π-Cyclopentadienyl(dithiolene)nitrosylmanganese and Related Sulphur Complexes

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THE reduction of monomeric π-cyclopentadienylmetal dithiolene complexes often results in the formation of the unsubstituted bis- or tris-dithiolenemetal compounds. Thus, such species as $[MoS_6C_6(CN)_6]^{2-}$ and $[Mn(NO)S_4C_4(CF_3)_4]^-$ have been obtained by treatment of $[\pi\text{-}C_5H_5MoS_4C_4(CN)_4]^-$,[1] and $[\pi\text{-}C_5H_5Mn(NO)S_2C_2(CF_3)_2]^0$,[2] with $Na_2S_2C_2(CN)_2$ and ethanolic hydrazine, respectively. In an attempt to produce a series of bisdithiolenenitrosylmanganese and related sulphur complexes analogous to the known iron and cobalt species,[3] $[M(NO)\text{–}(S\text{-}S)_2]^z$,† $z = \pm 1, 0, -2, -3$, we have investigated the reactions of $[\pi\text{-}C_5H_5Mn(NO)(CO)_2]^+(PF_6)^-$ with an excess of several different types of mono- and di-anionic bidentate sulphur ligands.

Treatment of $[\pi\text{-}C_5H_5Mn(NO)(CO)_2]^+(PF_6)^-$ with an equivalent or excess amount of $Na_2S_2C_2(CN)_2$ and its isomer, $Na_2S_2C{=}C(CN)_2$,‡ results in the formation only of the *monoanionic* species, $[\pi\text{-}C_5H_5Mn(NO)\text{–}(S\text{-}S)]^-$. Similarly, with toluene-3,4-dithiolate, tetrachlorobenzene-1,2-dithiolate and dialkyldithiocarbamates, the *neutral* species, $[\pi\text{-}C_5H_5Mn(NO)\text{–}(S\text{-}S)]^0$, are readily formed. Even in the presence of large excesses of the sulphur ligands, the $\pi\text{-}C_5H_5$–Mn bond was not cleaved.

A voltammetric examination§ of the π-cyclopentadienyl complexes has revealed that they undergo one-electron transfer reactions. Thus, the toluene- and tetrachlorobenzene-dithiolenes exist in a three-membered reversible electron transfer series: $[\pi\text{-}C_5H_5Mn(NO)\text{–}(S\text{-}S)]^+ \rightleftharpoons [\pi\text{-}C_5H_5Mn(NO)\text{–}(S\text{-}S)]^0 \rightleftharpoons [\pi\text{-}C_5H_5Mn(NO)\text{–}(S\text{-}S)]^-$, and, from a knowledge of the half-wave potentials for the formation of the mono-anions, chemical reducing agents have been chosen[3,4] which have successfully accomplished the one-electron change. The dicyano-1,2-dithiolene and the 1,1-dicyanoethylene-2,2-dithiolate exist in a two-membered series consisting of a neutral and monoanionic species, and chemical oxidation has afforded the 1,2-dithiolene $[\pi\text{-}C_5H_5Mn(NO)S_2C_2(CN)_2]^0$. The dialkyldithiocarbamato-species apparently can be oxidised in an irreversible one-electron step, thereby generating monocations.

The neutral dithiolene complexes are paramagnetic ($S = \frac{1}{2}$), their solid-state magnetic moments corresponding to one unpaired electron, and they exhibit six-line multiplet e.s.r. spectra in solution at room temperature due to nuclear hyperfine interaction with ^{55}Mn ($I = \frac{5}{2}$); ^{14}N ($I = 1$) hyperfine coupling was not resolved. The monoanionic dithiolenes, 1,1-dicyanoethylene-2,2-dithiolate, and dialkyldithiocarbamates are isoelectronic and are diamagnetic. The NO stretching frequencies of the neutral dithiolenes fall in the range 1770—1790 cm.$^{-1}$. Those of the monoanionic dithiolenes, 1,1-dicyanoethylene-2,2-dithiolate, and dithiocarbamates occur in the range 1690—1710 cm.$^{-1}$ and, on average, the NO stretching frequencies of the neutral species occur at the top end of this range and those of the monoanions at the bottom, although the overall difference is small.

The $\pi\text{-}C_5H_5$-ring in the cyclopentadienyldithiolene complexes could not be cleaved by the excess of the sulphur ligand, but conversion into the bis-dithiolenes, $[Mn(NO)\text{–}(S\text{-}S)_2]^{2-}$, may be achieved by using an excess of potassium ethoxide. These dianionic nitrosyl species can also be produced by treatment of $[Mn\text{–}(S\text{-}S)_2]^{2-}$ with NO gas.[5] Because of their instability, we have been unable, as yet, to establish unequivocally the exhibition of redox behaviour by these nitrosyl bis-dithiolenes.

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† The use of the abbreviation *S-S* is intended to refer to a bidentate sulphur ligand and not to diatomic sulphur.

‡ $Na_2S_2C_2(CN)_2$ is disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate and $Na_2S_2C{=}C(CN)_2$ is disodium 1,1-dicyanoethylene-2,2-dithiolate; the other ligands used in this study are derived from toluene-3,4-dithiol, tetrachlorobenzene-1,2-dithiol, and dialkyldithiocarbamates, NaS_2CNR_2.

§ Carried out in CH_2Cl_2 with a rotating Pt electrode.

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