Electron Spin Resonance Studies of Organometallic Manganese(0) Radicals Spin Trapped by 9,10-Phenanthroquinone and its Derivatives

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A series of manganese(0) radicals spin trapped by 9,10-phenanthroquinone ($C_{14}H_8O_2$) and its derivatives, $[Mn(^{\bullet}O_2C_{14}H_7X)(CO)_4]$, $[Mn(^{\bullet}O_2C_{14}H_7X)(CO)_3(PPh_3)]$, and $[Mn(^{\bullet}O_2C_{14}H_7X)(CO)_2(PPh_3)_2]$ (X = H, 3-CN, 2-NO_2, 4-NO_2, 3-Cl, 3-Br, 3-OMe, or 3-Pr^i), have been studied by e.s.r. spectroscopy. The hyperfine coupling constants A_{Mn} and A_P correlate well with the Hammett parameter σ_p. The larger the σ_p, the larger the coupling constant A_{Mn} or A_P. The proton hyperfine coupling constants, A_H for protons at positions 1, 3, 6, and 8 also correlate with σ_p, however, the trend is opposite to that observed for A_{Mn} or A_P. These correlations can be explained qualitatively by considering the mixing between the $O_2C_{14}H_7X$ π^* orbital which is occupied by an unpaired electron and the $d\pi$ orbital(s) of the $Mn(CO)_{4-n}(PPh_3)_n$ fragment, the influence of substituent X on the energy of the π^* orbital of 9,10-phenanthroquinone, and the influence of PPh_3 on the energy of the $d\pi$ orbital. It was estimated that *ca.* 30% spin density is delocalized from $^{\bullet}O_2C_{14}H_7X$ onto $Mn(CO)_{4-n}(PPh_3)_n$, depending on X and *n*.

Quinones play an important role in many biological electron-transfer processes.[1] Together with their reduced forms of semiquinone and catecholate they are potentially good ligands.[2] The catecholate ligand has an especially large complex formation constant of 10^{52} with iron(III)[3] and catecholate–iron complexes seem to occur in the catalytic oxidation of natural aromatic compounds.[4] Thus a study of the co-ordination chemistry of transition-metal quinone complexes could extend our understanding of the special role played by the quinones.

One general procedure for preparing transition-metal complexes of *o*-quinones is the reaction between some transition metal carbonyls (V, Cr, Mn, Fe, Co, Ni, Mo, or W) and *o*-quinones. The products are bis- or tris-semiquinone or oligomeric complexes.[5–7] However, the photochemical reaction between $[Mn_2(CO)_{10}]$ and *o*-quinones resulted in the formation of *o*-quinone trapped organometallic radicals.[8–10]

To shed light on the bonding of *o*-quinone organometallic radicals, we have studied[11] a series of radicals formed between $[Re(CO)_{4-n}(PPh_3)_n]$ (n = 0—2) and various substituted 9,10-phenanthroquinones. It was found that both A_{Re} and A_p correlated well with the Hammett parameter σ_p if the substituents were at position 3. However hyperfine coupling with the protons in the phenanthroquinone ring was not observed presumably due to the broad linewidth in the Re radical system. This hampered a detailed understanding about how the unpaired spin was distributed. This limitation was remedied when Re was replaced by Mn. Here we report our results on e.s.r. studies of a series of $[Mn(^{\bullet}O_2C_{14}H_7X)(CO)_{4-n}(PPh_3)_n]$ radicals.

Experimental

9,10-Phenanthroquinone ($O_2C_{14}H_8$) was purchased from the Aldrich Chemical Co. and used without further purification. 9,10-Phenanthroquinone derivatives $O_2C_{14}H_7X$, where X = 3-CN, 2-NO_2, 4-NO_2, 3-Cl, 3-Br, 3-OMe, or 3-Pr^i, were prepared according to the reported procedures.[11] $[Mn_2(CO)_{10}]$ was purchased from the Strem Chemical Co. and purified by vacuum sublimation.

Under nitrogen 9,10-phenanthroquinone (2×10^{-3} mmol) or its derivatives, purified $[Mn_2(CO)_{10}]$ (1×10^{-3} mmol), and benzene (1 cm^3) which was thoroughly dried by refluxing over sodium for 2 d, were introduced into a 5-mm quartz e.s.r. tube. Inside the e.s.r. cavity, the sample was irradiated with a 180-W medium-pressure mercury lamp. The duration of photolysis (*ca.* 3—5 min) was long enough to obtain e.s.r. spectra with a reasonable signal to noise ratio. Poor resolution could result from too lengthy an irradiation. The radicals were stable for *ca.* 30 min. After the e.s.r. measurement, excess triphenylphosphine was added to the sample tube to induce carbonyl substitution. Substitution of the first carbonyl was facile and completed within 10 min as judged by the e.s.r. signal. Substitution of the second carbonyl group was accomplished by heating the sample to 70 °C for 2 h.

