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ADDITION OF ORGANOMETALLIC RADICALS TO ORGANIC SUBSTRATES. REACTION BETWEEN MANGANESE DECACARBONYL AND α-DICARBONYL COMPOUNDS

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Summary

Some *o*-quinones and 1,2-diketones were allowed to react with manganese pentacarbonyl radicals generated in situ and the resulting persistent paramagnetic adducts studied by ESR spectroscopy. The evolution of carbon monoxide during the reaction together with the symmetrical distribution of the spin density in the organic framework (as implied by the spectral data) indicated chelation of a $Mn(CO)_4$ moiety by the two oxygens of the dicarbonyl substrates.

One or more carbon monoxide groups can be replaced by compounds containing nitrogen, phosphorus, arsenic or antimony as binding sites. A conjugative transfer of spin density is proposed for the last three classes of substituents, while a σ mechanism is probably involved in the case of nitrogen-containing ligands.

Introduction

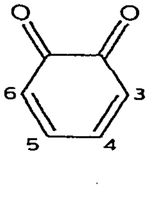
In recent years the reactions between organometallic radicals and organic substrates have been extensively investigated as synthetic routes to several classes of compounds. In some instances the paramagnetic intermediates formed in the course of these reactions are persistent enough to be studied by ESR spectroscopy, thus providing insight into their structures and into the mechanism of the reaction itself. A typical example [1] is the detection of paramagnetic species during the addition of group IVB organometallic radicals to aliphatic and aromatic substrates containing carbon—carbon, carbon—nitrogen, carbon—oxygen, and nitrogen—oxygen multiple bonds.

Although transition-metal-containing radicals are often easily generated, there have been few studies of their reactivities and ESR spectra in isotropic media [2].

Following a preliminary communication, [3] we report here further studies on the reaction of some manganese centred radicals with the mono-, di-, and tri-carbonyl derivatives 1—8:

R——CO——CO——R

1 , R = Me
2 , R = Bu^t
3 , R = Ph



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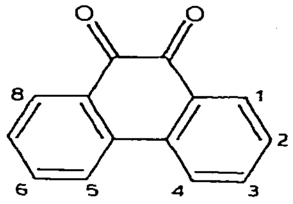

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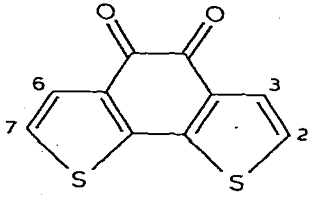

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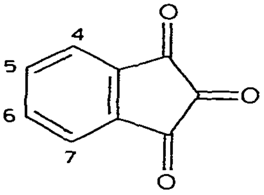

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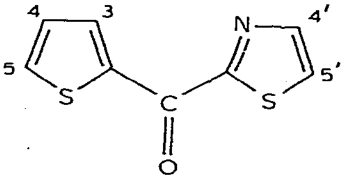

