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SYNTHESIS OF THE PENTACARBONYL(CHALCOCARBONYL)-CHROMIUM(0) COMPLEXES, $Cr(CO)_5(CX)$ ($X = S, Se$)

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Summary

The arene complexes, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ ($X = S, Se$), react with excess CO gas under pressure in tetrahydrofuran at about 60°C to produce the $Cr(CO)_5(CX)$ complexes in high yield. The IR and NMR (^{13}C and ^{17}O) spectra of these complexes are in complete accord with the expected C_{4v} molecular symmetry. Like the analogous $W(CO)_5(CS)$ complex, both compounds react with cyclohexylamine to give $Cr(CO)_5(CNC_6H_{11})$. However, while $W(CO)_5(CS)$ undergoes stereospecific CO substitution with halide ions (Y^-) to form *trans*-$[W(CO)_4(CS)Y]^-$, the two chromium chalcocarbonyl complexes apparently undergo both CO and CX substitution to afford mixtures of $[Cr(CO)_5Y]^-$ and *trans*-$[Cr(CO)_4(CX)Y]^-$.

Introduction

Sodium amalgam reduction of the Group VIB metal hexacarbonyls in tetrahydrofuran leads to mixture of metal carbonyl anions, chiefly $[M_2(CO)_{10}]^{2-}$ ($M = Cr, Mo, W$) [1], and addition of excess thiophosgene (Cl_2CS) to these solutions affords the $M(CO)_5(CS)$ complexes in very poor yields (usually <5%) [2]. Furthermore, these thiocarbonyl products are heavily contaminated with large amounts of $M(CO)_6$, which is regenerated during the reactions, thus necessitating tedious physical or chemical separations. Moreover, this route cannot be extended to the synthesis of the analogous selenocarbonyl complexes, $M(CO)_5(CSe)$, owing to the apparent non-existence of Cl_2CSe.

Earlier, we communicated [3] an alternative route to $Cr(CO)_5(CS)$ (eq. 1) in which the yield is approximately ten times greater than that via the thiophosgene route based on the amount of $Cr(CO)_6$ used, and there are no accompanying purification problems. In addition, the same route can be used to prepare the previously unknown selenocarbonyl complex, $Cr(CO)_5(CSe)$. In this paper, we present the complete details of these syntheses as well as some of the physicochemical properties of the two chalcocarbonyl products.

$$\begin{tikzcd} Cr(CO)_6 \arrow[r, "\text{Arene}", "h\nu"'] & (\eta^6\text{-Arene})Cr(CO)_3 + 3\,CO \arrow[d, "CX_2\,(X = S,\,Se)/PPh_3"] \\ Cr(CO)_5(CX) + \text{Arene} & (\eta^6\text{-Arene})Cr(CO)_2(CX) \arrow[l, "CO"', "10\text{--}200\ \text{atm}"] \end{tikzcd} \qquad (1)$$

Experimental

Chemicals were obtained from the sources indicated: $Cr(CO)_6$, CSe_2 (Strem Chemicals, Inc.); *cis*-cyclooctene (Eastman Kodak Co.); 2-picolene (Aldrich Chemical Co.). All procedures were performed routinely under a nitrogen atmosphere using standard Schlenk ware. Benzene, THF, Et_2O, hexanes, CS_2, and 2-picolene were refluxed under nitrogen over suitable drying agents (sodium metal strips in the presence of benzophenone, and P_2O_5 for 2-picolene) and were distilled immediately prior to use. *Cis*-cyclooctene was stored over molecular sieves (Linde 3A) and was used without further purification. Carbon diselenide was purchased in 1 g quantities in sealed ampoules which were mechanically broken directly in the reaction mixtures. (Caution: CSe_2 has a noxious odor and should be handled extremely carefully in closed systems at all times.)

