Journal of Organometallic Chemistry, 161 (1978) C63—C66
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

RADICAL ADDUCTS IN THE PHOTOREACTION BETWEEN DECACARBONYLDIMANGANESE AND 1,2-DICARBONYL COMPOUNDS

A. ALBERTI
Laboratorio dei composti del carbonio del C.N.R., Via Tolara di Sotto, 89-40064 Ozzano Emilia (BO) (Italy)
and C.M. CAMAGGI
Istituto di Chimica Organica dell'Università, Viale Risorgimento, 4-40136 Bologna (Italy)

(Received September 1st, 1978)

Summary

The radical adducts resulting from the photoreaction between decacarbonyldimanganese and some 1,2-dicarbonyl compounds have been generated and their ESR spectra recorded. Replacement of carbon monoxide moieties by other suitable ligands supports the formulation of these adducts as octahedral manganese complexes.

Photolysis* of a solution of decacarbonyldimanganese in the presence of 1,2-dicarbonyl compounds results in the formation of stable adducts, whose ESR spectra clearly show splittings due to the organic ligand and a ^{55}Mn nucleus.

In Table 1 are listed the hyperfine splitting constants for a series of radicals ob-

TABLE 1

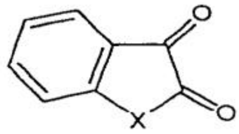
HYPERFINE SPLITTING CONSTANTS (*G*) FOR THE RADICAL ADDUCTS FROM Ia—Id (IIa—IId) AND II[a]

Substrate	Manganese adducts[b]		
	a (^{55}Mn)	a (H_{aromatic})	Other HFSC
Ia	4.80	1.60, 1.28, 0.30, < 0.05	
Ib	3.08	3.97, 3.10, 1.07, 0.99	0.80 (a(N)), 0.46 ($a(H_{NH})$)
Ic	3.32	3.42, 3.05, 1.04, 1.04	
Id	4.10	2.78, 2.51, 0.80, 0.80	
II	5.22		7.57 ($a(H_{CH_3})$, 6H)

[a] As the aromatic proton couplings are very close to those reported by Russell et al. [2] for the corresponding radical anions, the assignment in the two cases should be similar. [b] Values at room temperature in C_6H_6 solution.

---

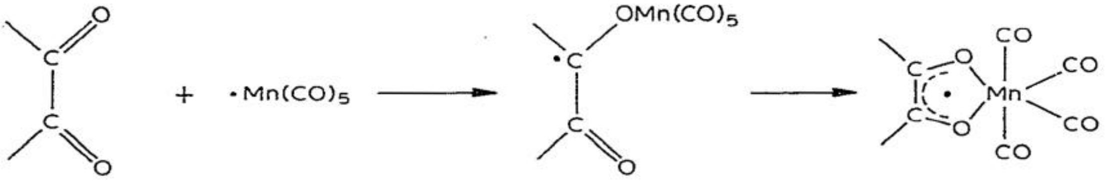
*A one kW high pressure mercury lamp was used as a source of UV light.



(Ia, X = CO ; Ib, X = NH ;
Ic, X = O ; Id, X = S)

tained from various substrates of general formula I, and from biacetyl (II), an exemple of a symmetrical aliphatic diketo derivative.

A similar adduct, formed in the photoassisted reaction between 9,10-phenanthraquinone (PQ) [1] and $Mn_2(CO)_{10}$, was recently formulated as a symmetrical "$^{\bullet}$PQ—$Mn(CO)_5$". The symmetry of this species (as deduced by its measured hyperfine splitting constants) can be due either to an actual symmetry of the adduct, with a heptacoordinated manganese bonded to both the oxygen atoms at one time, or to an averaging of two equivalent unsymmetrical structures resulting from a rapid (on the ESR time scale) exchange of the $Mn(CO)_5$ group between the two carbonyls (as is the case for the similar adduct from $^{\bullet}GePh_3$ and PQ [3]). However, the spectra do show no variation in pattern down to −90°C, except for a small increase of the ^{55}Mn HFSG, suggesting that the second hypothesis is unlikely. On the other hand, derivatives containing a heptacoordinated manganese are uncommon, and we believe that these radical adducts are octahedral manganese tetracarbonyl complexes, formed by the following sequence:



(Ia–Id) (IIa–IId)

In this sequence the conversion of I into II is favoured by the gain in entropy associated with the release of a carbon monoxide molecule*.