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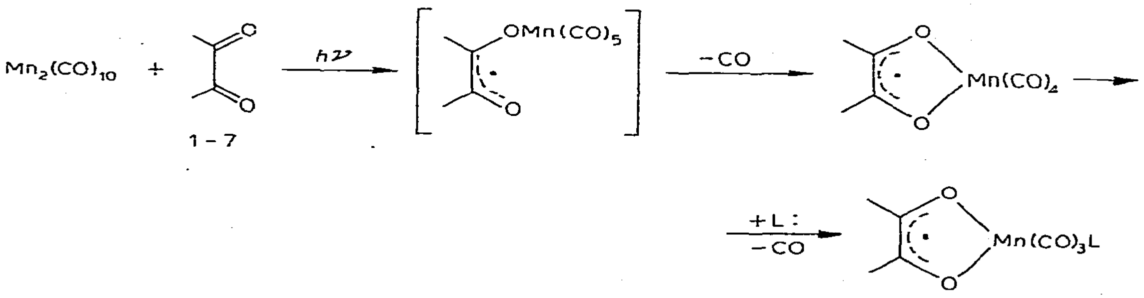
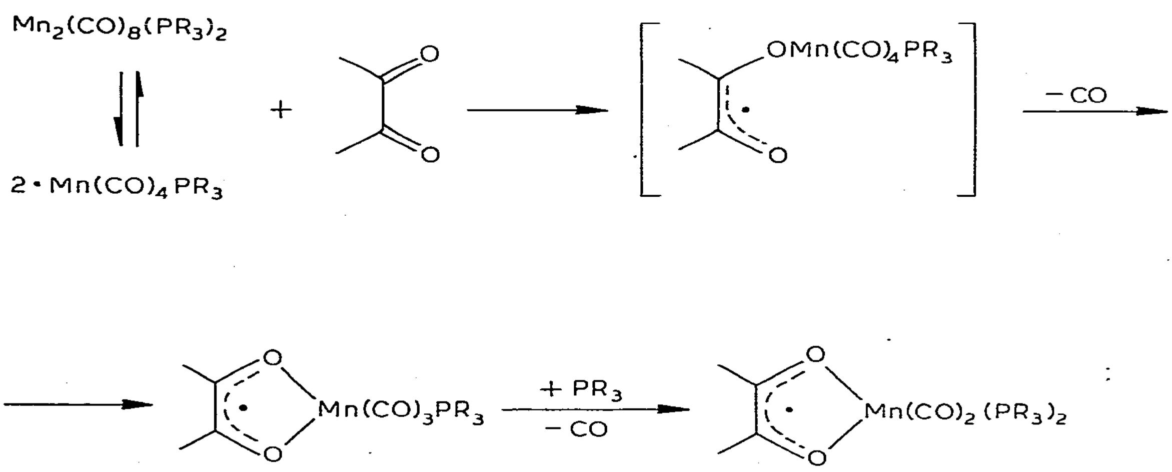
according to Scheme 1 and 2:

SCHEME 1



with L: = NPh_3 , $AsPh_3$, $SbPh_3$, $OP(NMe_2)_3$, Pyridine , Pyrazine

SCHEME 2



Experimental

The ESR spectra were recorded on a Varian E-104 spectrometer equipped with standard variable temperature accessories; the temperature was measured by means of a copper-constantan thermocouple before and after each scan.

A 100 W halogen lamp or a 1 kW high pressure mercury lamp was used indiscriminately as source of UV light, which was focused unfiltered on the centre of the microwave cavity. Except with compounds 1 and 2, which required constant irradiation, the quality of the spectra was found to be improved by switching off the light after a few minutes. The g factors of radical adducts VI, VIa, VIb and of the corresponding radical anion $6^{-\cdot}$ were measured relative to a sample of solid DPPH * ($g = 2.0037$).

All commercially available products were purchased from Fluka and used without further purification. Bipivaloyl [4], *o*-quinone [5], and benzo-[2,1-b;3,4-b′]dithiophen-4,5-dione [6] were prepared by published methods.

Results

(a) Photoreaction between dimanganese decacarbonyl (MDC) and compounds 1–8

As previously reported [3], the irradiation of solutions of α-dicarbonyl compounds containing small amounts of MDC results in the formation of stable paramagnetic species. During the photolysis carbon monoxide (which was characterized by mass spectroscopy) is evolved.

No major variations occurred in the ESR spectra of the radical adducts to compounds 1–8 on varying the temperature in the range −60° C to +120° C, except for a small increase of the $a(^{55}Mn)$ coupling constants and a progressive broadening of the low field lines of the manganese sextet at lower temperatures.

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* DPPH = diphenylpicrylhydrazyl.

TABLE 1

HYPERFINE SPLITTING CONSTANTS FOR RADICAL ADDUCTS I-VIII.