E.s.r. spectra were obtained using a Bruker ER 200D-SRC spectrometer equipped with a microwave frequency counter (Bruker model 271), ER 035 NMR gaussmeter, and Aspect 2000 computer. In most cases, *g* values were obtained using diphenylpicrylhydrazyl (dpph) as reference, in a dual cavity to avoid crowding near the cavity during photogeneration of the radical under study. The magnetic field difference between the two sampling positions in the dual cavity was carefully measured and included in all subsequent *g*-value calculations. All spectra were measured at room temperature.

Results and Discussion

The photochemical reaction between 9,10-phenanthroquinone or its derivatives with $[Mn_2(CO)_{10}]$ results in trapped organometallic radicals [equation (1), X = H, 3-CN, 2-NO_2, 4-NO_2, 3-Cl, 3-Br, 3-OMe, or 3-Pr^i]. They are stable for *ca.* 30 min under nitrogen and exhibit well resolved e.s.r. spectra. A typical spectrum and its simulation for $[Mn(^{\bullet}O_2C_{14}H_7Cl\text{-}3)(CO)_4]$ are shown in Figure 1(*a*). The radical formation mechanism has been suggested to be charge transfer in nature.[8] However, photochemical homolytic cleavage[12] of the metal–metal σ bond to form a pentacarbonylmanganese radical which subsequently reacts with $O_2C_{14}H_7X$ to form a radical adduct cannot be ruled out under our experimental conditions.

The carbonyl groups of $[Mn(^{\bullet}O_2C_{14}H_7X)(CO)_4]$ are labile with respect to phosphine or phosphite substitution.[13,14] In the presence of an equivalent amount of triphenylphosphine, the

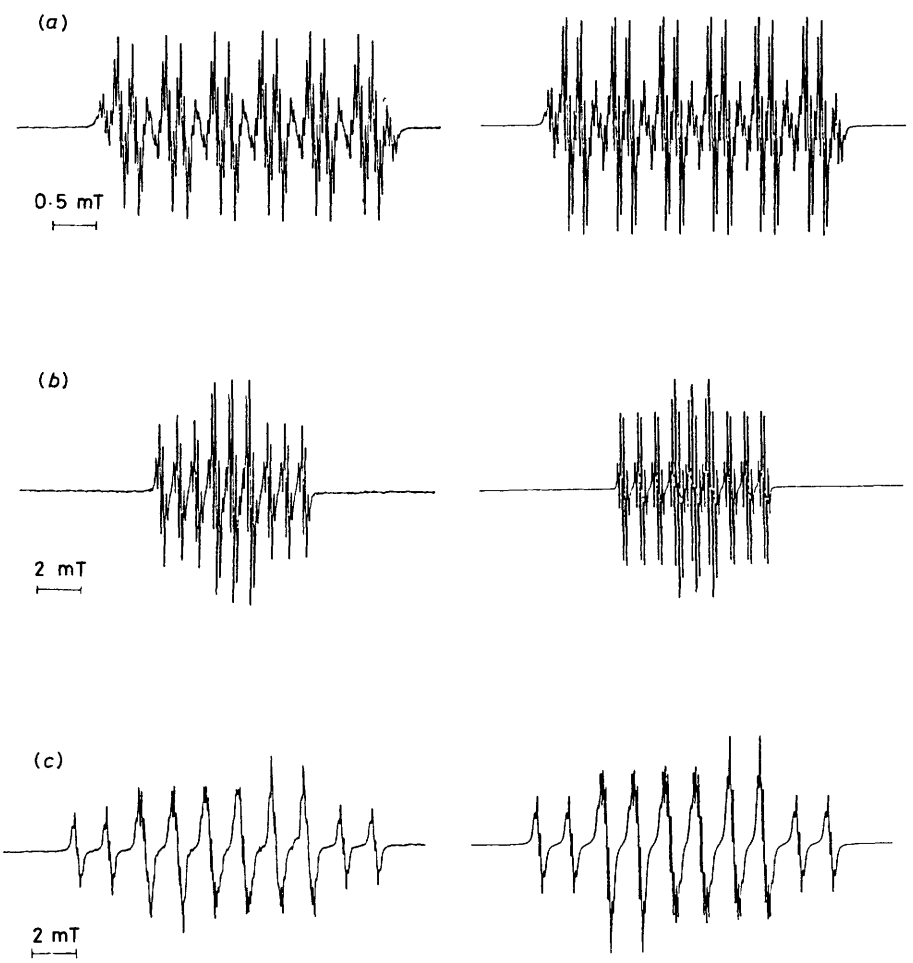
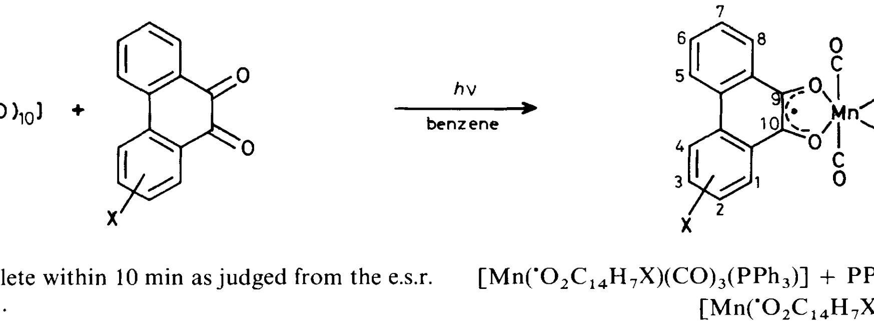


