Electrophilic Addition of Oxygen, Sulphur, and Selenium to η^2-CS_2 and η^2-CS_2Me Cobalt Complexes

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The reactions of oxygen, sulphur, and selenium with the complexes [(triphos)Co(η^2-CS_2)] and [(triphos)Co(η^2-CS_2Me)]BPh_4 [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] are described; these reactions provide evidence for the carbenoid nature of the metal–(η^2-CS_2) and metal–(η^2-CS_2Me) moieties.

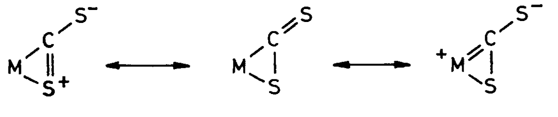
Much of the interest in CS_2 metal complexes comes from the versatile chemistry of the CS_2 molecule when it is co-ordinated to a metal in a bidentate fashion with carbon and sulphur atoms acting as donors. Co-ordination of CS_2 to metals makes it more electron rich, and in particular the sulphur atoms become potential nucleophilic centres, susceptible to attack by electrophilic reagents.[1,2] On the other hand, the dual nature of the metal–CS_2 moiety as an electrophilic and nucleophilic reagent has been demonstrated recently by 1,3-cycloadditions of activated alkynes.[3]

The chemical evidence indicates that a considerable electronic delocalization occurs over the three atoms of the η^2-CS_2 moiety. In particular, the canonical forms A, B, and C make significant contributions to the description of η^2-CS_2.

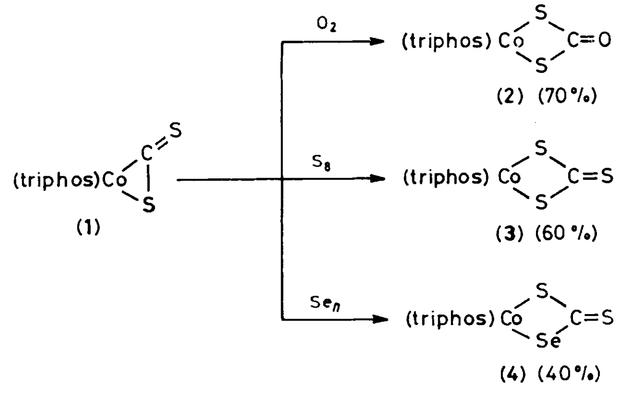
Structural data on η^2-CS_2 complexes confirm the contribution of the carbene-like canonical form C. The metal–carbon distances in many M–CS_2 moieties closely resemble those in related carbene complexes.[4,5]

To our knowledge, however, the carbenoid nature of η^2-CS_2 and η^2-CS_2Me metal complexes has not as yet been supported by chemical methods.

The present report concerns the reactions of oxygen, sulphur, and selenium with the cobalt complexes [(triphos)-Co(η^2-CS_2)],[2] (1) (Scheme 1), and [(triphos)Co(η^2-CS_2Me)]-BPh_4,† (5) (Scheme 3), [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$].