The UV-irradiation source was a 100-W Hanovia (No. 6515-30) high-pressure, quartz mercury-vapor lamp (Ace Glass, Inc.). A Pyrex irradiation vessel (capacity 350 ml) fitted with a water-cooled quartz finger to house the UV lamp was used in the photochemical steps of the reactions (for further details of the design of the apparatus, see refs. 4 and 5). Chromatographic separation of the various products was achieved by preparative thin-layer chromatography (TLC): five 20 × 20-cm TLC plates (1 mm thick) were prepared from a slurry of 80 g silica gel G (Macherey, Nagel and Co.) and 170 ml water, and these plates were activated before use by heating them at 100°C for 1 h. A maximum of 100 mg of product was spotted onto each plate.

Infrared spectra were recorded on either a Perkin-Elmer model 337 spectrophotometer coupled to a Texas instruments Serve-Riter model II expanded-scale recorder or a Nicolet model 6000 Fourier transform instrument (accuracy of band positions, at least $\pm 1\ cm^{-1}$). Complete details of instrumentation used to measure the ^{13}C and ^{17}O NMR spectra have been reported recently [6]. Mass spectra were recorded on an LKB 9000 spectrometer at 25°C/70 eV. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Preparation of $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$

The starting material, $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, was prepared from $Cr(CO)_6$ in 76%

yield by Rausch et al.'s C_6H_6/2-picolene route [7]. (η^6-C_6H_6)Cr(CO)$_3$ (0.35 g, 1.64 mmol) and excess *cis*-cyclooctene (20 ml) were added to 300 ml of C_6H_6 in the irradiation vessel. The mixture was continually agitated with a stream of nitrogen gas and, after wrapping the vessel with aluminium foil and placing it in an ice-water bath, the UV lamp was turned on. The solution gradually became dark wine-red owing to the formation of (η^6-C_6H_6)Cr(CO)$_2$(C_8H_{14}). The progress of the reaction was conveniently monitored by diluting a small sample of the reaction mixture with an equal volume of hexane and following changes in the IR spectrum of the reaction mixture in the CO stretching region. The ν(CO) bands were: (η^6-C_6H_6)Cr(CO)$_3$, 1970 (a_1) and 1900 (e) cm^{-1}; (η^6-C_6H_6)Cr(CO)$_2$-(C_8H_{14}), 1900 (a') and 1850 (a'') cm^{-1}. After ca. 50 min, the a_1 mode of the tricarbonyl had disappeared and the irradiation process was terminated. The mixture was then allowed to stand for 30 min with a steady stream of nitrogen gas bubbling through it in order to flush out any remaining CO. Carbon disulfide (25 ml) or CSe_2 (1 g, ca. 6 mmol) was added to the reaction mixture and the ice-water bath was removed. The solution slowly turned dark-yellow and some brownish-black decomposition product was evident. After standing for 2—3 h, the mixture was filtered through a medium-porosity, sintered-glass filter to remove the decomposition product. The benzene solvent and excess *cis*-cyclooctene were removed from the clear orange filtrate on a rotary evaporator using a mechanical vacuum pump protected by a liquid nitrogen trap. The residue contained (η^6-C_6H_6)Cr(CO)$_2$(CX) mixed with about 10% (η^6-C_6H_6)Cr(CO)$_3$; the desired chalcocarbonyl product was isolated by preparative TLC. The crude product was dissolved in a minimum quantity of Et_2O and then spotted onto three TLC plates and eluted with a hexanes/Et_2O mixture (3/1 for the thiocarbonyl and 2/1 for the selenocarbonyl derivative). The trailing, dark-yellow product band was quickly scraped off with a spatula and the scrapings were placed in a medium-porosity, sintered-glass filter and washed repeatedly with Et_2O. The resulting filtrate was reduced to dryness at room temperature on the rotary evaporator when orange crystals formed. The thio- and selenocarbonyl products were further purified by recrystallization from hexanes/Et_2O mixtures. (η^6-C_6H_6)Cr(CO)$_2$(CS): 0.20 g, 53% yield; m.p. 123°C (dec.). Mass spectrum: *m/e* 230 (P^+). IR (CS_2): ν(CO) 1962s (a'), 1932s (a''); ν(CS) 1220s (a') cm^{-1}. NMR (CH_2Cl_2) δ: 99.3 ($^{13}C_6H_6$), 231.5 (^{13}CO), 346.3 (^{13}CS), 374.1 ppm ($C^{17}O$). (η^6-C_6H_6)Cr(CO)$_2$(CSe): 0.15 g, 33% yield; m.p. 99°C (dec.). Mass spectrum: *m/e* 278 (P^+). IR (CS_2): ν(CO) 1975s (a'), 1932s (a''); ν(CSe) 1061s (a') cm^{-1}. NMR (CH_2Cl_2) δ: 98.5 ($^{13}C_6H_6$), 229.0 (^{13}CO), 363.7 (^{13}CSe), 375.7 ppm ($C^{17}O$). Anal. Found: C, 39.2; H, 2.26; Se, 28.1. Calcd for $C_9H_6O_2SeCr$: C, 39.0; H, 2.18; Se, 28.5%.

