Reactions of Pentacarbonyliron(0) and Hexacarbonylmolybdenum(0) Complexes with Thiocyanogen

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The reactions of pentacarbonyliron(0) and hexacarbonylmolybdenum(0) with thiocyanogen yield the polymeric complexes $[Fe(CO)_2(SCN)_2]$ and $[Mo(CO)_4(SCN)_2]$ respectively. The complexes are thermally and hydrolytically unstable. I.r. spectra are reported.

REACTIONS between metal carbonyl complexes and halogens have been the subject of detailed investigations. The following iron and molybdenum complexes have been prepared this way: $[Fe(CO)_5X_2]$, $[Fe(CO)_4X_2]$ ($X = Cl$, Br, or I); $[Fe(CO)_2I_2]$; $[Fe(CO)_2I]$; $[Fe(CO)_4I]_2$;[1-6] and $[Mo(CO)_4X_2]_2$ ($X = Cl$ or Br).[5,6] In all these complexes the iron is believed to be octahedrally co-ordinated, whereas the molybdenum is seven-co-ordinate. Metal carbonyl complexes have also been treated with ClN_3 and BrN_3.[7] The resulting complexes are believed to be either ionic, as for example the azido-bridged $[Fe(CO)_2N_3]_2^{2+}\ 2Cl^-$ with tetrahedrally co-ordinated iron, or polymeric as the azido- and chloro-bridged $[Mo(CO)_2(N_3)Cl]_n$ with octahedrally co-ordinated molybdenum.

Some metal carbonylthiocyanato-complexes have been prepared such as $[Fe(CO)_2(PPh_3)_2(CNS)_2]$ [8] and $[Rh(CO)L_2(CNS)]$ [9] ($L = PPh_3$, $AsPh_3$, or $SbPh_3$; CNS indicates that it is not established whether this group is *N*- or *S*-bonded). The complex $[NaMn(CO)_5]$ and ClSCN [10,11] or $(SCN)_2$ [11] yield monomeric $[Mn(CO)_5SCN]$. In solution there is an equilibrium between the forms $[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$. Pentacarbonyliron(0) is said to react with thiocyanogen with evolution

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of carbon monoxide, affording a product containing no CO.[11] The present paper deals with the re-investigation of this reaction together with that of $[Mo(CO)_6]$ with $(SCN)_2$.

RESULTS AND DISCUSSION

When a solution of thiocyanogen in an organic solvent was added to a solution of the metal carbonyl complex in a 1 : 1 mol ratio, carbon monoxide was evolved and a dark brown precipitate formed. Gas evolution is vigorous in reaction (1) and moderate in (2). Similarly, the complexes $[Fe_3(CO)_{12}]$ and $[W(CO)_6]$ were treated with $(SCN)_2$; in both cases gas evolution was observed, but it was not possible to obtain reproducible reaction products.

$$[Fe(CO)_5] + (SCN)_2 \longrightarrow [Fe(CO)_2(SCN)_2] + 3CO \quad (1)$$

$$[Mo(CO)_6] + (SCN)_2 \longrightarrow [Mo(CO)_4(SCN)_2] + 2CO \quad (2)$$

Dicarbonyldithiocyanatoiron(II), $[Fe(CO)_2(SCN)_2]$, is a brown powder, which is very sensitive to moist air, where rapid decomposition with loss of carbon monoxide takes place. It also is rather unstable thermally, releasing CO with an appreciable rate at 70 °C. After heating the complex for several hours to 120 °C in a nitrogen atmosphere, a product was obtained which showed no CO absorption bands in the i.r. spectrum and which according to analysis was impure $[Fe(SCN)_2]$. Even at room temperature the rate of CO evolution from $[Fe(CO)_2(SCN)_2]$ is so high that within 24 h *ca.* 10%, and within 2 weeks *ca.* 50%, of the carbon monoxide is released. Because of its instability $[Fe(CO)_2(SCN)_2]$ has to be prepared in a solvent of low boiling point, so that it can be dried quickly *in vacuo*, and all analyses and investigations must be performed with a freshly prepared product. It appears that Farona and Wojcicki[11] did not realize the instability of $[Fe(CO)_2(SCN)_2]$ and therefore reported erroneously that in the reaction between pentacarbonyliron(0) and thiocyanogen no $[Fe(CO)_2(SCN)_2]$ was formed. The complex $[Fe(CO)_2(SCN)_2]$ is insoluble in non-polar organic solvents such as benzene, carbon tetrachloride, and hexane, whereas it dissolves with decomposition in polar organic solvents such as ethanol, acetone, and pyridine. Water or aqueous solutions decompose the complex with total evolution of the carbon monoxide; this reaction can be used for volumetric quantitative analysis.