Substrate	Radical	Solvent	a (^{55}Mn) (G)	Other h.f.s.c. (G)
1	I	Toluene	5.25	7.65(6H)
1	I	Benzene	5.21	7.71(6H)
1	I	Me-Cyclohexane	5.36	7.50(6H)
2	II	Toluene	6.12	0.31(18H)
3	III	Toluene	5.75	0.90(4H_o), 0.40(4H_m), 0.90(2H_p)
4	IV	Toluene	7.71	0.45(2H, $H_{3,6}$), 3.37(2H, $H_{4,5}$)
5	V	Toluene	5.44	1.70(4H, $H_{1,3,6,8}$), 0.40(4H, $H_{2,4,5,7}$)
6	VI	Toluene	5.74	0.79(2H, $H_{2,7}$), 0.23(2H, $H_{3,6}$)
7	VII	Toluene	4.80	1.60(H_6), 1.30(H_4), 0.30(H_7), <0.1(H_5)
7	VII	Chloroform	4.86	1.58(H_6), 1.16(H_4), 0.40(H_7), <0.1(H_5)
8	VIII	Toluene	4.30	4.30(N), 3.90(H_3), 4.20($H_{5'}$), 2.70(H_5), 0.69(2H, $H_{4,4'}$)

TABLE 2

HYPERFINE SPLITTING CONSTANTS FOR RADICAL ADDUCTS I-VII AFTER LIGAND EXCHANGE.

Unsubstituted	Substituted	Ligand	T(°C)	a (^{55}Mn) (G)	a (Ligand) (G)	Other h.f.s.c. (G)
I	Ia	PPh_3	−40 to +60	6.50	26.2 (1 P)	7.25(6 H)
I	Ib	PPh_3	+60	8.75	26.3 (2 P)	6.65(6 H)
I	Ie	Pyridine	Room	3.62	1.87(1 N)	7.50(6 H)
I	If	Pyrazine	Room	3.75	1.87(1 N)	7.57(6 H)
II	IIa	PPh_3	−40 to +30	7.22	33.1 (1 P)	<0.2
II	IIb	PPh_3	+30	10.80	33.0 (2 P)	<0.2
II	IId	$P(OEt)_3$	+60	9.47	44.9 (2 P)	<0.2
III	IIIa	PPh_3	−10 to +60	7.48	27.3 (1 P)	0.80(4 H_o), 0.36(4 H_m), 0.80(2 H_p)
III	IIIb	PPh_3	+60	11.8	30.2 (2 P)	hyperfine structure not interpreted
III	IIIc	$P(OEt)_3$	−50 to +40	7.40	34.2 (1 P)	0.80(4 H_o), 0.36(4 H_m), 0.80(2 H_p)
III	IIId	$P(OEt)_3$	+40	10.5	40.7 (2 P)	hyperfine structure not interpreted
IV	IVc	$P(OEt)_3$	−50 to −30	11.2	41.7 (1 P)	0.68(2 H, $H_{3,6}$), 3.12(2 H, $H_{4,5}$)
IV	IVd	$P(OEt)_3$	−30	24.3	58.5 (2 P)	<0.2($H_{3,6}$), 1.12(2 H, $H_{4,5}$)
IV	IVe	Pyridine	Room	6.80	2.05(1 N)	0.45(2 H, $H_{3,6}$), 3.35(2 H, $H_{4,5}$)
V	Vg	$AsPh_3$	+100	7.15	32.5 (1 As)	1.62(4 H, $H_{1,3,6,8}$), <0.2($H_{2,4,5,7}$)
V	Vh	$SbPh_3$	+120	7.45	99.0 (1 ^{121}Sb) 54.0 (1 ^{123}Sb)	1.56(4 H, $H_{1,3,6,8}$), <0.2($H_{2,4,5,7}$)
VI	VIa	PPh_3	−60 to +60	8.2	26.3 (1 P)	0.71(2 H, $H_{2,7}$), <0.2($H_{3,6}$)
VI	VIb	PPh_3	+60	15.0	32.0 (2 P)	<0.3($H_{2,3,6,7}$)
VI	VIc	$P(OEt)_3$	−30 to +60	8.10	32.6 (1 P)	0.50(2 H, $H_{2,7}$), <0.2($H_{3,6}$)
VI	VId	$P(OEt)_3$	+60	13.5	41.7 (2 P)	<0.3($H_{2,3,6,7}$)
VI	VIe	Pyridine	Room	4.80	1.60(1 N)	0.76(2 H, $H_{2,7}$), <0.3($H_{3,6}$)
VI	VIg	$AsPH_3$	100	7.47	33.5 (1 As)	0.74(2 H, $H_{2,7}$), <0.3($H_{3,6}$)
VI	VIh	$SbPh_3$	120	7.95	102.0 (1 ^{121}Sb) 56.0 (1 ^{123}Sb)	<0.3($H_{2,3,6,7}$)
VI	VIl	NPh_3	100	4.81	1.62(1 N)	0.76(2 H, $H_{2,7}$), <0.3($H_{3,6}$)
VI	VIm	HMPTA	Room	3.10	0.72(1 P)	0.82(2 H, $H_{2,7}$), <0.3($H_{3,6}$)
VI	VIn	*G*	Room	5.45	2.35(1 N)	0.71(2 H, $H_{2,7}$), <0.3($H_{3,6}$)
VII	VIIa	PPh_3	−50 to +20	6.6	18.0 (1 P)	1.25(H_6), 1.00(H_4), 0.37(H_7), <0.2(H_5)