Preparation of Cr(CO)$_5$(CX)

Before describing the syntheses of these complexes, it should be emphasized that the crude (η^6-C_6H_6)Cr(CO)$_2$(CX) products from the previous reactions can be used directly. Removal of traces of (η^6-C_6H_6)Cr(CO)$_3$ is not necessary because Cr(CO)$_6$ is not formed under the mild conditions employed and the relatively low volatility of the tricarbonyl prevents it co-subliming with the volatile pentacarbonyl complexes.

A solution of (η^6-C_6H_6)Cr(CO)$_2$(CX) (0.50 g, 2.2 mmol, X = S; 1.8 mmol, X = Se) in THF (50 ml) was syringed into a 75-ml stainless-steel bomb (Matheson, Ltd.) fitted with a valve. This valve was securely tightened to the bomb and, after degassing the solution by repeated freeze-thaw cycles using liquid nitrogen, CO gas (22 mmole) was admitted to the bomb at liquid nitrogen temperature from a calibrated vacuum manifold. The valve was closed and the bomb was placed in an oil bath at 70° C for 3 days for the thiocarbonyl complex. In the case of the selenocarbonyl complex, a 50° C oil bath was used and the reaction was complete in 4 h. Under these conditions and assuming that no CO gas dissolves, the pressure in the bomb is approximately 20 atm. At the end of the reaction, the bomb was cooled to liquid nitrogen temperature before opening the valve. The remaining CO gas was slowly pumped off under vacuum in a well-ventilated area. The contents of the bomb were then allowed to warm up to room temperature following which they were syringed out into a 250-ml round-bottomed flask. The flask was shielded from light as much as possible because the products (especially the selenocarbonyl) are photosensitive. The THF solvent was removed at —25 to —15°C (C_6H_5Cl/dry-ice slush bath) on a rotary evaporator using a mechanical pump protected by a liquid nitrogen trap (the temperature was kept close to the lower limit during solvent removal from $Cr(CO)_5(CSe)$ while the upper limit was maintained for the much less volatile $Cr(CO)_5(CS)$ complex). Sublimation of the residue under vacuum (0.1 Torr/25° C) onto an ice-water cooled finger inserted into the flask gave analytically pure samples of the deep-yellow complexes. $Cr(CO)_5(CS)$: 0.45 g, 87% yield; m.p. 87—88° C. Mass spectrum: *m/e* 236 (P^+). IR (gas phase): ν(CO) 2097.5ms (a_1^{eq}), 2032.7s (a_1^{ax}), 2070.6vs (e); ν(CS) 1279.7s (a_1); IR (CS_2): ν(CO) 2088.4m (a_1^{eq}), 2017.3s (a_1^{ax}), 1989.0vs (e); ν(CS) 1261.0s (a_1) cm^{-1}. NMR (CH_2Cl_2) δ: 212.4 (*cis*-^{13}CO), 209.4 (*trans*-^{13}CO), 332.2 (^{13}CS), 373.0 (*cis*-$C^{17}O$), (*trans*-$C^{17}O$) not observed; NMR ($CDCl_3$, ref. 2) δ: 211.4 (*cis*- and *trans*-^{13}CO), 331.1 ppm (^{13}CS). $Cr(CO)_5(CSe)$: 0.23 g, 45% yield. Mass spectrum: *m/e* 284 (P^+). IR (gas phase): ν(CO) 2097.8ms (a_1^{eq}), 2037.8s (a_1^{ax}), 2010.5vs (e); ν(CSe) 1095.4s (a_1); IR (CS_2): ν(CO) 2087.6m (a_1^{eq}), 2023.4s (a_1^{ax}), 1991.8vs (e); ν(CSe) 1077.4s (a_1) cm^{-1}. NMR (CH_2Cl_2) δ: 211.7 (*cis*-^{13}CO), 208.1 (*trans*-^{13}CO), 360.7 (^{13}CSe), 373.4 (*cis*-$C^{17}O$), 385.3 ppm (*trans*-$C^{17}O$). Anal. Found: C, 25.6; Se, 27.8. Calcd for C_6O_5SeCr: C, 25.5; Se, 27.9%.

