Pentacarbonyl(thione) Complexes of Chromium and Tungsten Prepared by Unusual Methods†

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The synthesis of pentacarbonyl(thione) complexes of chromium and tungsten *via* reaction of carbene complexes with lithium sulfides is reported.

The standard method for the preparation of $M(CO)_5L$ compounds (L = heterocyclic thione) utilises photochemical carbonyl substitution.[1] We have reported a number of reactions which afford thione complexes by the modification of an existing ligand.[2] While studying the interaction of Fischer-type carbene complexes with anionic organosulfur compounds, we discovered two new conversions which also afford thione complexes. Although the yields are rather low, the unique interactions involved, as well as the fact that one of the thiones is unstable in uncoordinated form and has not been prepared before, merit this brief report.

Reactions of organolithium compounds with CS_2[3,4] have not been researched as well as those of Grignard reagents[5] but, nevertheless, the outcome seems identical in that dithioesters are formed on alkylation of the reaction product. We have embarked upon a study to determine whether the product of the reaction between BuLi and CS_2 is a strong enough nucleophile to bind to the carbene carbon in carbene complexes in the way that RS^- is routinely used to prepare thiocarbene complexes.[6] With a similar purpose in mind, we also converted lithiated thiazoles, previously used in carbene complex syntheses,[7] into their corresponding sulfides by treatment with elemental sulfur.
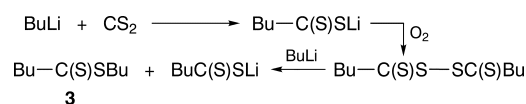
Reaction of BuLi with CS_2 (1:1 molar ratio) yielded a deep red solution in diethyl ether which was subsequently reacted with a methoxy(methyl)carbene complex of either chromium or tungsten. The resulting mixture was either acidified (with CF_3SO_3H) or treated with alkylating agent (CF_3SO_3Me) to give unexpected oily products with the same sulfur-containing ligand:

$$[(CO_5)M\{S{=}C(SBu)Bu\}] \qquad (\textbf{1}, \text{M} = \text{Cr}; \textbf{2}, \text{M} = \text{W})$$
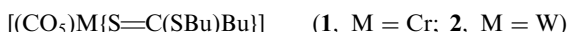
Since neither the proton or the methyl group appeared in the product, the procedure was repeated using the chromium carbene complex, but omitting the protonation or alkylation step. Product **1** could be isolated in essentially the same yield. In the absence of carbene complex, the relatively unstable free dithioester, $Bu(BuS)C{=}S$ (**3**) was separated as an oil by column chromatography and isolated as an unstable, yellow oil. The total procedure was repeated with MeLi and PhLi as starting reagents, but no stable products could be isolated. The physical characterisation data of the new complexes showed no discrepancies.

In the absence of any mechanistic evidence, we rationalised the ligand formation in terms of an oxidation step[8] by small amounts of oxygen present, followed by reaction with a second BuLi molecule (Scheme 1).

In the presence of the metal carbene complex, substitution by the dithioester then leads to the isolated product. It is known that dialkyl sulfides readily react with carbene com-

plexes to produce neutral pentacarbonyl(thioether) metal complexes.[9] Reaction of BuLi and CS_2 in the presence of excess oxygen did not lead to a higher yield of the product. Treatment of the reaction mixture with BuBr did, however, increase the yield, which can be interpreted in terms of a reaction with the initial adduct BuC(S)Li.

Reaction of the same carbene complexes with 4-methylthiazolyl sulfide or benzothiazolyl sulfide gave bright orange solutions, the contents of which remained on the origin during development on SiO_2 thin layer plates with both diethyl ether and dichloromethane as eluents, confirming the formation of ionic adducts. Protonation or alkylation afforded the products shown in Scheme 2.

