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PARAMAGNETIC ADDUCTS BETWEEN MANGANESE-CENTRED RADICALS AND NITRO DERIVATIVES. A NEW CLASS OF MANGANESE-CONTAINING RADICALS

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Summary

The photolytic or thermal reaction of pentacarbonylmanganese radicals with either aromatic or aliphatic nitro compounds in the presence of PBu_3, and in one case of pyridine, gives spin adducts which have been studied by ESR spectroscopy. On the basis of the spectral parameters these paramagnetic species, which represent the first example of a new class of transition metal-containing radicals, have been assigned a cyclic structure, with the manganese atom acting as a bridge between the two oxygens of the nitro group; this implies the loss of a CO unit during complexation.

The role of the phosphine in stabilizing these radicals by replacing one or two CO moieties is critical; doubly-substituted species are much more persistent than their mono-substituted analogues. In the absence of PBu_3 the corresponding paramagnetic adduct could be observed only with 2-methyl-2-nitropropane.

Introduction

Iron- [1], cobalt- [2], manganese- [3] and rhenium-centered [1b,3a,4] radicals are readily scavenged by nitroso compounds, and a number of reports have dealt with the resulting nitroxides. The manganese derivatives, however, show a rather low stability, and in some istances doubts arise as to their actual nature, owing to the simultaneous presence of more than one paramagnetic species.

In contrast, radicals centered at a Group IVB element, such as silicon or tin, are not trapped by nitroso compounds [5]; instead, they add to nitro derivatives affording the corresponding relatively stable oxynitroxides [6].

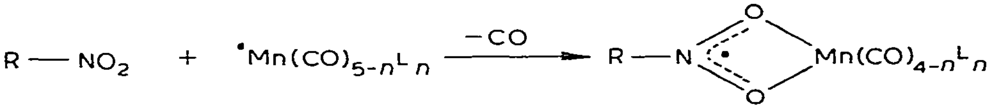
Such a process has not yet been reported for transition metals; indeed, nitroarenes are known to react with cobalt-centered radicals [2], such as ${}^{\bullet}Co(CN)_5{}^{3-}$, to give paramagnetic species, but these have been unambiguously identified as arylcobalto nitroxides, formed according to the following reaction scheme:

$$R{-}NO_2 + {}^{\bullet}Co(CN)_5{}^{3-} \rightarrow R{-}NO_2{}^{\dot{-}} + Co(CN)_5{}^{2-}$$

$$2\,R{-}NO_2{}^{\dot{-}} + H^+ \rightarrow R{-}NO + R{-}NO_2 + OH^-$$

$$R{-}NO + {}^{\bullet}Co(CN)_5{}^{3-} \rightarrow [R{-}N(O^{\bullet})\,Co(CN)_5]^{3-}$$

We have now found that persistent spin adducts are formed in the reaction between some aliphatic or aromatic nitro derivatives and in situ generated ${}^{\bullet}Mn(CO)_{5-n}L_n$ radicals (where L = PBu_3 or Pyridine). Although the nitro group does not commonly behave as a bidentate ligand towards the manganese nucleus, we think that the present results are indicative of a chelated structure for these species:



(1–6)

(I–VI)

(1) R = t-butyl
(2) R = isopropyl
(3) R = phenyl

(4) R = 3,5-dichlorophenyl
(5) R = 2-thienyl
(6) R = 3-thienyl

The high stability of the spin adducts (I—VI) when L = PBu_3 and $n = 2$ is presumably due to conjugative interactions between the single occupied molecular orbital (SOMO) and the phosphorus atoms of the ligand moieties.

Experimental

Decacarbonyldimanganese (MDC), tri-n-butylphosphine and most of the nitroso and nitro compounds were commercially available. Octacarbonylbis-(tri-n-butylphosphine)dimanganese [7], 2- and 3-nitrothiophen, 2-methyl-2-nitropropane, *o*-nitrophenylmethyl sulphoxide and *o*-nitrophenylphenyl sulphoxide were prepared by published methods.

The ESR spectra were recorded on a Varian E-104 spectrometer and standard accessories were used to control the temperature, which was measured before and after each scan by means of a copper-constantan thermocouple positioned at the centre of the microwave cavity.

An 1 kW high pressure mercury lamp was used as the UV light source. Though in a few instances steady photolysis was necessary while recording the spectra, in most cases irradiation was interrupted as soon as good ESR signals were obtained.

No particular care was found to be necessary in the preparation of the samples, undegassed solutions of the reactants in t-butylbenzene contained in quartz tubes. Bubbling of nitrogen or degassing by the freeze-thaw technique did not lead to any improvement of the quality of the spectra.