^{G} *i*-propyliden-cytidine

The room temperature hyperfine splitting constants (h.f.s.c.) of radical adducts I—VIII are listed in Table 1. The assignment of the h.f.s.c. to the various positions was made by comparison with the corresponding radical anions and and alkali ion pairs.

(b) Ligand exchange on radicals I—VII and addition of $[Mn(CO)_4PPh_3]^\bullet$ to compounds 1—7

Small quantities of a suitable ligand were added in the absence of UV light to solutions containing radicals I—VII. The ESR spectra showed the formation of new radicals, characterized by splittings due to the ligands, the increase in the concentration of which was paralleled by a progressive disappearance of the original species and evolution of carbon monoxide. Whilst with pyridine, pyrazine, triphenylamine, triphenyl arsine, triphenyl stibine or hexamethyl phosphoric acid triamide (HMPTA) a single new species was obtained independent of the experimental conditions, with triphenyl phosphine and triethylphosphite two substitution products were detected. At lower temperature the original spectra were replaced by new ones showing an additional splitting due to one phosphorus atom; increasing the temperature eventually resulted in the formation of species which exhibited a coupling from two equivalent phosphorus nuclei. In one case [3], addition of $P(OEt)_3$ resulted in the formation of two radicals, each containing two equivalent phosphorus atoms. In Table 2 we report the spectral data of the radicals detected after ligand exchange.

The PPh_3-containing adducts were also obtained by an alternative method. In this a solution of MDC and PPh_3 was photolysed under the conditions under which $Mn_2(CO)_8(PPh_3)_2$ was formed in equilibrium with the monomer $[Mn(CO)_4PPh_3]^\bullet$ and after shutting off the irradiation a small quantity of one of the compounds 1—6 was added. The resulting radicals were identical with those obtained by addition of PPh_3 to I—VI.

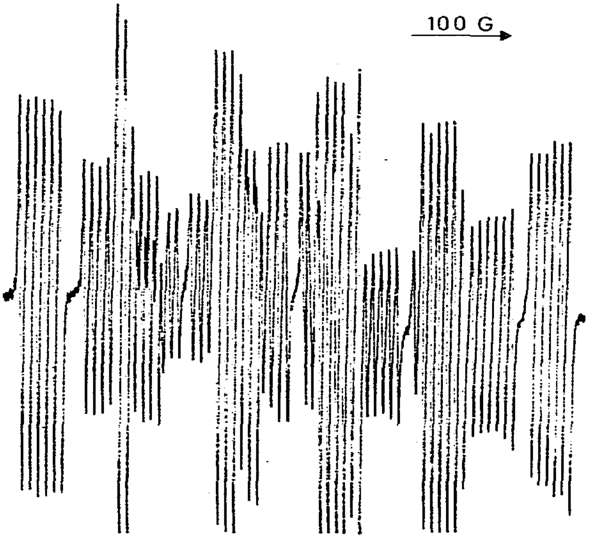


Fig. 1. ESR spectrum of radical adduct VIh in toluene at +120°C.