In the absence of a carbene complex, alkylation of these sulfides leads to formation of the corresponding alkyl derivative,[10] as shown in eqn. (1).
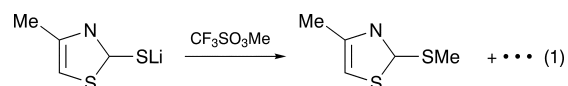
Reaction of $[W(CO)_5\{CMe(OCOMe)\}]$[11] with 2-benzothiazolyl sulfide led to an orange–red salt that on acidification also formed the thione complex **6**. This again confirmed the presence of an anionic intermediate that, through rearrangement and bond-breaking during acidification, formed a thione capable of substituting the carbene ligand. We thus propose the general mechanism (Scheme 3) for thione formation.
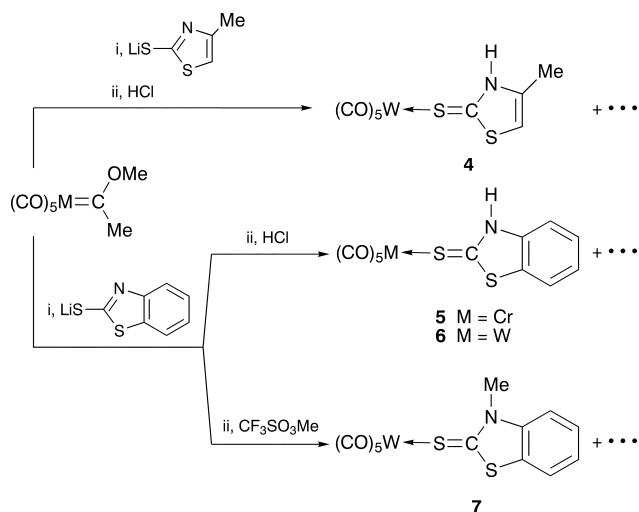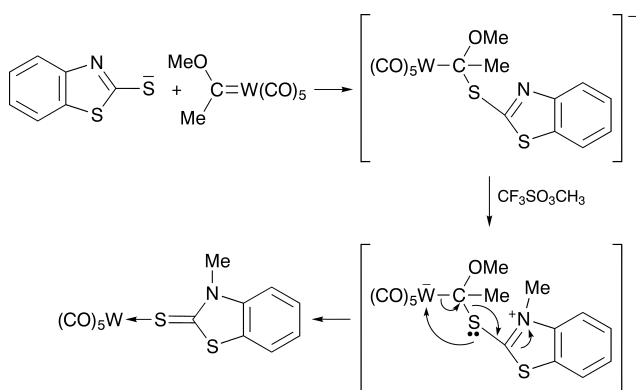
Scheme 1

Scheme 2

Table 1 Physical, infrared and ^{1}H NMR data (J/Hz) for complexes **1**–**7**

| Complex | Yield (%) | Mp/°C | ν(CO)(cm^{-1}) | | | | δ_H/ppm |
			A$_{1(m)}$	B$_{1(w)}$	E$_{(vs)}$	A$_{1(s,sh)}$	
1	14	oil	2076	1985	1948	1934	3.00 (t, 2 H, H1, J = 8), 1.57–1.73 (m, 2 H, H2), 1.29–1.52 (m, 4 H, H3,7), 0.92 (t, 3 H, H4, J = 7), 3.2 (t, 2 H, H5, J = 7), 1.73–1.88 (m, 2 H, H6), 0.93 (t, 3 H, H8, J = 7)
2	23	oil	2073		1943	1929	3.00 (t, 2 H, H1, J = 8), 1.42–1.56 (m, 2 H, H2), 1.21–1.33 (m, 4 H, H3,7), 0.83 (t, 3 H, H4, J = 7), 3.24 (t, 2 H, H5, J = 7), 1.67–1.80 (m, 2 H, H6), 0.96 (t, 3 H, H8, J = 7)
3	10	oil					3.19 (t, 2 H, H5), 2.99 (t, 2 H, H1), 1.86–1.68 (m, 2 H, H2), 1.52–1.67 (m, 2 H, H6) 1.31–1.50 (m, 4 H, H3,7), 0.91 (t, 3 H, H8), 0.90 (t, 3 H, H4)
4	14	71–73	2071	1982	1933	1912	9.96(br, 1 H, N–H), 2.31(s, 3H, Me), 6.52(s, 1H, H5)
5	20	127–129	2067		1942	1924	13.3 (br, 1H, N–H), 7.97 (d, 1H, H4, J = 8) 7.38–7.56 (m, 3H, H5,6,7)
6	15	132–134	2071	1982	1936	1915	10.26 (br, 1H, N–H), 7.62 (d, 1H, H4, J = 8), 7.34–7.52 (m, 3H, H5,6,7)
7	17	135–137	2072		1934	1918	4.0 (s, 3H, N–Me), 7.72 (d, 1H, H4, J = 8), 7.32–7.56 (m, 3H, H5,6,7)