Reactions of $Cr(CO)_5(CX)$ with cyclohexylamine

In a typical experiment, a mixture of $Cr(CO)_5(CX)$ (ca. 0.5 mmol) and $C_6H_{11}NH_2$ (0.07 ml, 0.7 mmol) in hexane (25 ml) was stirred at room temperature for 6 h. The color of the solution gradually changed from golden- to lemon-yellow. Following filtration and solvent removal from the filtrate on a rotary evaporator, a yellow crystalline solid was obtained. Spectroscopic data established this product to be $Cr(CO)_5(CNC_6H_{11})$ (ca. 0.1 g, 85% yield; m.p. 48.5° C). Mass spectrum; *m/e* 301 (P^+). IR (hexane): ν(CO) 2063w (a_1^{eq}), 1955vs (e), 1945s(sh) (a_1^{ax}); ν(CN) 2152w (a_1) cm^{-1}. ^{13}C NMR (CH_2Cl_2, —60° C) δ: 215.0 (*cis*-^{13}CO), 217.3 (*trans*-^{13}CO), 159.6 ppm (^{13}CN, $^1J(^{14}N—^{13}C)$ = 14.5 Hz).

Similar reactions of $Cr(CO)_5(CX)$ with $(C_6H_{11})_2NH$ and MeCN only resulted in gradual decomposition of the starting material, as evidenced by changes in the IR and ^{13}C NMR spectra of the reaction mixtures.

Reactions of $Cr(CO)_5(CX)$ with halide ions

A THF solution (25 ml) containing $Cr(CO)_5(CS)$ (0.144 g, 6.1 mmol) and Bu_4NI (0.150 g, 7.6 mmol) was heated gently at 50°C for 4 h. At this time, the ν(CO) bands in the IR spectrum of the reaction mixture had reached their maximum intensities. The solvent was then removed in vacuo and the solid residue was taken up in a minimum quantity of CH_2Cl_2. Addition of Et_2O caused the immediate formation of yellow crystals (0.21 g) which ^{13}C NMR and subtractive FT-IR showed to be a 2/3 mixture of the tetra-n-butylammonium salts of $[Cr(CO)_5I]^-$ and *trans*-$[Cr(CO)_4(CS)I]^-$. $Bu_4N[Cr(CO)_5I]$: IR (CH_2Cl_2): ν(CO) 2053.9w (a_1^{eq}), 1969.2w(sh) (b_1), 1923.0vs (e), 1864.9w (a_1^{ax}) cm^{-1}. ^{13}C NMR (CH_2Cl_2) δ: 227.9 (*cis*-^{13}CO), 217.6 ppm (*trans*-^{13}CO). *trans*-$Bu_4N[Cr(CO)_4(CS)I]$: IR (CH_2Cl_2): ν(CO) 2054.8vw (a_1), 1955.2vs (e) cm^{-1}. ^{13}C NMR (CH_2Cl_2) δ: 215.4 (^{13}CO), 330.0 ppm (^{13}CS).

