H stretching) in CCl_4.

DISCUSSION

The structure of the $Fe_3(CO)_9X_2$ complexes has already been reported[6]. The Fe and chalcogen atoms are arranged in a distorted tetragonal pyramid, at the apex of which is the Fe atom with the unusual coordination number 7. It seems likely that the structures of both the mono- and the disubstituted derivatives are similar to those of the starting compounds because of the ease of interconvertibility from one to the other upon reaction with ligands or CO (1 and 2). It is, therefore, reasonable to assume that the ligand replaces the CO molecule without altering the Fe_3X_2 cluster, even though the available data do not offer precise structural details; *e.g.* in the case of monosubstituted derivatives, it is not known whether L is bonded to the Fe atom at the apex or to one of the two Fe atoms at the base. Even though their presence cannot be demonstrated, there may be steric isomers in both the mono- and the disubstitutes. Their properties are probably so similar that separation by means of the methods used (fractional crystallization, thin-layer chromatography, etc.) was not possible for us.

With respect to the structure of the $Fe_3(CO)_9LTe_2$, similar reasoning may be employed to support the assumption that the unaltered Fe_3X_2 cluster coordinates a ligand molecule. One possibility is that L is bonded to one of the two Fe atoms at the base; this atom would thus have the same coordination number as the apical Fe atom. The resulting complex is probably rendered unstable by steric reasons, and may lose the L molecule and return to the starting compound or expel a CO group so as to form the monosubstituted derivative. However, it is thought more likely that the ligand attaches itself to one of the Te atoms by an overlap of the ligand orbitals of P or As and the 5 *d* orbitals of Te.

In effect the electronegativity of S and Se is greater than that of Te, which should mean that the Fe atoms bonded to them are becoming more positive, and hence an easier coordination between them and basic ligands. The fact that $Fe_3(CO)_9S_2$ and $Fe_3(CO)_9Se_2$ do not form these adducts, even with very nucleophilic ligands such as tributylphosphine, indicates that coordination of L on the chalcogen atom is preferred; this, however, is only possible in the case of Te which has less electron-attracting power.

It is also known that the covalent Te may act like a weak Lewis acid by means of the empty 5 *d* orbitals. Te halides, for example, may bond two molecules of ligands such as pyridine[7a], thiourea[7b], and tetramethylthiourea[7c]. TeF_6 certainly behaves like a Lewis acid and, with the bases, gives $2B\cdot TeF_6$-type adducts, where B may be an alkaline halide[8a] or trialkylamine[8b]. Coordination on Te of this type would finally be favoured sterically since it would be less impeded by the steric hindrance presented by the CO groups bonded to the Fe atoms.

EXPERIMENTAL

The $Fe_3(CO)_9X_2$ complexes were prepared and purified according to methods that have already been reported[1a]; their purity and that of their derivatives was checked by means of IR spectra, elemental analysis and thin-layer chromatography (adsorbent: Kieselgel G, according to Stahl; developers: heptane, 1:1 CS_2 and petroleum ether, 10% ethyl ether in petroleum ether). The ligands $P(OC_6H_5)_3$, $As(C_6H_5)_3$ and $P(n\text{-}C_4H_9)_3$ were Fluka A.G., Alfa Inorganics and K & K laboratories products and were used without further purification. CO and N_2 were dried before use by being passed through a column of $CaCl_2$ and silica gel.

The solvents (heptane and petroleum ether) were dried over sodium wire, purified by fractional distillation and held on sodium. IR spectra were obtained with a Mod. IR 12 double beam Beckman spectrophotometer with KBr optics. C and H analysis was performed on a Mod. 185 Carbon, Hydrogen and Nitrogen Analyser (F and M Scientific Co.); Fe was analysed by means of a Perkin-Elmer Model 303 atomic absorption spectrophotometer, with DCR1. Molecular weights were determined by the vapour tension method with a Hewlett Packard Mod. 302 Mechrolab vapor pressure osmometer. Melting points were determined microscopically using a Leitz Mod. 350 heating plate.