Carbonyl containing octahedral complexes of manganese are expected to undergo CO replacement by suitable nucleophiles [4]. When ethers, such as 1,2-dimethoxyethane (DME), diethyleneglycol dimethyl ether (Diglyme), 15-crown-5 or 18-crown-6 ethers, are added to the solution, either before or after the formation of the radical adducts, decreases of the ^{55}Mn HFS constant are observed, paralleled by an increase of the couplings due to the aromatic protons (see Table 2). This can be tentatively rationalized in terms of a weakening of the Mn—quinone interaction due to the replacement of carbonyl ligands by ether molecules.

---

*In principle it should be possible to obtain direct information on the structure of these complexes by analyzing ^{13}C satellites in their ESR spectra. This analysis, however, is complicated in our systems because of the presence of many carbon atoms. The use of ^{13}C labelled $Mn_2(CO)_{10}$ would provide the best solution to this problem.

TABLE 2

HYPERFINE SPLITTING CONSTANTS (*G*)

Radical/ligand	a($H_{aromatic}$)	a(^{55}Mn)	Other HFSC
IIa/DME [a]	1.60, 1.26, 0.32, < 0.05	3.15	
IId/18-C-6	2.81, 2.53, 0.82, 0.82	2.78	
IId/DME [a]	2.86, 2.57, 0.82, 0.82	2.65	
IId/Diglyme	2.84, 2.62, 0.82, 0.82	2.64	
IId/15-C-5	2.83, 2.55, 0.82, 0.82	2.63	
IIId/P(OEt)$_3$	3.10, 2.85, 0.95, 0.89	2.20	7.66(2^{31}P)
IVd/P(OEt)$_3$	2.80, 2.50, 0.80, 0.80	7.00	27.00(2^{31}P)

[a] The spectrum of the uncomplexed IIa or IId is still present.

A better understanding of this process can be achieved by using nucleophiles whose coordinating atom has a nuclear spin quantum number different from zero, such as phosphorus or nitrogen, so that additional information can be derived from the hyperfine splitting.

In addition of triethylphosphite to a solution of the Mn adduct with Id in methylcyclohexane at 0°C, a new radical species (IIId) replaces IId, its ESR spectrum showing an additional splitting due to two equivalent phosphorus atoms (see Table 2). When the sample is warmed to +60°C, IIId slowly disappears giving place to a new radical (IVd), which still exhibits splitting due to two ^{31}P nuclei, though much larger in value (see Table 2). No further variations are observed on re-cooling the sample.

By analogy with the well known substitution reaction of phosphines and phosphites on octahedral manganese carbonyl complexes [4], these results can be interpreted by assuming an initial kinetically controlled replacement of two CO groups by the same number of phosphite molecules to afford radical III, which thermally rearranges to the more stable IV.

This assignment is consistent with the measured ^{31}P HFSC. The relatively low spin density on P atoms in IIId is due to spin polarization through the Mn nucleus.