Similar reactions of both $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$ with other halide ions ($Y^- = Cl^-, I^-$) in THF solution at room temperature also gave mixtures of $[Cr(CO)_5Y]^-$ and *trans*-$[Cr(CO)_4(CX)Y]^-$: X = Se, $Y^- = I^-$, 3/1; X = S, $Y^- = Cl^-$, 2/3; X = Se, $Y^- = Cl^-$, 5/4. ^{13}C NMR δ: *trans*-$Bu_4N[Cr(CO)_4(CSe)I]$: 214.0 (^{13}CO), (^{13}CSe) not observed; $[Ph_3P{=}N{=}PPh_3][Cr(CO)_5Cl]$: (*cis*-$^{13}CO$), 224.9 (*trans*-$^{13}CO$); *trans*-$[PPh_3{=}N{=}PPh_3][Cr(CO)_4(CS)Cl]$: 217.0 ($^{13}CO$), 330.4 ($^{13}CS$); *trans*-$[PPh_3{=}N{=}PPh_3][Cr(CO)_4(CSe)Cl]$: 215.7 ($^{13}CO$), 359.4 ppm ($^{13}CSe$).

Results and discussion

Although only the reactions of the benzene complexes were described in the Experimental section, various complexes of the type (η^6-Arene)$Cr(CO)_2(CX)$ react smoothly with CO under pressure to give high yields of the $Cr(CO)_5(CX)$ derivatives (eq. 1). The reaction rates depend critically on the nature of the substituents on the arene ring (e.g., $PhCO_2Me > o\text{-}C_6H_4Me_2 > C_6H_6$) and the selenocarbonyl compounds react significantly faster than the corresponding thiocarbonyls. A detailed kinetic investigation of the analogous arene replacement reactions with tertiary phosphines and phosphites is currently in progress [8]. The arene replacement reactions reported here are directly analogous to those of (η^6-Arene)$M(CO)_3$ (M = Cr, Mo, W) with various monodentate ligands (L) to form *fac*-$M(CO)_3L_3$ [9,10], and most probably proceed by similar mechanisms involving η^4- and η^2-Arene intermediates.

The new route to $Cr(CO)_5(CS)$ is much easier and gives a far better yield than the thiophosgene route described earlier. The spectroscopic properties of the two $Cr(CO)_5(CX)$ complexes leave no doubt as to their formulation. The IR spectra are closely similar and are in complete accord with the expected C_{4v} molecular symmetry, as are the ^{13}C and ^{17}O NMR data — the intensities due to the *cis* and *trans* carbonyls are in the predicted 4/1 ratio. The new selenocarbonyl complex, $Cr(CO)_5(CSe)$, is the first example of a transition metal complex containing only CO and CSe ligands. Selenocarbonyl complexes are extremely rare [11—13] and provide a unique opportunity to study the properties of CSe which appears to be unstable as a diatomic species even at very low temperatures unlike its congeners CO and CS. $Cr(CO)_5(CSe)$ is a highly-volatile, air-stable, deep-yellow crystalline solid that sublimes before melting and has a characteristic odor reminiscent of CSe_2; it is readily soluble in all common organic solvents. The major fragments in its mass spectrum are P^+, $(P - 2\,CO)^+$, $Cr(CSe)^+$, and Cr^+ providing tentative evidence for strong Cr—CSe bonding.

