

Preliminary Communication

A FACILE ROUTE TO $\text{Cr}(\text{CO})_5(\text{CX})$ ($\text{X} = \text{S}, \text{Se}$) COMPLEXES

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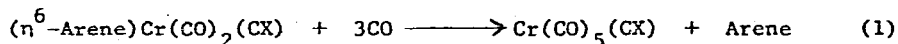
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Summary

Reaction of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CSe})$ with excess CO under pressure gives $\text{Cr}(\text{CO})_5(\text{CSe})$, the first example of a selenocarbonyl complex containing only CO and CSe ligands. Similar reactions of $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$ ($\text{R} = \text{H}, \text{CO}_2\text{CH}_3$) with CO afford $\text{Cr}(\text{CO})_5(\text{CS})$ in much higher yield than the literature method.

While numerous thiocarbonyl complexes have been reported for almost all the Group VIB, VIIB and VIII metals [1,2], metal selenocarbonyls are still extremely rare and are restricted to complexes of the type, $(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_2(\text{CSe})$, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{CSe})$ ($\text{M} = \text{Mn}, \text{Re}$) [3,4] and *cis*- $\text{RuCl}_2(\text{CO})(\text{CSe})(\text{PPh}_3)_2$ [5]. We now report the synthesis of $\text{Cr}(\text{CO})_5(\text{CX})$ ($\text{X} = \text{S}, \text{Se}$) by the method in reaction 1. The reactions are



directly analogous to the substitution of arene ligands in $(\eta^6\text{-Arene})\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by various monodentate ligands (L) to form *fac*- $\text{M}(\text{CO})_3\text{L}_3$ complexes [6,7].

Reaction 1 may be carried out under either low or high pressure

conditions. In a typical low pressure experiment, a tetrahydrofuran solution (50 ml) of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CSe})$ (0.3 g, 1 mmol) [3,8] is placed in a Carius tube (capacity ~70 ml) and the solution is degassed by repeated freeze-thaw cycles. Carbon monoxide (8 mmol) is then introduced into the tube from a calibrated vacuum manifold and the tube is sealed off and placed in a 50° oil bath. Under these conditions, the maximum pressure in the tube assuming that no CO gas is dissolved is 8 atm and formation of $\text{Cr}(\text{CO})_5(\text{CSe})$ is complete in 3.5 h. Only the thiocarbonyl reactions have so far been studied at high pressure. For example, when $(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_2(\text{CS})$ (1.0 g, 3.5 mmol) [9] dissolved in acetone (70 ml) is reacted with CO in an autoclave at 70° and under 150 atm pressure, the reaction is complete in 3 h. During product work up, the solvents must be removed extremely carefully owing to the high volatility of the $\text{Cr}(\text{CO})_5(\text{CX})$ complexes. We found that this is best accomplished on a vacuum line using a sequence of three cold traps: chlorobenzene/liquid nitrogen slush (-45°), chloroform/liquid nitrogen slush (-63°) and acetone/dry ice (-78°). Analytically pure samples of the $\text{Cr}(\text{CO})_5(\text{CX})$ complexes can be obtained by vacuum sublimation ($25^\circ/1 \times 10^{-4}$ torr) of the solid residues remaining in the two higher temperature traps onto an ice-cooled finger. The yields are typically 70-95% based on $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_2(\text{CX})$ and 30-50% based on $\text{Cr}(\text{CO})_6$. The latter range is appreciably higher than the 3-6% yield obtained for $\text{Cr}(\text{CO})_5(\text{CS})$ by the current literature method [10] which involves sodium amalgam reduction of $\text{Cr}(\text{CO})_6$ in tetrahydrofuran and treatment of the resulting carbonyl anions with excess Cl_2CSe . Moreover, unlike the thiophosgene route, the new method described here for $\text{Cr}(\text{CO})_5(\text{CS})$ does not necessitate physical or chemical separation of the thiocarbonyl product from the large amounts of $\text{Cr}(\text{CO})_6$ regenerated in the reactions. It should also be mentioned that the literature approach would be impossible for the synthesis of $\text{Cr}(\text{CO})_5(\text{CSe})$ owing to the non-existence of Cl_2CSe .

The new selenocarbonyl complex, $\text{Cr}(\text{CO})_5(\text{CSe})$, is a highly volatile, deep-yellow, crystalline solid that sublimes before melting and has a characteristic odour reminiscent of CSe_2 . It is air-stable and soluble without decomposition in all common organic solvents. The parent ion in its mass spectrum is consistent with the abundances of the naturally occurring isotopes of chromium and selenium. The initial fragmentation is $\text{Cr}(\text{CO})_5(\text{CSe})^+ \xrightarrow{-2\text{CO}} \text{Cr}(\text{CO})_3(\text{CSe})^+$, following which there is stepwise loss of CO to give $\text{Cr}(\text{CSe})^+$. That there is no evidence for CSe loss until $\text{Cr}(\text{CSe})^+$ degrades to Cr^+ is tentatively indicative of strong Cr-CSe bonding. The non-appearance of a peak attributable to CSe^+ is in line with the known instability of CSe itself [11]. The vibrational spectra of the complex are closely similar to those of $\text{Cr}(\text{CO})_5(\text{CS})$ [12] and are in accord with the expected C_{4v} molecular symmetry. In its IR spectrum in *n*-hexane, the complex exhibits three $\nu(\text{CO})$ modes at 2093m ($\underline{a}_1^{\text{eq}}$), 2031m ($\underline{a}_1^{\text{ax}}$) and 2000vs (\underline{e}) cm^{-1} and one $\nu(\text{CSe})$ mode at 1077s (\underline{a}_1) cm^{-1} . The $\nu(\text{CO})$ region in the Raman spectrum (Kr^+ excitation, 568.2 nm) of the solid is complicated by extensive solid-state splittings indicative of more than one molecule per unit cell; the $\nu(\text{CSe})$ mode appears as a broad, medium-intense peak at 1093 cm^{-1} .

In principle, reaction 1 could be extended to the synthesis of the other Group VIB $\text{M}(\text{CO})_5(\text{CX})$ complexes provided that suitable examples of the presently unknown (η^6 -Arene) $\text{M}(\text{CO})_2(\text{CX})$ precursors could be prepared. There has been considerable interest lately in the chemistry of metal thiocarbonyls with the $\text{M}(\text{CO})_5(\text{CS})$ complexes receiving particular attention because of their high symmetry and close structural similarity to the metal hexacarbonyls [e.g., 10,12-14]. We anticipate that $\text{Cr}(\text{CO})_5(\text{CSe})$ will be subject to similar attention in the future, especially since diatomic CSe has never been isolated [11], and the discovery of this relatively simple selenocarbonyl complex affords the best opportunity to date for comparing the bonding properties of CSe with those of the isoelectronic ligands, CO and CS.

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