Cyclopentadienylmanganese Dicarbonyl Thiocarbonyl

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Summary The thiocarbonyl complex, $C_5H_5Mn(CO)_2(CS)$, has been isolated from the reaction of $C_5H_5Mn(CO)_2$-(*cis*-cyclo-octene) with carbon disulphide.

Following the discovery in 1966 of the first thiocarbonyl complex of a transition metal,[1] a molecular orbital calculation indicated[2] that transition-metal thiocarbonyl complexes should be more stable than their carbonyl analogues. Despite this, surprisingly few thiocarbonyl complexes have been reported and then only for the Group VIII metals, rhodium,[1-4] irridium,[4] cobalt,[5] iron,[6] and ruthenium.[7]

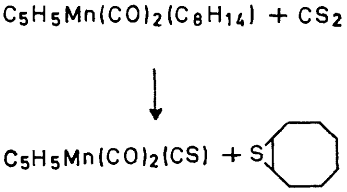
We have been attempting to extend the range of the known thiocarbonyl complexes and have succeeded in isolating in low yield the first thiocarbonyl complex of manganese, $C_5H_5Mn(CO)_2(CS)$ (I), from the reaction of $C_5H_5Mn(CO)_2$(*cis*-cyclo-octene) with carbon disulphide. The reaction is complex owing to the concomitant formation of $C_5H_5Mn(CO)_3$ and an, as yet, unidentified compound. The new compound, (I), forms fairly air stable, pale-green crystals, m.p. 53°. It analyses correctly and from its mass spectrum it has the correct molecular weight and the expected fragmentation pattern. The i.r. spectrum exhibits two strong terminal C–O stretching absorptions and one strong terminal C–S stretching absorption (Table). These frequencies may be compared with those also shown in the Table for the isoelectronic and presumably isostructural cationic iron thiocarbonyl complex, $[C_5H_5Fe(CO)_2(CS)]^+$. The absence of the positive charge on (I) would be expected to result in an increase in the extent of back-bonding between the metal and the CO and CS groups when compared to that for the iron complex. Consequently, the C–O and C–S stretching frequencies of (I) would be expected to be lower than those of the iron complex, as is observed.

I.r. spectra (cm^{-1}) of cyclopentadienylmetal dicarbonyl thiocarbonyl complexes in Nujol mull

Compound	ν_{CO}		ν_{CS}
$C_5H_5Mn(CO)_2(CS)$[a]	2010s	1959s	1271s
$[C_5H_5Fe(CO)_2(CS)]PF_6$ [b] ..	2093s	2064s	1348s

[a] In CS_2 solution: ν_{CO} 2006s 1954s; ν_{CS} 1266s.
[b] From ref. 6a.

The formation of (I) from $C_5H_5Mn(CO)_2$(*cis*-cyclo-octene) and CS_2 is a novel reaction as it provides the first example of the substitution of a co-ordinated olefin by the two-electron ligand CS. Most probably the olefin acts as a sulphur acceptor in the reaction and in doing so it is converted into an episulphide



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