Results

The photoreaction between nitrosobenzene, MDC, and tri-n-butylphosphine in thoroughly degassed solutions led to a relatively weak and poorly resolved ESR spectrum (characterized by an overall splitting of 89.3 gauss) which we were unable to simulate satisfactorily; moreover, the lack of a center of symmetry clearly indicated the simultaneous presence of more than one paramagnetic species. Similar results were obtained with the 3,5-dichloro derivative, which was examined with the aim of getting simpler spectra because of the absence of the *meta*-triplet splitting. In both cases the spin adducts were also thermally labile; however, lowering the temperature did not help, since the quality of the spectra became even worse owing to a drastic increase in linewidth.

In contrast, nitro compounds (1—6) under the same conditions gave the particularly stable radicals (I—VI) in the range 30 to 140°C. Their ESR spectra were all characterized by hyperfine couplings with a manganese, a nitrogen and

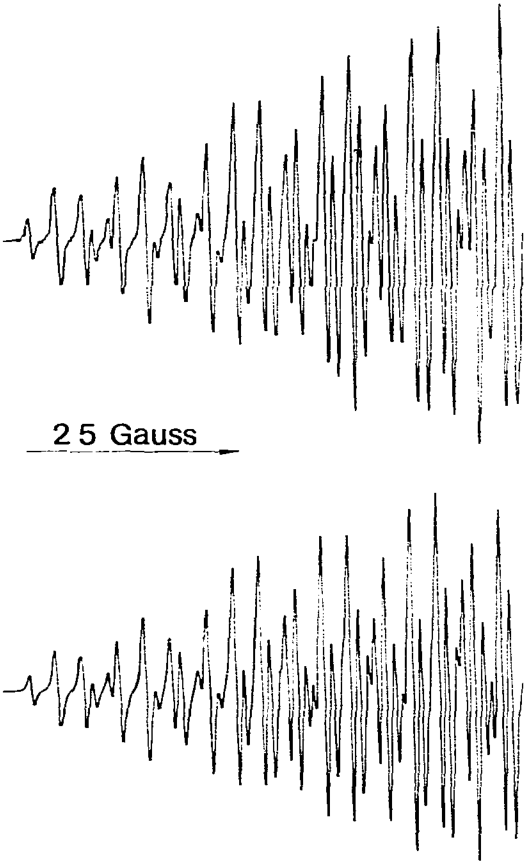


Fig. 1. Experimental (above) and computer simulated (below) low field half of the ESR spectrum of radical IV in t-butylbenzene.

TABLE 1

HYPERFINE SPLITTING CONSTANTS (G) FOR RADICALS I—VIII

Compound	Radical	Ligand	*a*(Mn)	*a*(N)	*a*(L)	
1	Ia	—	5,15	27,0	—	
1	Ib	PBu_3	6,40	23,2	23,5 (1 P)	
1	Ic	PBu_3	5,75	24,0	23,0 (2 P)	
1	Id	Pyridine	4,20	26,6	2,25 (1 N)	
2	II	PBu_3	7,25	24,0	27,5 (2 P)	14,57 (H_2)
3	III	PBu_3	6,10	12,4	22,8 (2 P)	3,14 (2 H_o), 1,06 (2 H_m), 3,40 (H_p)
4	IV	PBu_3	7,74	11,08	26,3 (2 P)	3,14 (2 H_o), 3,44 (H_p)
5	V	PBu_3	5,18	11,68	19,2 (2 P)	5,40 (H_3), 1,14 (H_4), 4,40 (H_5)
6	VI	PBu_3	5,66	13,74	22,0 (2 P)	5,00 (H_2), 1,20 (H_4), 0,66 (H_5)
7	VII	—	6,45	9,10	—	0,98 (2 H), 3,00 (1 H), 3,32 (1 H), 0,38 (3 H)
8	VIII	—	6,45	9,08	—	0,98 (2 H), 2,91 (1 H), 3,30 (1 H)

two equivalent phosphorus nuclei, plus additional splittings from other protons of the nitro substrates (see Table 1 for h.f.s.c.). Although, in some cases, at lower temperature two radicals were at first actually detected, the one characterized by the smaller overall splitting quickly disappeared. Insufficient data concerning these latter species is available to establish whether they are the monophosphorus analogues of I—VI or instead the corresponding alkyl- or arylmanganeso nitroxides resulting from deoxygenation of the nitro substrates.

A few experiments were carried out by photolyzing solutions of the nitro compounds in the presence of $Mn_2(CO)_8(PBu_3)_2$, with the aim of obtaining the adducts in which only one CO unit had been replaced by a phosphine moiety. In all cases the spectra were characteristic of a mixture of radicals, and an unambiguous interpretation was impossible. Only with the simplest nitro derivative, i.e. 1, could the three species Ib, Ic and X be clearly identified.