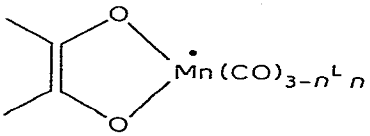
The ESR spectra of Sb-containing radicals Vh and VIh deserve special comment, because free radicals which can be observed in solution seldom have large h.f.s.c. from nuclei with spin greater than $\frac{1}{2}$. Figure 1 shows the ESR spectrum of VIh, whose asymmetry is well accounted for by perturbation theory. To second order the midpoints of the $M_I = +\frac{1}{2}$ and $M_I = -\frac{1}{2}$ transitions are shifted downfield by $\frac{1}{2}\,(I(I+1) - \frac{1}{4})(a^2/H_0)$ from the field corresponding to the g factor, i.e. by ca. 7.3 gauss for the spectrum showing the $a(^{121}\mathrm{Sb})$ coupling and by ca. 13.4 gauss for the one with $a(^{123}\mathrm{Sb})$ coupling. In addition, the sextets due to ^{55}Mn are no longer equally spaced, their separation increasing with the magnetic field.

Discussion

It is generally accepted that photolysis of $\mathrm{Mn_2(CO)_{10}}$ in organic non-ethereal solvents gives rise to $[\mathrm{Mn(CO)_5}]^{\cdot}$ radicals, which can be trapped by suitable reagents. Thus, they react with nitroso derivatives giving fairly stable nitroxides [7], while in the presence of phosphites and phosphines the products are dimeric $\mathrm{Mn_2(CO)_{10-n}(PPh_3)_n}$ complexes in thermal equilibrium with the corresponding monomers observed by ESR spectroscopy [8a].

It has been suggested that $[\mathrm{Mn(CO)_5}]^{\cdot}$ radicals add to α-dicarbonyl compounds with loss of carbon monoxide (Scheme 1). Several items of evidence now support the proposed structure for radicals I—VII.

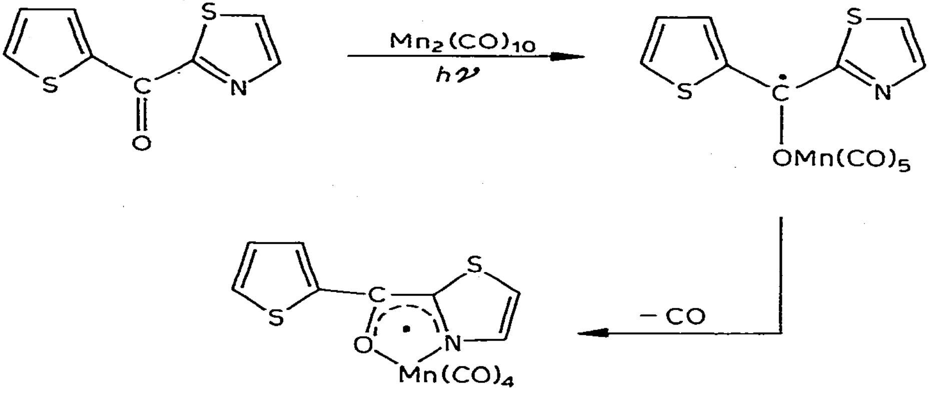
The g factors measured for radical VI, VIa and VIb are 2.00397, 2.00357 and 2.00243, respectively, while the radical anion of 6 has a g factor of 2.00517, which is typical of an organic radical containing atoms with low energy empty orbitals. The lower g values of VI, VIa and VIb indicate that in these adducts there is a transfer of spin density from the organic framework towards the $\mathrm{Mn(CO)_{4-n}L_n}$ moiety. However these values are still characteristic of "organic radicals", in contrast with those shown by closely related Mn-centered species such as $[\mathrm{Mn(CO)_3(Pbut_3)_2}]^{\cdot}$, whose isotropic g factor has been measured as 2.03 [8b]. This precludes the possibility of structures such as



for the species we are dealing with.