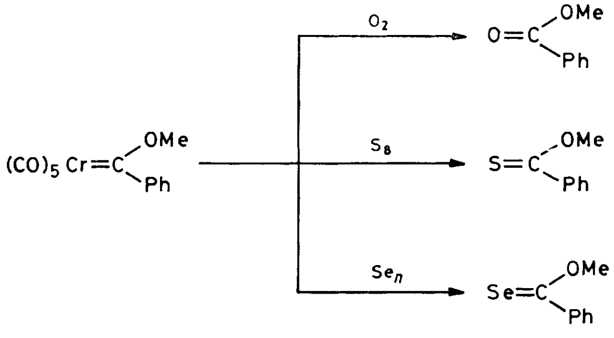
A B C



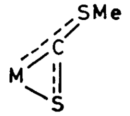
Scheme 1

A tetrahydrofuran solution of (1) reacted at room temperature with molecular oxygen, to produce a solution from which yellow-green crystals of (2) were obtained in good yield. The red sulphur and selenium compounds (3) and (4) were obtained analogously, but reflux temperatures and a large excess of finely powdered cyclo-octasulphur or amorphous selenium were required to give satisfactory yields.‡ Compounds (2) and (3) have been synthesised previously in this laboratory by different routes,[6] but (4) represents an unprecedented metal complex containing a bidentate monoselenodithiocarbonate ligand. The similarity of the spectroscopic properties of (4) with those of (3) and in particular (2), whose structure has been established by *X*-ray analysis,[6] suggests a distorted square pyramidal co-ordination around the cobalt atom, the three phosphorus atoms of the triphos ligand and the selenium atom and one sulphur atom of the monoselenodithiocarbonate ligand serving as donor atoms.

The reactions outlined in Scheme 1 may be viewed as providing evidence for the carbenoid nature of the metal–CS_2 moiety. A close analogy, in fact, can be found in the reactions of the Fischer-type carbene complex [$(CO)_5Cr{=}C(Ph)OMe$] with Group 6B elements[7] (Scheme 2).



Scheme 2



D

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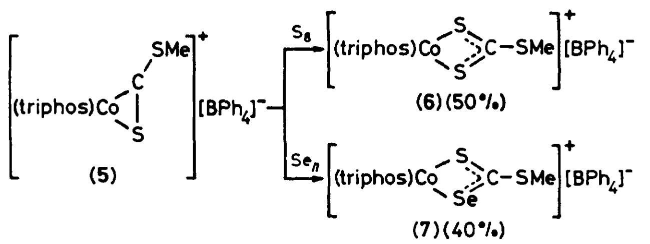
† Compound (5) was prepared under nitrogen by treatment of a CH_2Cl_2 solution of (1) with a slight excess of $MeSO_3F$ and $NaBPh_4$. Satisfactory elemental analytical data were obtained. [ν_{C-S} (Nujol) 1120 cm^{-1}; μ_{eff} (293 K) 2.08 μ_B; yield 85%.]

‡ Satisfactory elemental analytical data were obtained. Compound (2): ν^a(Nujol) 1690, $\nu_{C=O}$ 1600 cm^{-1}; μ_{eff} (293 K) 1.97 μ_B. Compound (3): $\nu_{C=S}$ (Nujol) 1040, ν_{C-S} 855 cm^{-1}; μ_{eff} (293 K) 2.10 μ_B. Compound (4): $\nu_{C=S}$ (Nujol) 1040, ν_{C-S} 790 cm^{-1}; μ_{eff} (293 K) 2.03 μ_B.

[a] Fermi resonance between the carbon–oxygen stretching mode and the first overtone band of the carbon–sulphur asymmetric stretching mode.



Scheme 3

The nature of the metal-(η^2-CS$_2$Me) bonding (D) in dithiomethoxycarbonyl complexes can be regarded in the same way as that of the CS$_2$ precursor.[5] Hence, it was not surprising that a tetrahydrofuran solution of (5) reacted at reflux temperature with an excess of cyclo-octasulphur or amorphous selenium to give green crystals of (6) and (7),§ respectively. The methyltrithiocarbonate complex (6) has been synthesised previously in this laboratory by a different route.[8] On the basis of spectroscopic and magnetic determinations, and an *X*-ray analysis performed on (6) a structure can be assigned to (7), where the cobalt atom is five-co-ordinated by the three phosphorus atoms of the triphos ligand and the selenium and the free sulphur atoms of the novel *S*-methyl monoselenodithiocarbonate ligand.

Solutions of (5) reacted with molecular oxygen, but no product has so far been isolated.

The reactions reported in this paper represent unprecedented reaction paths for η^2-CS$_2$ and η^2-CS$_2$Me metal complexes. What is more, they constitute a new, and, in some cases, the only method for the preparation of mixed thio- and selenocarbonate metal complexes, whose chemistry has only recently become the focus of increased attention.[8–10]

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§ Satisfactory elemental analytical data were obtained. Compound (6): ν_{C-S} (Nujol) 970 cm^{-1}; μ_{eff} (293 K) 2.09 μ_B. Compound (7): ν_{C-S} (Nujol) 960 cm^{-1}; μ_{eff} (293 K) 2.10 μ_B.