Activation of Carbon Diselenide by Transition-metal Complexes. Selenocarbonyl Derivatives of Chromium and Manganese

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Summary Carbon diselenide reacts in the presence of PPh_3 with $(\pi\text{-}C_5H_5)Mn(CO)_2(THF)$ or $(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_2(THF)$ to give $(\pi\text{-}C_5H_5)Mn(CO)_2(CSe)$ and $(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$, the first examples of transition-metal selenocarbonyls.

Although the chemistry of transition-metal carbonyls has been developed rapidly, the existence of the corresponding thiocarbonyl complexes was not demonstrated until 1966, when Baird and Wilkinson[1] isolated *trans*-$RhCl(CS)(PPh_3)_2$ and related compounds. There is increasing interest in metal thiocarbonyl chemistry,[2] and we now wish to report the synthesis of the first complexes incorporating co-ordinated carbon monoselenide.

Reaction of the complex $(\pi\text{-}C_5H_5)Mn(CO)_2(THF)$, prepared by photolysis of $(\pi\text{-}C_5H_5)Mn(CO)_3$ in THF,[3] with an equimolar quantity of CS_2 gives a green solution. After addition of triphenylphosphine (1 mol. equiv.) and removal of THF, extraction with hexane followed by sublimation (40°, 10^{-3} mm Hg) gives yellow, air-stable crystals of $(\pi\text{-}C_5H_5)Mn(CO)_2(CSe)$ (I) (40%, m.p. 67—68°; ν_{CO}, 2015s, 1963vs; 1105vs ν_{CSe}, cm^{-1}); further extraction

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with benzene yields Ph_3PSe (identified by m.p. and i.r. spectrum[4]). This suggests that (I) is formed as in equation (1). The red complex $(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$ (II) (20%, m.p. 185° (decomp.); ν_{CO}, 1990vs, 1947s; ν_{CSe}, 1071vs cm^{-1}) has been synthesized similarly from $(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_3$ in THF. Complex (I) can also be formed by refluxing equimolar amounts of CSe_2 and PPh_3 with the *cis*-cyclooctene complex $(\pi\text{-}C_5H_5)Mn(CO)_2(C_8H_{14})$ in benzene (*ca.* 10% yield).

$$(\pi\text{-}C_5H_5)Mn(CO)_2(THF) \xrightarrow{CSe_2} (\pi\text{-}C_5H_5)Mn(CO)_2(CSe_2)$$

$$\xrightarrow{PPh_3} \underset{(I)}{(\pi\text{-}C_5H_5)Mn(CO)_2(CSe)} + Ph_3PSe \qquad (1)$$

The formation of carbon monoselenide has been investigated by Steudel who has reported[5] that, unlike its sulphur analogue, CSe cannot be isolated. Compounds (I) and (II) thus show the stabilization of a previously uncharacterized entity by co-ordination to a transition metal. The complexes allow a direct comparison of the spectroscopic properties of co-ordinated CO, CS, and CSe. All three types of complex give rise to strong, sharp i.r. absorptions attributable to ν_{CX} decreasing in energy in the order $X = O \gg S > Se$. Little is known about selenoketones[6] and a wavenumber range for $\nu_{C=Se}$ has not been established. Further vibrations of the Mn–C–Se linkage can tentatively be identified with features at 515s, 508s [i.r., δ(Mn–C–Se)] and 363m cm^{-1} [Raman, $\nu(Mn\text{–}C_{Se})$]. In the mass spectrum of complex (I), fragments arising from the molecular ion and from $C_5H_5Mn(CSe)^+$ and $Mn(CSe)^+$ are prominent while those due to CSe loss with retention of CO are of very low abundance. This may be taken as indirect evidence for strong metal to CSe bonding.

The spectroscopic data are consistent with the presence of a metal–C–Se sequence in (I) and (II), analogous to the sequences confirmed by diffraction methods for metal carbonyls and thiocarbonyls. However, it is difficult to discount the possibility of *iso*-selenocarbonyl bonding without crystallographic evidence, and for this reason we are starting an *X*-ray structure determination for compound (I).

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