An indirect proof for the structure proposed in Scheme 1 is the lack of formation of stable paramagnetic adducts with monocarbonyl compounds in a broad range of experimental conditions unless a second chelating group is present in a strategic position. *p*-benzoquinone or 9,10-anthraquinone do not give any ESR spectrum upon reaction with $[\mathrm{Mn(CO)_5}]^{\cdot}$; even 1,3-diketones like dibenzoyl methane, benzoyl acetone or acetyl acetone, do not give stable complexes, presumably because of the absence of conjugation between the two carbonyls. The same is true for 2,2′-dithienyl ketone, whilst the corresponding 2-thienyl 2-thiazolyl ketone gives the stable radical adduct VIII, owing to the presence of the lone pair of the heterocyclic nitrogen (see Scheme 3).

SCHEME 3



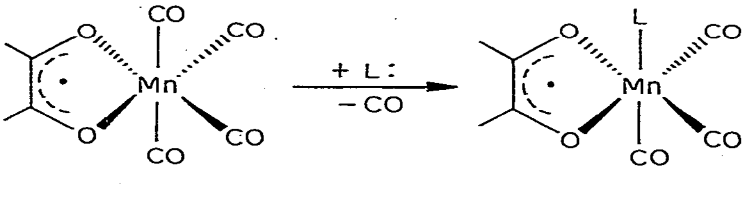
VIII

This behaviour seems to be quite general: preliminary studies on the addition of $[\mathrm{Mn(CO)_5}]^{\bullet}$ radicals to nitro-derivatives show that even in this case the paramagnetic adducts are stable only if intramolecularly chelated. Another important feature of radicals I—VI is that their ESR spectra are characteristic of symmetric species down to —100°C. Although a rapid migration, with a small energy barrier, of a $\mathrm{Mn(CO)_5}$ group between the two carbonyls would give the same results, this does not appear to be the case, because for the tricarbonyl derivative VII the spectra indicate an asymmetric structure up to +200°C (biphenyl as solvent). In the light of these arguments we think that the structure proposed in Scheme 1 for radicals I—VII can be considered correct.

An analysis of the h.f.s.c. values reported in Table 1 shows that the spin density distribution in the organic framework in I—VIII is relatively close to that found for the corresponding radical anions [9]; this is not surprising since these complexes can, in the limit, be compared to very tight ion-pairs. In the present case the spin density is probably acquired by the manganese atom at the expense of the two carbonyl oxygens, with little effect on the rest of the molecule, in agreement with the smaller g value of VI compared to that shown by the anion $6^{-\bullet}$ (vide supra).

Nitrogen containing radicals (Ie, If, IVe, VIe and VII) obtained by ligand exchange show a decrease of the $a(\mathrm{Mn}^{55})$ coupling, all other splittings being unchanged; whilst a similar behaviour was observed with ligands containing an oxygen atom as binding site, an increase of the manganese splitting is induced

SCHEME 4



by the replacement of carbon monoxide moieties by phosphorus, arsenic and antimony ligands. The persistence of the degeneracy of the h.f.s.c. of the dicarbonyl substrate after the ligand exchange is, in our opinion, an indication of substitution in one of the two axial positions, according to Scheme 4.

Such a facial configuration of the adducts would allow an overlap between the molecular orbital containing the unpaired electron and the σ manganese-phosphorus (arsenic or antimony) orbitals or an interaction between the π system and the vacant low-energy orbitals of these group V atoms. In pyridine- or pyrazine-substituted derivatives, the decrease of the Mn coupling and the absence of splittings due to the ligand molecule (except for the directly bonded nitrogen) suggest a σ-type spin transfer mechanism, which would explain the close similarity of the ESR spectra given by Ie and If, and by VIe and VIf.

Substitution of two ligand molecules for the same number of CO groups was achieved only in the case of phosphorus derivatives, and resulted in a further increase of the $a(^{55}\text{Mn})$ coupling constant through a mechanism similar to that proposed for the analogous monosubstituted adducts.

Finally we emphasize the interest of systems containing such ligands as compounds of potential biological importance (see for instance VIn). There is currently much interest in the binding of transition-metal complexes to nucleic acids and their constituents [10], and ESR spectroscopy can give valuable information about the nature of the binding process.

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