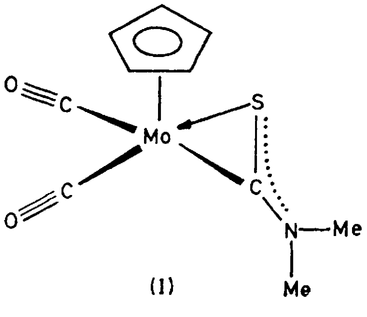
Thiocarboxamido Complexes of Manganese and Molybdenum

By P. M. Treichel* and W. K. Dean
(*Department of Chemistry, University of Wisconsin, Madison, Wisconsin* 53706)

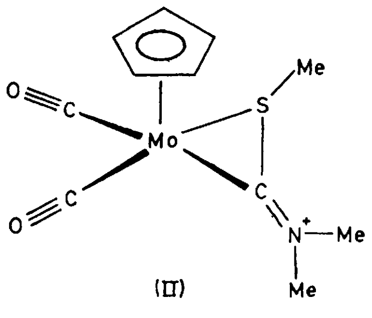
Summary Reaction of $CpMo(CO)_3^-$ and $ClCSNMe_2$ yields $CpMo(CO)_2CSNMe_2$ which gives $[CpMo(CO)_2C(SMe)NMe_2]^+$ (isolated eventually as the PF_6^- salt) with $[Me_3O]BF_4$; the same reactions are reported with $Mn(CO)_4PPh_3^-$; the structures of these complexes are believed to involve the C–S group as a bidentate three electron donor.

Thiocarbamoyl metal complexes have been prepared in reactions involving nucleophilic attack of amines[1] on $[CpFe(CO)_2CS]^+$ and of hydrosulphide ion[2] on $[Pt(PPh_3)_2(CNMe)_2]^{2+}$. No one has yet described studies on the obvious alternative route to such compounds from a metal carbonyl anion and a thiocarbamoyl halide, though an analogous reaction with dimethylcarbamoyl chloride is known.[3] We report here the preliminary results from such a study.



(I)

The reaction of either $CpMo(CO)_3^-$ or $CpMo(CO)_2PPh_3^-$ with $ClCSNMe_2$ (THF, 25°, 12 h) gave, unexpectedly, a red-brown crystalline dicarbonyl complex (I), $CpMo(CO)_2CSNMe_2$. Analogous products $Mn(CO)_4CSNMe_2$ and $Mn(CO)_3(PPh_3)CSNMe_2$ arise from $Mn(CO)_5^-$ and $Mn(CO)_4(PPh_3)^-$ respectively.



(II)

The i.r. spectrum of (I) contains ν_{CO} (1934, 1841 cm^{-1}), ν_{C-N} (1573 cm^{-1}) and ν_{CS} (1167 cm^{-1}); the ^1H n.m.r. spectrum of this compound contains resonances at τ 4·58 (int. 5), 6·27(3), and 6·40(3) assignable to (Cp) and non-equivalent Me protons. To accord with this data and with the stoicheiometry the structure shown in the Figure is proposed. The $CSNMe_2$ ligand is presumably acting as a $3e$ donor. This formulation provides for restricted rotation of the C–N bond leading to non-equivalent methyl groups.

Both CpMo(CO)$_2$CSNMe$_2$ and Mn(CO)$_3$(PPh$_3$)CSNMe$_2$ react with [Me$_3$O]BF$_4$, giving [CpMo(CO)$_2$C(SMe)NMe$_2$]$^+$, isolated as a PF$_6^-$ salt, (II), and [Mn(CO)$_3$(PPh$_3$)C(SMe)-NMe$_2$]BF$_4$. The molybdenum species (II) has ν_{CO} at 2006 and 1935 cm^{-1}, ν_{C-N} at 1616 cm^{-1} and ν_{CS} at 1155 cm^{-1}; and its ^{1}H n.m.r. spectrum contains singlet resonances at τ 3·98(5), 5·97(3), 6·07(3), and 7·65(3) assignable to the (Cp) protons, the two dissimilar N–Me groups, and the SMe group in structure (II).

(*Received*, 8*th May* 1972; *Com.* 782.)

[1] L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, 1971, **10**, 78.
[2] W. J. Knebel and P. M. Treichel, *Chem. Comm.*, 1971, 516.
[3] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometallic Chem.*, 1966, **5**, 341.