Dombek and Angelici have made extensive studies of the chemical properties of $W(CO)_5(CS)$ [14], and consequently we felt that it would be of interest to examine a few reactions of $Cr(CO)_5(CS)$ and $Cr(CO)_5(CSe)$ with nucleophiles for the purposes of comparison. While the reactions of $Cr(CO)_5(CX)$ with cyclohexylamine closely parallel those for $W(CO)_5(CS)$ [14] with the quantitative formation of $Cr(CO)_5(CNC_6H_{11})$, the reactions with halide ions do not. Previously, the tungsten derivative had been shown to give exclusively *trans*-$[W(CO)_4(CS)I]^-$ on reaction with I^- [2]. However, the chromium chalcocarbonyl complexes give mixtures of $[Cr(CO)_5Y]^-$ and *trans*-$[Cr(CO)_4(CX)Y]^-$ on reaction with Cl^- and I^-. In an attempt to see if the $[Cr(CO)_5Y]^-$ ions were produced by thermal decomposition of the *trans*-$[Cr(CO)_4(CX)Y]^-$ ions, we monitored the thermal decomposition of a $[Cr(CO)_5I]^-$/*trans*-$[Cr(CO)_4(CS)I]^-$ mixture in THF at 50°C by FT-IR spectroscopy. At no time was there any evidence for an increase in the intensities of the $\nu(CO)$ bands due to the $[Cr(CO)_5I]^-$ ion. Clearly, there must be both CO and CX replacement occurring during the reactions of $Cr(CO)_5(CX)$ with halide ions in direct contrast with the normal chemical behaviour of transition metal chalcocarbonyl complexes [13]. However, it should be mentioned that Dombek and Angelici noticed that on extended reaction with PPh_3, $W(CO)_5(CS)$ also undergoes some loss of CS [2]. The difference in the behaviour of $Cr(CO)_5(CS)$ and $W(CO)_5(CS)$ with halide ions in the line with the metal—CS force constants for these systems, viz., $f(Cr—CS) = 2.45$ mdyne $Å^{-1}$ and $f(W—CS) = 3.31$ mdyne $Å^{-1}$; the metal—CO force constants in both cases are appreciably lower perhaps reflecting the facility of CO substitution [15].

Following the successful preparation of the $Cr(CO)_5(CX)$ derivatives, we hoped to be able to extend reaction 1 to the synthesis of the analogous complexes of molybdenum and tungsten. However, although the $(\eta^6\text{-Arene})M(CO)_3$ precursors can readily be prepared, we were unable to form any suitable intermediate complex of the type $(\eta^6\text{-Arene})M(CO)_2L$ ($L = C_8H_{14}$, THF, etc.) for subsequent reaction with CX_2/PPh_3. It appears that the quantum yields of the photochemically-induced CO substitution reactions of $(\eta^6\text{-Arene})M(CO)_3$ are extremely low [16]. Consequently, while our route to the chromium compounds is the easiest, it is still necessary to resort to the thiophosgene route for $Mo(CO)_5(CS)$ and $W(CO)_5(CS)$, despite the poor yields obtained.

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References

1 J.E. Ellis, J. Amer. Chem. Soc., 96 (1974) 7825.
2 B.D. Dombek and R.J. Angelici, Inorg. Chem., 15 (1976) 1089.

3 A.M. English, K.R. Plowman, I.S. Butler, G. Jaouen, P. LeMaux and J.Y. Thépot, J. Organometal. Chem., 132 (1977) C1.
4 W. Strohmeier, Angew. Chem. Int. Ed. Engl., 3 (1964) 730.
5 I.S. Butler, D. Cozak and S.R. Stobart, Inorg. Synth., 19 (1979) 193.
6 D. Cozak, I.S. Butler, J.P. Hickey and L.J. Todd, J. Magn. Reson., 33 (1979) 149.
7 M.D. Rausch, G.A. Moser, E.J. Zaiko and A.L. Lipman, Jr., J. Organometal. Chem., 23 (1970) 185; see also C.A. Mahaffy and P.L. Pauson, Inorg. Synth., 19 (1979) 154.
8 A. Ismail and I.S. Butler, unpublished results.
9 A. Pidcock, J.D. Smith and B.W. Taylor, J. Chem. Soc. (A), (1966) 1604.
10 G.R. Dobson, I.W. Stolz and R.K. Sheline, Adv. Inorg. Chem. Radiochem., 8 (1966) 1.
11 G.C. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) 1206.
12 J.-P. Battioni, D. Mansuy and J.-C. Chottard, Inorg. Chem., 19 (1980) 791.
13 (a) I.S. Butler, Acc. Chem. Res., 10 (1977) 359. (b) P. Yaneff, Coord. Chem. Rev., 23 (1977) 183.
14 B.D. Dombek and R.J. Angelici, Inorg. Chem., 15 (1976) 2403, and references cited therein.
15 A.M. English, K.R. Plowman and I.S. Butler, Inorg. Chem., submitted for publication.
16 M. Wrighton, Chem. Rev., 74 (1974) 401.