The complex tetracarbonyldithiocyanatomolybdenum(II), $[Mo(CO)_4(SCN)_2]$, is considerably less reactive than $[Fe(CO)_2(SCN)_2]$. It is a dark brown powder, which is sensitive to moist air and is slowly decomposed by water, only a fraction of the carbon monoxide being released. At room temperature no significant thermal decomposition takes place, whereas at 70 °C a volume contraction was observed. After heating the complex for 12 h to 150 °C, a product containing no CO absorption bands in the i.r. spectrum was obtained.

I.r. Spectra.—I.r. spectra of the metal carbonylthiocyanato-complexes are given in the Table. The bands were assigned by comparison with related complexes.[2,3,6,7,11-15] From the i.r. spectra it can be concluded that metal carbonylthiocyanato- and not carbonylisothiocyanato-complexes have been formed. For the latter complexes a strong CN valence vibration at *ca.* 1 900—2 000 cm^{-1} and a CS valence vibration between 700 and 900 cm^{-1} would be expected;[12,13] these are not present in the present spectra. Instead CN vibration absorption bands between 2 050 and 2 150 cm^{-1} and CS vibration bands between 600 and 700 cm^{-1} were found, which are typical for thiocyanato-complexes.

As the complexes are insoluble in organic solvents, they must be either polymers or ionic species. Non-ionic molecules of low molecular weight would be expected to be soluble in organic solvents, as is the case for monomeric $[Mn(CO)_5(SCN)]$[11] and dimeric $[Mo(CO)_4X_2]_2$ (X = Cl or Br).[5,6] But ionic species also have to be excluded, as they would require the absence of CO absorption bands below 2 000 cm^{-1}, whereas bands between 1 800 and 2 000 cm^{-1} are found in the spectra of the complexes $[Fe(CO)_2(SCN)_2]$ and $[Mo(CO)_4(SCN)_2]$. In ionic molecules the carbon monoxide would be expected to be part of the cation as is the case in $[Fe(CO)_2N_3]_2^{2+}$ $2Cl^-$.[7] The positive charge on the cation precludes considerable back-donation from the metal to the carbon atom in the M–C bond

I.r. spectra/cm^{-1} of the complexes $[Fe(CO)_2(SCN)_2]$ and $[Mo(CO)_4(SCN)_2]$

$[Fe(CO)_2(SCN)_2]$	Assignment	$[Mo(CO)_4(SCN)_2]$	Assignment
3 680—3 200 ms,vb	ν(OH) (humidity)	3 600—3 200 w,vb	ν(OH) (humidity)
2 135vs	ν(CN) and ν(CO)	2 115s	ν(CN) and ν(CO)
2 118m,sh		2 050m	
2 101vs		1 990w	
2 060s		1 932w	
1 998w,sh		1 905vw	
1 818m	(?)	1 870m	
1 750vw		1 630—1 590w,vb	δ(H_2O) (humidity)
1 606w	δ(H_2O) (humidity)		
1 402w		1 408vw	
1 269w		990mw	
745vw		736vw	
		686vw,sh	
608vs	ν(CS)	672m	ν(CS)
570s	δ(FeCO)	668vw,sh	
486m,b	$\nu_{asym}(FeC_2)$, δ(SCN) and δ(FeCO) (?)	472w,b	δ(SCN) and ν(MoC)
		450vw,sh	
439m,b	$\nu_{sym}(FeC_2)$, δ(SCN)	360vw	
		330vw	
		308vw,sh	
		290m	ν(MoS)
		225vw,sh	

