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Preliminary communication

^{13}C HYPERFINE SPLITTING IN THE RADICAL COMPLEX OF BIS(ETHOXYTHIOCARBONYL)SULFIDE AND DIMANGANESE DECACARBONYL

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Summary

A close examination of the ESR spectrum of a paramagnetic complex formed from bis(ethoxythiocarbonyl)sulfide and dimanganese decacarbonyl has revealed, for the first in this type of radical adduct, ^{13}C hyperfine coupling in natural abundance from the carbonyl ligands.

Paramagnetic species derived from transition metal carbonyls have been the subject of numerous investigations in recent years. However, many of the primary radicals formed during photolysis or thermolysis are too reactive [1] for direct ESR detection in fluid solution. For example, the ESR spectrum of the 17-electron species $^{\cdot}Mn(CO)_5$ has only been observed in solid matrices [2] and the crystal structure reported is the $Mn(CO)_4(\eta\text{-}C_4H_6)$ [3]. ESR evidence, however, has been obtained for the formation of moderately stable organophosphorus substituted manganese carbonyl radicals by photosubstitution reactions [4,5]. Further studies have shown that many of these metal carbonyl radicals can be 'stabilized' by complexing with organic substrates, especially when the organic substrates can act as bidentate ligands. Examples include the following radical complexes (I—III) resulting from the reactions of $^{\cdot}Mn(CO)_{5-n}L_n$ radicals with α-diones [6,7], with aliphatic or aromatic nitroso derivatives [8], and with 1,4-diaza-1,3-butadiene [9], respectively.

In all of these complexes it has been assumed that there are four carbonyl ligands, thus preserving the octahedral coordination of the metal atom. These paramagnetic molecules are then 19 electron species in which the odd electron

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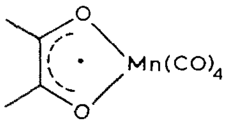
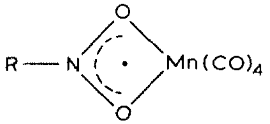


(I)



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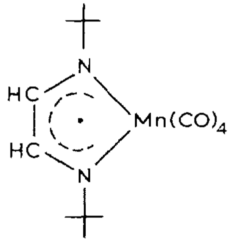
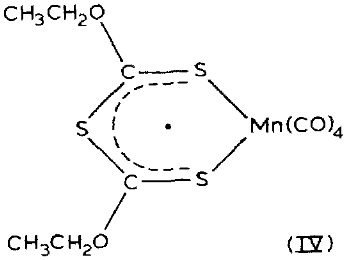


(III)

is largely confined to a π-orbital on the organic moiety. In many cases support for this formulation has been obtained by observing substitution reactions of the labile CO ligands with phosphines and similar Group VA compounds. Unfortunately, none of the complexes (I—III) exhibited detectable ^{13}C satellites from the CO groups.

We now report the first observation of ^{13}C satellites from CO ligands in a radical complex derived from $^{\cdot}Mn(CO)_5$. The photochemical and thermal reactions of metal carbonyls with bis(ethoxythiocarbonyl)sulfide (BETS) have recently been shown to provide a new class of metal carbonyl radical complexes [10]. Under high gain the paramagnetic species BETS—$^{\cdot}Mn(CO)_4$ (4) clearly exhibits ^{13}C satellites in its ESR spectrum recorded in toluene solution at room temperature.



(IV)

A ^{13}C doublet splitting of 8.73 gauss was evident in addition to the original sextet from ^{55}Mn (4.13 gauss) and the quintet from four equivalent protons (2.46 gauss) (Table 1). The relative intensity of the ^{13}C satellite lines was about twice that expected for any pair of equivalent carbon atoms in the organic ligand and is thus assigned to the four CO ligands. This implies that the structure of IV is fluxional and that the observed splitting is in fact an average over the *cis* and *trans* positions. The contribution of the two *cis* CO's to the observed coupling constant of 8.37 gauss is expected to be very small, since they lie in the nodal plane of the singly occupied MO which is mainly π in character and associated with the organic moiety. It follows that the coupling constant for a *trans* ^{13}CO in the radical complex should lie within the range of 15—17 gauss. In order to support this assignment we have substituted one of the CO ligands in IV with triphenylphosphine. As previously observed in similar complexes such as I or II, substitution occurs at the *trans* position leading to a substantial ^{31}P coupling constant of 43.7 gauss. For this substituted radical complex no ^{13}C satellites could be unambiguously resolved.