Table 2 Analytical and ^{13}C NMR data

| Complex | Formula | Found (calcd.) | | | | δ_c/ppm |
		C	H	N	S	
1	C$_{14}$H$_{18}$O$_5$S$_2$Cr	44.0 (44.3)	4.7 (4.5)	– –	16.8 (16.5)	239.5 (C=S), 214.8 (*cis* CO), 223.3 (*trans* CO), 49.5 (C1), 33.1 (C2), 22.3 (C3), 13.6 (C4), 52.0 (C5), 36.9 (C6), 29.1 (C7), 13.7 (C8)
2	C$_{14}$H$_{18}$O$_5$S$_2$W	32.7 (32.4)	3.5 (3.2)	– –	12.3 (12.0)	216.0 (C=S), 196.9 (*cis* CO), 204.1 (*trans* CO), 37.4 (C1), 28.9 (C2), 22.1 (C3), 13.6 (C4), 50.6 (C5), 32.8 (C6), 22.2 (C7), 13.7 (C8)
4	C$_9$H$_5$O$_5$NS$_2$W	23.8 (23.6)	1.1 (1.0)	3.1 (3.2)	–	191.6 (C=S), 197,7 (*cis* CO), 201.1 (*trans* CO), 139.7 (C4), 111.47 (C5), 14.0 (C6)
5	C$_{12}$H$_5$O$_5$NS$_2$Cr	40.1 (40.4)	1.4 (1.3)	3.9 (3.5)	–	194.4 (C=S), 216.6 (*cis* CO), 223.5 (*trans* CO), 129.0 (C4), 125.1 (C5), 123.3 (C6), 126.1 (C7), 130.7 (C8), 142.7 (C9)
6	C$_{12}$H$_5$O$_5$NS$_2$W	29.3 (29.2)	1.0 (1.1)	2.9 (2.7)	–	190.9 (C=S), 197,4 (*cis* CO), 202.2 (*trans* CO), 128.2 (C4), 122.3 (C5), 112.8 (C6), 125.6 (C7), 130.2 (C8), 140.4 (C9)
7	C$_{13}$H$_7$O$_5$NS$_2$W	30.9 (30.6)	1.4 (1.2)	2.8 (3.0)	–	191.5 (C=S), 197.6 (*cis* CO), 201.6 (*trans* CO), 128.0 (C4), 122.3 (C5), 112.9 (C6), 126.0 (C7), 130.2 (C8), 142.7 (C9), 34.1 (N–Me)

Scheme 3

In contrast to the preparation of the dithioester complexes **1** and **2** above, the first step involves a nucleophilic addition which is followed by nitrogen protonation or alkylation and C′–S bond cleavage. The nitrogen atom in the anionic intermediate appears to have a higher proton affinity than the oxygen of the methoxy group, thus preventing elimination of HOMe upon protonation. Carbene substitution by a thione has also been included in the final step.

Experimental

All reactions involving organometallic reagents were performed under an atmosphere of argon using standard vacuum-line and Schlenk techniques.

Typical Procedure for Preparing Dithioester Complexes.— Complex **1** (carbon disulfide 0.12 cm^3, 2 mmol, 1.26 g cm^{-3}) was dissolved in diethyl ether (40 cm^3) and cooled to −80 °C. *n*-Butyllithium (1.25 cm^3, 2 mmol, 1.6 mol dm^{-3}) was added dropwise. The solution immediately turned dark red and was stirred at −80 °C for 30 min. Subsequently, [Cr(CO)$_5${CMe(OMe)}] (500 mg, 2 mmol) was dissolved in diethyl ehter (10 cm^3) and added slowly to the first solution. The colour changed from red to yellow. The mixture was stirred for 2 h while the temperature increased to 0 °C and the colour deepened to orange–red. The solution was cooled to −50 °C and either alkylated with methyl triflate (0.23 cm^3, 2 mmol) or

acidified with CF$_3$SO$_3$H (0.18 cm^3, 2 mmol). The temperature was allowed to rise to 25 °C, after which the solution was evaporated to dryness, the residue extracted with hexane and the complex mixture chromatographed to yield the main product as a red oil.

Typical Procedure for Preparing Thione Complexes.—Complex **4**. 4-Methylthiazole (0.18 cm^3, 2 mmol) was dissolved in THF (30 cm^3) and cooled to −80 °C. *n*-Butyllithium (1.25 cm^3, 2 mmol, 1.6 mol dm^{-3}) in hexane was added dropwise to the solution and stirred for 30 min. Sulfur (0.06 g, 2 mmol) was added to the bright yellow solution and the mixture stirred for 1 h. Subsequently, [W(CO)$_5${CMe(OMe)}] (764 mg, 2 mmol) in THF (20 cm^3) was added dropwise and the temperature allowed to increase to −10 °C. The colour changed from orange to orange–red. After 2 h HCl (9.37 cm^3, 0.438 mol dm^{-3}) was added dropwise. The dark red solution was stirred at room temperature for 1 h, evaporated to dryness and the residue extracted with CH$_2$Cl$_2$. Chromatography on silica gel yielded a red product that crystallised from CH$_2$Cl$_2$– hexane (1:3) at −80 °C. The other thione complexes were prepared similarly.

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