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Preliminary communication

ACTIVATION OF CARBON DISULPHIDE BY METAL CARBONYL ANIONS: FORMATION OF TRITHIOCARBONATE COMPLEXES

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Summary

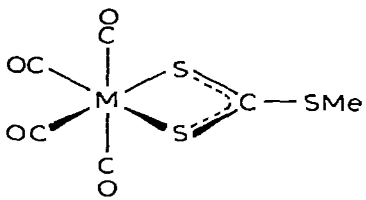
Trithiocarbonate complexes are formed when metal carbonyl anions are treated consecutively with carbon disulphide and a neutralising agent such as methyl iodide or $Re(CO)_5Br$.

Although activation of carbon disulphide by transition metal complexes is an area much studied of late (and recently reviewed [1] for the first time), no reports have appeared of attempts to directly exploit the electrophilic reactivity of carbon in the molecule. Nucleophiles such as cyanide ion do attack CS_2 at carbon [2], and it seemed likely that transition metal carbonyl anions might act similarly. We describe here such reactions, which unexpectedly provide trithiocarbonate complexes.

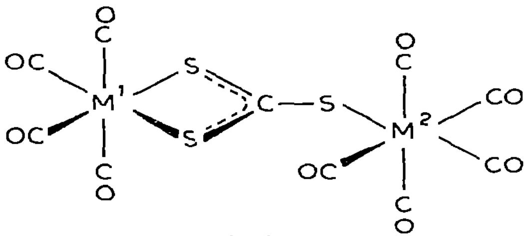
Treatment of tetrahydrofuran solutions of the sodium salts of $[M(CO)_5]^-$ (M = Mn, Re) with excess CS_2 for 1 h, followed by methylation with methyl iodide, gave (5-10%) trithiocarbonate complexes $M(CO)_4S_2C(SMe)$ (I; M = Mn, Re); for I (M = Re) m.p. 94°; ν(CO) (hexane) 2109m, 2014s, 1999s, 1963s cm^{-1}; τ 7.42s; *m/e* $(M - nCO)^+$ (n = 0-3). Analogous products $Fe(CO)(C_5H_5)S_2C(SMe)$ [3] and $Mo(CO)_2(C_5H_5)S_2C(SMe)$ [4] were obtained from $[Fe(CO)_2(C_5H_5)]^-$ and $[Mo(CO)_3(C_5H_5)]^-$ respectively.

The reaction of $[Re(CO)_5]^-$ with CS_2/MeI also gave small amounts of a yellow crystalline complex $(CO)_4ReS_2CSRe(CO)_5$ (m.p. 135-140° (dec.); ν(CO) (hexane) 2147w, 2103m, 2046s, 2005s, 1992s, 1955s cm^{-1}; *m/e* $(M - nCO)^+$ (n = 0-9)). A trithiocarbonate-bridged structure II (M^1 = M^2 = Re) is strongly indicated by the carbonyl IR spectrum, which is composed of bands typical of both the $(CO)_4ReS_2C$ (2103m, 2005s, 1992s, 1955s cm^{-1}) and $(CO)_5ReS$ (2147w, 2046s, 1992s cm^{-1}) structural units, by comparison with the spectra of I (M = Re) and III respectively.

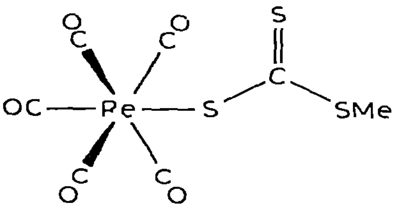
The apparent structural relationship of I (M = Re) and II (M^1 = M^2 = Re) led us to treat $[Re(CO)_5]^-$ with CS_2 and $Re(CO)_5Br$ consecutively in the hope of



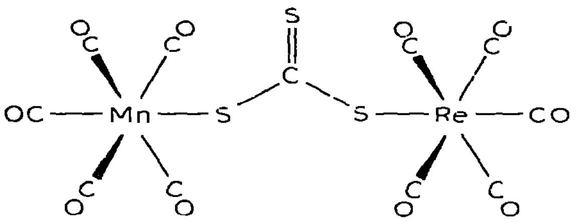
(I)



(II)



(III)



(IV)

forming the dirhenium complex. That this reaction yielded II (M^1 = M^2 = Re) readily (45%) provides further support for the structural assignment. Only IR spectroscopic evidence was obtained for formation of $(CO)_4MnS_2CSMn(CO)_5$ (II; M^1 = M^2 = Mn) by a similar route. Mixed metal analogues are obtained, however, if either $[Mn(CO)_5]^-$ or $[Re(CO)_5]^-$ is allowed to react with CS_2, and is subsequently treated with $Re(CO)_5Br$ or $Mn(CO)_5Br$, respectively. The major product (5%) in each case is II (M^1 = Mn, M^2 = Re), with minor formation of II (M^1 = Re, M^2 = Mn), suggesting that each reaction sequence involves a common intermediate. Most likely is $(CO)_5ReSC(S)SMn(CO)_5$ (IV) which would be expected to form II (M^1 = Mn, M^2 = Re) preferentially on CO elimination.

Another example of this tendency towards trithiocarbonate formation has been presented in the very recent report [5] of the determination of the molecular structure of $[(CO)_4ReS_2CSRe(CO)_4]_2$, prepared from $Re(CF_3)(CO)_5$ and CS_2. It is interesting that this complex can be envisaged as arising from dimerisation of $(CO)_4ReS_2CSRe(CO)_5$, with sulphur bridge formation and CO elimination, though we have not yet established that this can occur. A complex $(PPh_3)(NO)NiS_2CSNi(PPh_3)_2(NO)$, apparently related to II, has been prepared [6] from CS_3^{2-} and $Ni(I)(PPh_3)_2(NO)$, but it was not possible for us to obtain II (M^1 = M^2 = Mn or Re) by a similar route.

The activation by metal carbonyl anions of other molecules (e.g. CO_2 and RNCS) containing electrophilic carbon atoms, and the process by which trithiocarbonate complexes are formed from CS_2 in the reactions described here, are under investigation. It is noteworthy to record in connection with the latter that addition of sulphur to the $[Re(CO)_5]^-/CS_2/MeI$ reaction, prior to MeI addition, serves to promote formation (9%) of $Re(CO)_5SC(S)(SMe)$ (III) {m.p. 83°; ν(CO) (hexane) 2140w, 2038s, 1991s cm^{-1}; τ 7.27s; m/e $(M - nCO)^+$ (n = 0-4)} over I (M = Re) (5%).

References

1 I.S. Butler and A.E. Fenster, J. Organometal. Chem., 66 (1974) 161.
2 G. Bähr, Angew. Chem., 70 (1958) 606.
3 R. Bruce and G.R. Knox, J. Organometal. Chem., 6 (1966) 67.
4 R. Havlin and G.R. Knox, Z. Naturforsch. B, 21 (1966) 1108.
5 G. Thiele, G. Liehr and E. Lindner, J. Organometal. Chem., 70 (1974) 427
6 H. Brunner, Z. Naturforsch. B, 24 (1969) 275.