We also tried to generate radicals I—VI in the presence of different phosphorus-containing ligands, such as triphenylphosphine or trialkyl phosphites, but complex mixtures were always obtained even at very low PR_3 concentrations. The fact that a number of paramagnetic species were simultaneously detected may possibly be due to the formation of the corresponding nitroxides in addition to the radicals I—VI. This is not surprising in view of the fact that aryl- and oxyalkyl-phosphorus derivatives exhibit a much higher reactivity towards nitro compounds than their alkyl analogues [8].

Among ligands other than phosphorus derivatives, pyridine is one of the more important. The room temperature reaction of 1 in the presence of this amine gave a radical whose spectrum (see Table 1) indicated the replacement of only one CO moiety by a pyridine molecule; increasing the temperature resulted in a sudden disappearance of the ESR signal.

Photolysis of solutions of compounds 1—2 and MDC in the absence of a ligand gave negative results for 2 but led to the unsubstituted manganeso adduct with (1).

The presence of the phosphine proved to be essential in the case of nitroarenes 3—6. However with *o*-nitrophenylmethyl sulphoxide (7) and *o*-nitrophenylphenyl sulphoxide (8) persistent radicals were observed (see Table 1). The presence of other *ortho*-substituents such as NHR, NO_2, COR and SR led to the formation of more labile and short-lived species.

Discussion

The data reported in Table 1 indicate that, in contrast with what happens in the case of $^\bullet Co(CN)_5^{3-}$ radicals, deoxygenation does not take place in the reaction between Mn-centered radicals and aliphatic nitro derivatives *, the manganese and nitrogen coupling constants measured for radicals Ia—d being quite dissimilar to those previously reported for t-butylpentacarbonylmanganeso nitroxide and its derivatives (see Table 2 for comparison); the nitrogen splittings in Ia—d are actually much closer to those measured for aliphatic oxynitroxide radicals of general formula $RN(O^\bullet)OR'$, where the nitrogen coupling

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* A substantial amount of the deoxygenated nitroxide radical X was detected only during steady photolysis of 1 in the presence of $Mn_2(CO)_8(PBu_3)_2$.

TABLE 2

HYPERFINE SPLITTING CONSTANTS (G) FOR RADICALS I, IX—XI

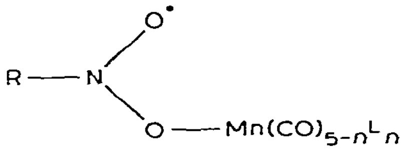
Scavenger	Radical source	Radical adduct	a(Mn)	a(N)	a(L)	T (°C)	Reference
1	MDC	Ia	5.15	27.0	—	—30	*b*
t-BuNO	MDC	IX	6.90	16.6	—	—30	3a
t-BuNO	MDC	IX	6.84	16.1	—	—40	*b*
i-BuNO	[a]	IX	12.56	17.39	—	Room	3b
t-BuNO	MDC	IX	9.96	18.91	—	0	*b*
1	MDC/PBu_3	Ic	5.75	24.0	23.0 (2 P)	—40/+140	*b*
t-BuNO	MDC/PBu_3	X	10.50	18.25	3.5 (1 P)	—10	*b*
1	MDC/Pyridine	Id	4.20	25.6	2.25 (1 N)	Room	*b*
t-BuNO	MDC/Pyridine	XI	11.69	17.92	0.58 (1 N)	Room	3c

[a] $Mn(CO)_5^-$ + tropilium cation in THF. [b] This work.

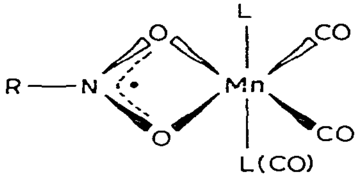
is in the range 22 to 29 gauss, depending on the nature of R and R′. Although no comparative data are available for radical II, the similarity of the h.f.s.c. with those measured for Ic leaves little doubt that the same type of paramagnetic species is involved.

A quite interesting feature of the data collected in Tables 1 and 2 is that the values of the $a(^{31}P)$ coupling shown by species Ib—c and II are almost an order of magnitude larger than those found for the corresponding nitroxides.