The general reaction procedure was as follows. A three-necked balloon with a gas inlet and outlet, reflux and a mercury valve was used. Air was expelled from this balloon by the passage of nitrogen for about 15 min. After expulsion of the air, the complex was introduced in an aliphatic hydrocarbon solution, with a boiling point 20–30° higher than that of the reaction. The ligand was then added and the reaction was allowed to continue at a constant temperature by keeping the balloon immersed in a water thermostat. The progress of the reaction was followed by the removal of small samples of solution with a syringe, and their analysis by thin-layer chromatography. Thin-layer chromatography was also used to separate the reaction products (eluent: 1:1 CS_2 and petroleum ether). In each case, the compounds moved in the order: starting product, monosubstitute, disubstitute, "adduct". A second purification by means of the same method was necessary in most cases, especially where a large excess of ligand had been used in the reaction; some complexes were then crystallized from n-heptane at −20°.

Reaction of $Fe_3(CO)_9S_2$ with $As(C_6H_5)_3$

1.30 g of $Fe_3(CO)_9S_2$ (2.7 mmoles) was reacted with 1.23 g of $As(C_6H_5)_3$ (4.0 mmoles) at 50° for 3 days. The solution was examined by means of thin-layer chromatography and two bands were observed: the first, a dark red (starting product); the second, a brown colour. The latter was collected and crystallized from n-heptane at −20°. 0.86 g (42% yield) of $Fe_3(CO)_8As(C_6H_5)_3S_2$ was obtained. A mixture containing 0.90 g of $As(C_6H_5)_3$ (2.9 mmoles) and 0.45 g of $Fe_3(CO)_8As(C_6H_5)_3S_2$ (0.59 mmoles), prepared as just described, was allowed to stand for 3 days at 70°. Separation and crystallization as before gave 92 mg (15% yield) of $Fe_3(CO)_7[As(C_6H_5)_3]_2S_2$.

Reaction of $Fe_3(CO)_9S_2$ with $P(OC_6H_5)_3$

3.40 g of $Fe_3(CO)_9S_2$ (7.0 mmoles) dissolved in n-heptane were reacted with 7.5 ml of $P(OC_6H_5)_3$ (~28 mmoles) for 2 days at 60°. Chromatographic separation showed, besides the starting product, one deep red-brown and one paler red-brown band. After further purification, 2.8 g (52% yield) of $Fe_3(CO)_8P(OC_6H_5)_3S_2$ and 0.88 g of $Fe_3(CO)_7[P(OC_6H_9)_3]_2S_2$ were obtained.

Reaction of $Fe_3(CO)_9S_2$ with $P(n\text{-}C_4H_9)_3$

10 ml of an 0.50 *M* solution of $P(n\text{-}C_4H_9)_3$ were added to 200 ml of a 2.5 m*M* solution of the complex and allowed to stand for 1 day at 50°. Two dark red-brown chromatographic bands were separated; these were purified several times to remove the excess of ligand. 0.11 g of $Fe_3(CO)_8P(n\text{-}C_4H_9)_3S_2$ and 0.10 g of $Fe_3(CO)_7[P(n\text{-}C_4H_9)_3]_2S_2$ were obtained.

Reaction of $Fe_3(CO)_9Se_2$ with $As(C_6H_5)_3$

A mixture containing 3.2 g of the complex (5.5 mmoles) and 3.4 g of ligand (11 mmoles), dissolved in n-heptane, was reacted at 70° for 3 days. Chromatographic separation and purification gave 2.0 g (42% yield) of $Fe_3(CO)_8As(C_6H_5)_3Se_2$ which was crystallized from petroleum ether.

Reaction of $Fe_3(CO)_9Se_2$ with $P(OC_6H_5)_3$

A solution containing 4.0 g of $Fe_3(CO)_9Se_2$ (6.9 mmoles) and 7.4 ml of $P(OC_6H_5)_3$ (~28 mmoles) was reacted for 2 days at 65°. Chromatographic separation produced 2 red-brown bands, corresponding to the mono- and disubstituted derivatives. The yields were 2.14 (36%) and 1.2 g (19%), respectively.