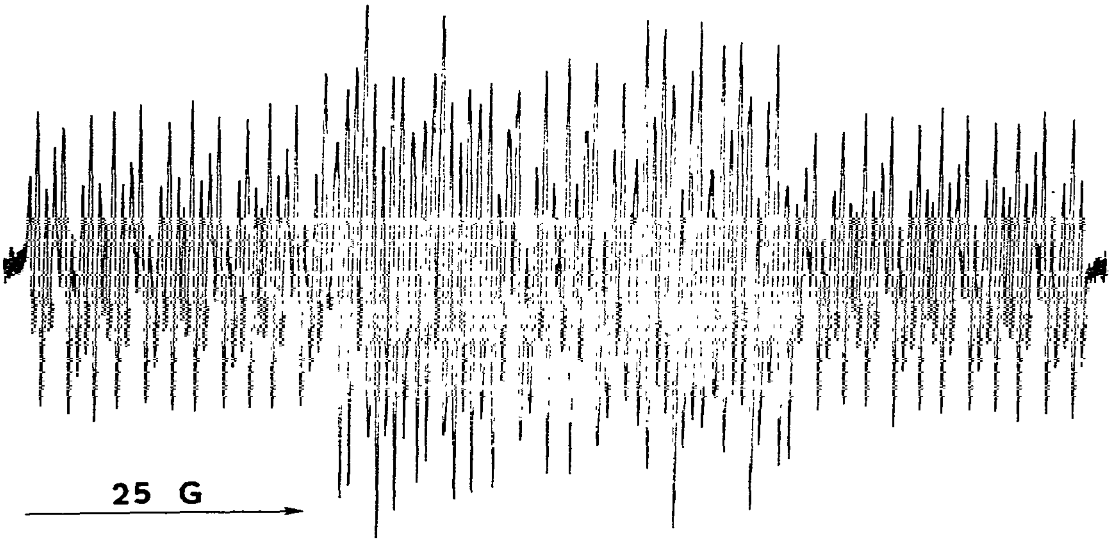
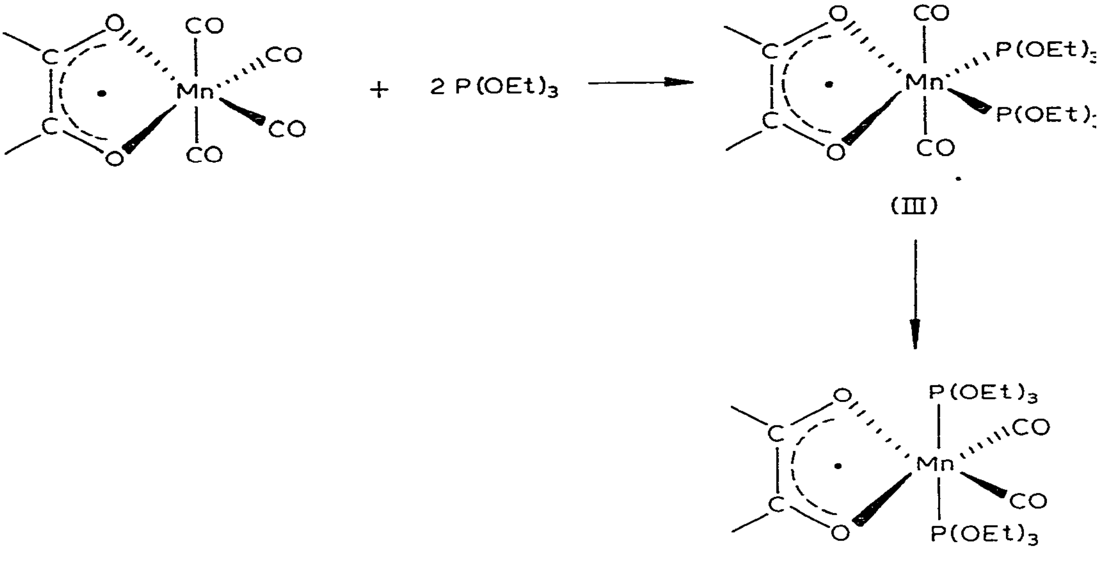


Fig. 1. ESR spectrum of radical IVd in methylcyclohexane at 60°C.



(III)

(IV)

Once again the large value of the aromatic protons HFSCs as well as the small one for ^{55}Mn are in agreement with the donating effect of P(OEt)$_3$ groups whic replaces two CO ligands. A direct interaction between the π system containing the unpaired electron and the Mn—P $\sigma^\star$ antibonding orbitals may be the cause (the large ^{55}Mn and ^{31}P HFSC in IVd, and for its greater thermodynamic stabilit with respect to IIId.

With the aim of better elucidating the structure of radicals II—IV, further work is in progress with other 1,2-dicarbonyl compounds and different ligands. Extended Hückel Molecular Orbital (EHMO) calculations are also being carried out on these systems.

References

1 K. Mochida, J.K. Kochi, K.S. Chen and J.K.S. Wan, J. Amer. Chem. Soc., 100 (1978) 2927.
2 G.A. Russell, C.L. Myers, P. Bruni, F.A. Neugebauer and R. Blankespoor, J. Amer. Chem. Soc., 92 (19 2762; G.A. Russell and R.D. Stephens, J. Phys. Chem., 70 (1966) 1320.
3 A. Alberti and A. Hudson, J. Chem. Soc. Perkin II, in press.
4 J.P. Candlin, K.A. Taylor and D.T. Thompson, Reactions of Transition-Metal Complexes, Elsevier, Amsterdam, 1968; F. Bosolo and R.G. Pearson, Mechanism of Inorganic Reactions — A study of Metal Complexes in Solution, John Wiley, New York, 1968.