TABLE 1

ESR PARAMETERS OF SOME OBSERVED BETS—$^{\bullet}$Mn(CO)$_x$L$_y$ RADICAL COMPLEXES IN TOLUENE AT ROOM TEMPERATURE

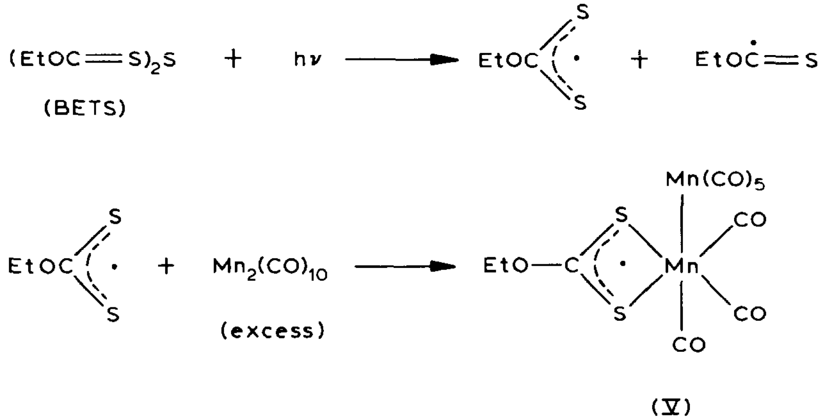
Radical Complex	g-Factor	Hyperfine coupling (G)
BETS—$^{\bullet}$Mn(CO)$_4$	2.0095 ± 0.0001	$a_{\mathrm{Mn}} = 4.13$ $a_{\mathrm{H}}(4\mathrm{H}) = 2.46$ $a_{^{13}\mathrm{C}}(\mathrm{CO}) = 8.73$
BETS—$^{\bullet}$Mn(CO)$_3$PPh$_3$	2.0096	$a_{\mathrm{Mn}} = 5.55$ $a_{^{31}\mathrm{P}} = 43.7$ $a_{\mathrm{H}}(4\mathrm{H}) = 2.17$ $a_{^{13}\mathrm{C}}(\mathrm{CO})$ not resolved
Radical Complex (V)	2.0128	$a_{\mathrm{Mn}(1)} = 4.14$ $a_{\mathrm{Mn}(2)} = 6.70$ $a_{\mathrm{H}}(2\mathrm{H}) = 2.46$ $a_{^{13}\mathrm{C}}(\mathrm{CO})$ not resolved.

Since the substitution does not significantly alter the spin densities in the BETS moiety, this suggests that the ^{13}C assignment to the CO ligands is correct. If our analysis is valid, when one of the *trans* CO ligands is replaced by PPh$_3$ the average ^{13}C coupling constant should drop to $17/3 = 5.6$ gauss. It would be difficult to see a coupling of this magnitude because of overlap with the main spectral lines.

A doublet satellite splitting of 11.2 gauss observed in the related radical complex formed [10] from BETS and Fe(CO)$_5$ is also probably attributable to the *trans* CO ligands. This complex is presumably [BETS—$^{\bullet}$Fe(CO)$_4$]$^+$ which is isoelectronic with BETS—$^{\bullet}$Mn(CO)$_4$ and structurally similar to a number of cationic iron-containing radicals prepared by Connelly and his co-workers [11].

During the course of the present study we have observed that when reacting BETS with an excess of Mn$_2$(CO)$_{10}$, a second radical species is formed in addition to IV. This radical is characterized by a rather high *g*-factor ($g = 2.0128$) and exhibits hyperfine couplings of 4.14 and 6.70 gauss to two different ^{55}Mn nuclei and a coupling of 2.46 gauss to two equivalent protons (Fig. 1).

A possible reaction sequence, based on the previously reported photochemistry of BETS [12], which leads to a paramagnetic species with two different Mn nuclei is:



(1)

(2)

(V)

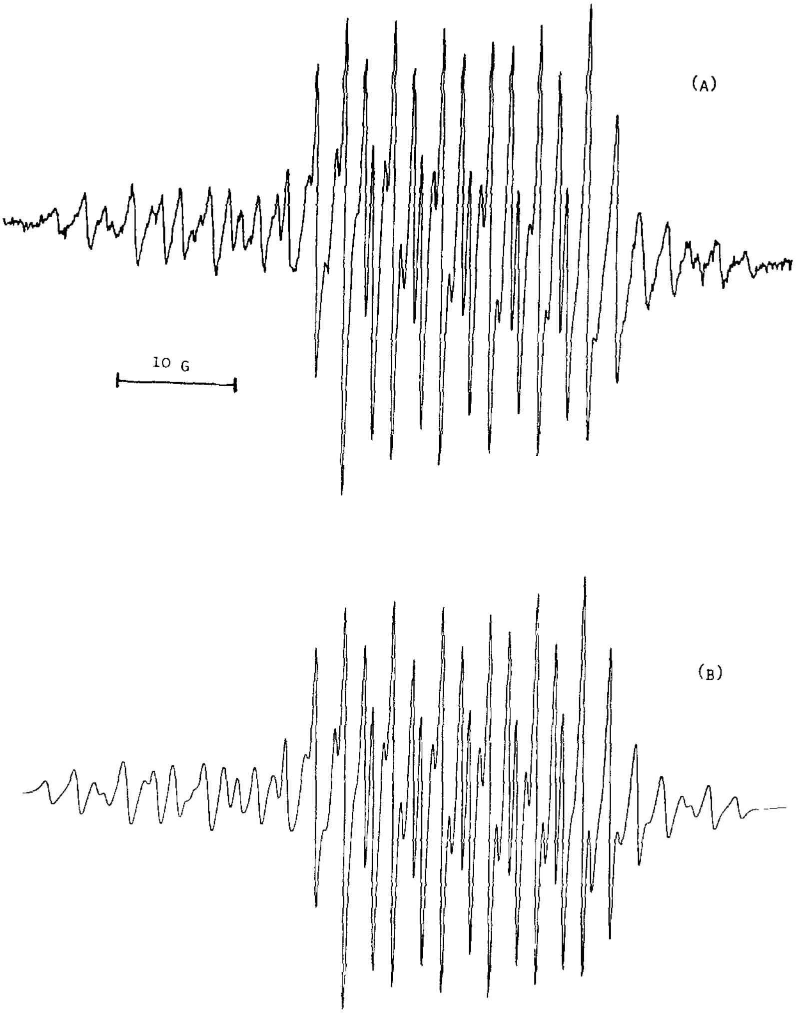


Fig. 1. (A) The ESR spectrum observed at room temperature during the photolysis of BETS in toluene with an excess of $Mn_2(CO)_{10}$; (B) Simulated spectrum consisting of 60% radical IV and 40% radical V.

While the identity of the radical complex containing two Mn nuclei in this reaction remains uncertain, the ESR evidence is not inconsistent with the structure V. It is interesting to note that a species with two non-equivalent Mn nuclei has also been observed in spin trapping experiments with nitroso compounds in the presence of excess $Mn_2(CO)_{10}$.

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