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Preliminary communication

Polynuclear iron carbonyl dithiolene complexes

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The synthesis of transition metal cluster compounds containing 1,2-dithiolato ligands and other groups suitable for use as spectroscopic "labels" (*e.g.* CO or NO) is not well systematised. The species which have been prepared, however, have interesting redox properties, *viz.* $\{Co(CO)[S_2C_2(CF_3)_2]\}_3$ [1] and $\{Fe(NO)[S_2C_2(CF_3)_2]\}_3$ [2] may be reduced[3] in one, and two, one-electron steps, respectively. In order to extend the range and type of polynuclear metal dithiolene complexes containing CO, and to attempt to discover some general route to their syntheses, we have investigated the reactions of di- and tri-nuclear iron carbonyl compounds with $S_2C_2(CF_3)_2$.

Treatment of $Fe_2(CO)_6(XR)_2$ (X = S, R = Me, Et or Ph; X = Se, R = Ph) with $S_2C_2(CF_3)_2$ in n-pentane/benzene afforded the deep green neutral complexes $\{Fe(XR)(CO)[S_2C_2(CF_3)_2]\}_n^0$. Molecular weight determinations established that in $CHCl_3$ $n = 4$ whereas in acetone $n = 2$. The complexes were insufficiently volatile for mass spectrometric studies, but their IR spectra in $CHCl_3$ solution exhibited carbonyl stretching frequencies (Table 1) which are consistent with either structure I or II.

Voltammetric studies of $\{Fe(XR)(CO)[S_2C_2(CF_3)_2]\}_4^0$ in CH_2Cl_2 revealed that the species could be oxidised irreversibly, and reduced reversibly, in a one-electron process; multiple electron reduction processes occurred between −0.3 and −0.8 V. There was a small, but barely significant, dependence of $E_{1/2}$ on the group R. Dissolution of $\{Fe(XR)(CO)[S_2C_2(CF_3)_2]\}_n^0$ in dimethylsulphoxide, which might have been expected to cause reduction of these species to the monoanions[3,4], resulted in the formation of deep red solutions. In the species X = S, R = Me or Et, the shape and position of $\nu(CO)$ did not change, but when X = S or Se and R = Ph, $\nu(CO)$ moved to lower frequencies; the nature of these reactions is not fully understood since dissociation of the tetramer (as in acetone), as well as reduction, could have occurred.

Reaction of $Fe_3(CO)_9S_2$ with $S_2C_2(CF_3)_2$ afforded, in low yields, $\{Fe_3S_2[S_2C_2(CF_3)_2]_4\}^0$, which has already been reported[3]. This synthesis, however, represents the first direct route to this trinuclear species.

Treatment of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $S_2C_2(CF_3)_2$ has afforded

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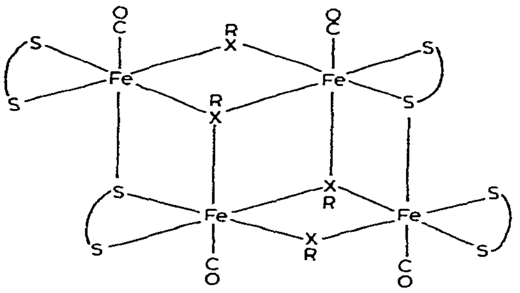
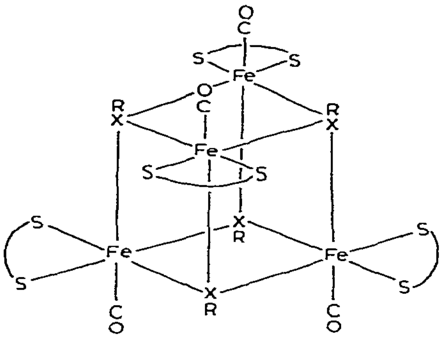


(I)



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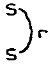
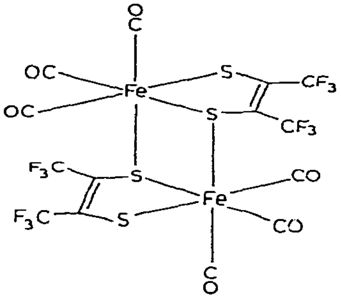


represents $S_2C_2(CF_3)_2$

$\{Fe_2(CO)_6[S_2C_2(CF_3)_2]\}^0$ [5] and $\{Fe[S_2C_2(CF_3)_2]_2\}^0_2$ [6]. However, reaction of $Fe_2(CO)_9$ with $S_2C_2(CF_3)_2$, under carefully controlled conditions in n-pentane/n-hexane, afforded a violet, volatile, crystalline solid, $\{Fe(CO)_3[S_2C_2(CF_3)_2]\}^0_n$. Solution molecular weight determinations indicated that $n = 2$, but a parent ion could not be detected in the mass spectrum; only ions corresponding to $[Fe(CO)_xS_2C_2(CF_3)_2]^+$, $x = 3$, 2, 1, or 0, were observed. The IR spectrum of the compound in the carbonyl region was



(III)

TABLE 1 [a]

	$\nu(CO)$ [b]	$E_{1/2}$ [c]	
		0 ↔ +1	0 ↔ −1
$\{Fe(SMe)(CO)[S_2C_2(CF_3)_2]\}_4^0$	2100 2048	+0.97	+0.47
$\{Fe(SEt)(CO)[S_2C_2(CF_3)_2]\}_4^0$	2102 2065	+1.00	+0.46
$\{Fe(SPh)(CO)[S_2C_2(CF_3)_2]\}_4^0$	2110 2075	+1.01	+0.49
$\{Fe(SePh)(CO)[S_2C_2(CF_3)_2]\}_4^0$	2100 2062	+1.00	+0.47
$\{Fe(CO)_3[S_2C_2(CF_3)_2]\}_2$ [d]	2030 2036 2089		

[a] All complexes described were analysed satisfactorily for C, H and S. [b] In $CHCl_3$ solution, cm^{-1}. [c] In CH_2Cl_2, *vs.* SCE at 20±2° with rotating Pt electrode and $[Et_4N][ClO_4]$ as supporting electrolyte. [d] In n-pentane solution.

consistent with a structure III for this binuclear species. The compound is extremely reactive, and readily loses CO in the presence of Lewis bases.

It would appear, therefore, that $S_2C_2(CF_3)_2$ may easily replace two CO groups in metal carbonyl species (*cf.* also the syntheses of $\{M[S_2C_2(CF_3)_2]_3\}^0$ [7] from $M(CO)_6$ (M = Cr, Mo or W and $S_2C_2(CF_3)_2$), and that this can be used as a method of obtaining polynuclear bis(trifluoromethyl)dithiolene complexes. As a further example, reaction of $Co_3(CO)_9CY$ (Y = Cl or Me) with $S_2C_2(CF_3)_2$ afforded $\{Co_3(CO)_3[S_2C_2(CF_3)_2]_3CY\}^0$ in which the tetrahedral Co_3C cluster appears to remain intact.

Attempts to extend this type of reaction using other bidentate sulphur ligands have been less sucessful. Thus, treatment of $[Fe_2(CO)_6(SR)_2]$ with $Me_2NC({=}S)S{-}SC({=}S)NMe_2$ afforded only $Fe(S_2CNMe_2)_3$. The syntheses of other polynuclear dithiolene and related complexes are being further studied.

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