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which would be required to explain values of $\tilde{\nu}$(CO) below 2 000 cm^{-1}. So it is concluded that the carbonylthiocyanato-complexes of iron and molybdenum are polymers. In these polymers the bridging can be effected by the SCN and/or the CO groups. Chemical evidence (no complexes with CO bridges are known when other more appropriate ligands such as the SCN group are present) and the i.r. spectra [CO bridges require strong $\tilde{\nu}$(CO) bands at *ca.* 1 800 cm^{-1} or less] indicate that bridging is effected by the S atoms of the SCN groups. Therefore the following structures are proposed.

[$Fe(CO)_2(SCN)_2$]. The iron atoms have octahedral co-ordination with four bridging SCN and two terminal CO ligands. A possible *trans*-configuration of the two CO groups cannot be distinguished from the also possible *cis*-configuration, such as is found in the similar complex [$Fe(CO)_2(SMe)_2$]$_n$.[2,14] The complex [$Fe(CO)_2I_2$]$_n$ is also believed to belong to one of these two types.[4,15]

[$Mo(CO)_4(SCN)_2$]. For a polymer-structure model a co-ordination number higher than six must be formulated for molybdenum. As other carbonyl complexes of molybdenum, *e.g.* dimeric [$Mo(CO)_4Cl_2$]$_2$, exhibit the co-ordination number of seven,[5,6,16] it can be assumed that seven-co-ordination also exists in [$Mo(CO)_4(SCN)_2$]. The seven co-ordination sites are occupied by four terminal CO, one terminal SCN, and two bridging SCN ligands.

EXPERIMENTAL

All experimental operations were performed in an atmosphere of dry oxygen-free nitrogen. Solvents were carefully purified and distilled before use. [$Fe(CO)_5$] (Fluka) was distilled and [$Mo(CO)_6$] (Alfa-Inorganics) was recrystallized from benzene before use. $(SCN)_2$ was prepared from AgSCN and Br_2.[17]

Dicarbonyldithiocyanatoiron(II), [$Fe(CO)_2(SCN)_2$].—To a stirred ice-cooled solution of the complex [$Fe(CO)_5$] [5 cm^3 in 50 cm^3 light petroleum (b.p. 30—40 °C)], a solution of $(SCN)_2$ (2·8 g in 40 cm^3 benzene) was added dropwise within 15 min. A voluminous, brown solid precipitated and vigorous gas evolution was observed; the stirring was continued for 30 min. The *precipitate* was filtered, washed with light petroleum, and dried for 30 min *in vacuo* {Found: Fe, 23·5 (complexometric); CO, 22·4 (gas volumetric after hydrolysis); SCN, 49·7 (as AgSCN and $BaSO_4$). [$Fe(CO)_2(SCN)_2$] requires Fe, 24·5; CO, 24·55; SCN, 50·95%}.

Tetracarbonyldithiocyanatomolybdenum(II), [$Mo(CO)_4(SCN)_2$].—To a stirred solution of the complex [$Mo(CO)_6$] (1·75 g in 250 cm^3 benzene), a solution of $(SCN)_2$ in benzene (from 2·57 g AgBr and 0·3 cm^3 Br_2) was added dropwise. A dark brown solid precipitated with gas evolution. Stirring was continued for 1 h. The *precipitate* was filtered, washed with benzene, and dried *in vacuo* for several hours {Found: Mo, 28·3 (as oxinate); N, 8·2 (ignition); S, 19·3 (as $BaSO_4$). [$Mo(CO)_4(SCN)_2$] requires Mo, 29·6; N, 8·65; S, 19·8%}.

I.r. spectra were recorded in both Nujol and perfluorocarbon mulls between KBr and CsI plates. Perkin-Elmer spectrophotometers, models 225, 337, and 621 were used.

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