Two alternative structures can be envisaged for these manganese-containing spin adducts, i.e. the "open" structure (A) or the "cyclic" (B). Spin density at the phosphorus atoms can originate from indirect spin polarization and/or

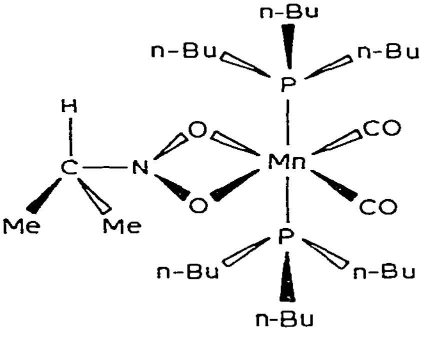


(A)



(B)

conjugative interactions. The former mechanism will result in a small $a(^{31}P)$ coupling, given the large distance between the phosphorus atoms and the radical centre. However, if overlap can occur between the SOMO and either the σ orbitals associated with the Mn—P bonds or the empty d orbitals centered at the phosphorus nuclei, large $a(^{31}P)$ splittings would be expected. We think that in the rigid structure (B) such an overlap can be much more effective than in the flexible structure (A), where free rotation about the N—O and O—Mn bonds is expected to take place. This is also in agreement with the finding that the $a(^{31}P)$ splittings in Ic and II are practically temperature independent over all the examined range (—40 to +140°C). Furthermore, indirect evidence in favour of the "cyclic" structure B is provided by the value of the aliphatic proton splitting exhibited by radical II. This is unusually large, since in the known isopropyl oxynitroxides $(CH_3)_2HCN(O^{\bullet})OR$ the a(CH/H) coupling is always smaller [9a,9c,10] than 6 gauss, and in no cases * is expected to exceed the value of 10—11 gauss which, being the splitting found for the methyl protons in methylalkoxy nitroxides $CH_3N(O^\bullet)OR'$, must represent the upper limit for the coupling from freely rotating protons β to the nitrogen atom. This finding would be nicely explained by assuming that the radical II has the "cyclic" structure C, in which, because of the steric repulsion due to the bulky PBu_3 groups, the isopropyl moiety is forced into a position such that the C—H bond eclipses the orbital containing the unpaired electron. The cyclic structure of these species implies of course a two step reaction, elimination of a CO moiety following the initial trapping of the manganese centered radical by the nitro substrate. A similar mechanism has been invoked for the photoreaction between MDC and α-diketones [11].



(C)

The observed decrease of the nitrogen splittings observed upon replacement of the alkyl by an aryl group is expected on the basis of delocalization of the unpaired electron into the unhindered aromatic systems. Thus, the nitrogen couplings in radicals III—VI decrease along the sequence: 3-thienyl > phenyl > 2-thienyl, which represents the reverse of the delocalizing ability of these aromatic groups towards an unpaired π electron. Unfortunately there are no corresponding unhindered arylmanganeso nitroxides to test the magnitude of the nitrogen splittings in III—VI. We think, however, that also these species are well described by structure B, in agreement with the values of the $a(^{31}P)$ couplings which are similar to those measured for Ib—Ic and II. Such a structure also accounts for our failure to detect any evidence of restricted rotation of the aryl group around the C—N bond in V and VI down to —20°C although it is known that in the corresponding triethylsilyloxy nitroxides the two rotational isomers can be detected just below room temperature [12].

The stabilizing role of PBu_3 in radicals I—VI should be emphasized. As already pointed out, only the doubly phosphine-substituted spin adducts could be detected during the reaction of nitro derivatives 1—6 with MDC and PBu_3. The monosubstituted analogue could be obtained, and then in small amounts at

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* To have a larger set of comparative data we also examined the previously unreported triphenylsilyl-, triphenylgermyl-, triphenylstannylisopropyl oxynitroxides and found a(CH/H) values of 4.85, 5.17 and 5.76 gauss respectively. The nitrogen splittings for these radicals were 28.42, 28.36 and 28.49 gauss.

low temperatures, only in the case of 2-methyl-2-nitropropane upon reaction with $Mn_2(CO)_8(PBu_3)_2$; the radical Ib was however rather short-lived and disappeared as soon as the irradiation was cut off.

No ESR signals were ever detected during the reaction of nitroarenes and MDC in absence of PBu_3. An apparent exception was observed during the photolysis of MDC in solutions containing 7 or 8. In fact, although no radical species were observed during irradiation, very intense spectra characterized by rather small nitrogen splittings (see Table 1) appeared as soon as the UV light was switched off. This, together with the finding that no spin adducts could be obtained from the corresponding *para*-substituted nitro compounds provides evidence that radicals VII and VIII can not be assigned a structure such as B. These species might possibly be considered as arylmanganeso nitroxides in which chelation of the Mn atom is achieved by the *ortho*-sulphoxide group. This is, however, only speculation, and an unequivocal elucidation of the structure of these radicals must be delayed until more data have been collected.

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