Reaction of $Fe_3(CO)_9Se_2$ with $P(n\text{-}C_4H_9)_3$

4.8 g of $Fe_3(CO)_9Se_2$ (8.3 mmoles) and 20 ml of $P(n\text{-}C_4H_9)_3$ (~82 mmoles) react very quickly at room temperature. The yield 4.6 g (74%) consists almost entirely of the monosubstitute. The mixture must be heated to 40° for approx. 10 h if an appreciable quantity of the disubstitute is required; in this case, the same initial reagent quantities yield 2.2 g of mono- and 1.7 g of disubstitute.

Reaction of $Fe_3(CO)_9Te_2$ with $As(C_6H_5)_3$

1.75 g of $Fe_3(CO)_9Te_2$ (2.6 mmoles) and 4.76 g of $As(C_6H_5)_3$ (15.6 mmoles) were left to stand for 1 day at 30°. A deep orange band was separated. The solid, which slowly decomposed even under nitrogen, was repeatedly washed in petroleum ether to remove traces of the starting product. Yield: 1.63 g of $Fe_3(CO)_9As(C_6H_5)_3Te_2$. In a second reaction, the same initial quantities were kept at 50° for 2 days. On this occasion, the deep orange band was entirely replaced by a deep brown and a paler green-brown band. After purification and crystallization from n-heptane, these bands yielded 1.12 g (45%) of the monosubstitute and 0.28 g (12%) of the disubstitute.

Reaction of $Fe_3(CO)_9Te_2$ with $P(OC_6H_5)_3$

These compounds were reacted at room temperature for about 1 h and their yield was almost entirely formed of the "adduct", which separated as an instable red-orange band. 2.5 g of $Fe_3(CO)_9Te_2$ (3.7 mmoles) and 5.0 ml of $P(OC_6H_5)_3$ (~19 mmoles) yielded about 1.1 g (30%) of "adduct" after purification and washing in small volumes of petroleum ether. Heating for some hours at 40° is necessary before the substitutes can be obtained. These separate as a red-brown band (monosubstitute) and a vivid red band (disubstitute). Yields: about 40% and 25%, respectively.

Reaction of $Fe_3(CO)_9Te_2$ with $P(n\text{-}C_4H_9)_3$

This reaction behaves in the way described above: after a few minutes, the complex is completely transformed into the orange "adduct"; after some hours at 40°, appreciable quantities of the substitutes are obtained in the form of brown bands. Yields: (a) 1.9 g of $Fe_3(CO)_9Fe_2$ (2.8 mmoles) and 6.0 ml of $P(n\text{-}C_4H_9)_3$ ($\sim$25 mmoles) reacted for 15 min at room temperature gave 1.2 g (50%) of the adduct (purified as just described); (b) 4.4 g (6.5 mmoles) of complex and 16 ml ($\sim$65 mmoles) of phosphine yielded 2.1 g (38%) of monosubstitute and 1.7 g (26%) of disubstitute after 8 h at 40°.

Reaction of $Fe_3(CO)_9Te_2$ with CO

100 ml of 2.0 m*M* solution of $Fe_3(CO)_9Te_2$ in n-heptane were introduced into a small (200 ml internal capacity) autoclave. The air was pumped out and CO introduced to a pressure of 70–80 atm. The autoclave was then placed in an air oven and held at 30° for about 2 days. The gas was then carefully removed and the autoclave was opened. A solid compound, consisting of shiny black microcrystals, was collected by filtration. This was found to be very poorly soluble in n-heptane and poorly soluble in other organic solvents. Repeated washings in petroleum ether were used to remove all traces of the starting product. Yield: 80 mg of $Fe_3(CO)_{10}Te_2$ (25%).

Decomposition reactions of the "adducts"

70–80 mg of the "adduct" under examination were introduced into a glass vial with a rubber cap, similar to that previously reported[4a]. A current of nitrogen was passed through the vial for 10 min to expel the air and it was then sealed over a flame. A syringe was used to insert 10 ml of CCl_4 through the rubber cap and the vial was then placed in a thermostat set at 25°. A microsyringe was used to draw off small quantities of the solution at convenient intervals. These were then subjected to IR spectrophotometric and thin-layer chromatographic analysis.

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