Figure 1. Solution (left) and simulated (right) e.s.r. spectra of (*a*) $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_4]$, (*b*) $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$, and (*c*) $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$



(1)

substitution is complete within 10 min as judged from the e.s.r. signal [equation (2)].

$$[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_4] + \mathrm{PPh_3} \longrightarrow [\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_3(\mathrm{PPh_3})] \quad (2)$$

A typical spectrum and its simulation for $[\mathrm{M}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$ is shown in Figure 1(*b*). The phosphorus hyperfine coupling constants lie in the range 2.425—2.840 mT, indicating that the phosphorus is *cis* to $\mathrm{O_2C_{14}H_7X}$.[15] The *X*-ray structure of a related radical $[\mathrm{Re(dtbq)(CO)_3(PPh_3)}]^{\bullet}$[16] (dtbq = 3,5-di-t-butyl-*o*-benzoquinone), where phosphine is established to be *cis* to dtbq, also supports the structural assignment.

In contrast with the Re radicals, the second substitution by triphenylphosphine is facile thermally, and the reaction is complete within 2 h at 70 °C [equation (3)]. Hyperfine splitting

$$[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_3(\mathrm{PPh_3})] + \mathrm{PPh_3} \longrightarrow [\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_2(\mathrm{PPh_3})_2] \quad (3)$$

due to two equivalent phosphines can be observed. The large hyperfine coupling constants (2.915—3.781 mT) again indicate the two phosphines are *cis* to $\mathrm{O_2C_{14}H_7X}$.

The e.s.r. parameters, which were confirmed by satisfactory spectral simulation of the radicals $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_4]$, $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_3(\mathrm{PPh_3})]$, and $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$, are summarized in the Table. It is clear that as the number of phosphines increase, the e.s.r. parameters follow regular patterns, *i.e.* *g* decreases, A_{Mn} increases, A_{P} increases, and A_{H} decreases.

To understand the relationship between A_{Mn} and substituent, A_{Mn} was plotted against the substituent Hammett parameter σ_{p} and the results are shown in Figure 2. Linear correlations were observed for all three radical systems: $[\mathrm{Mn}(^{\bullet}\mathrm{O_2C_{14}H_7X})(\mathrm{CO})_4]$,

Table. E.s.r. parameters of $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_{4-n}(PPh_3)_n]$ in benzene solution at 25 °C

X	n	g	A_{Mn}/mT	A_P/mT	A_H/mT
H	0	2.003 75	0.5501		$4A_H = 0.1692$, $4A_H = 0.0414$
	1	2.003 61	0.7775	2.568	$4A_H = 0.1563$, $4A_H = 0.0342$
	2	2.002 98	1.359	3.083	$4A_H = 0.1354$
3-CN	0	2.003 87	0.5960		$3A_H = 0.1602$, $2A_H = 0.0564$, $2A_H = 0.0319$
	1	2.003 41	0.8825	2.683	$3A_H = 0.1435$, $2A_H = 0.0233$
	2	2.002 95	1.713	3.411	$3A_H = 0.1220$
2-NO_2	0	2.003 84	0.6005		$4A_H = 0.1570$, $3A_H = 0.0359$
	1	2.003 58	0.8850	2.650	$4A_H = 0.1528$, $3A_H = 0.0289$
	2	2.002 89	1.696	3.438	$4A_H = 0.1235$
4-NO_2	0	2.003 84	0.5928		$4A_H = 0.1578$, $3A_H = 0.0345$
	1	2.003 50	0.8776	2.689	$4A_H = 0.1435$, $3A_H = 0.0256$
	2	2.003 01	1.655	3.388	$4A_H = 0.1175$
3-Cl	0	2.004 04	0.5595		$3A_H = 0.1670$, $4A_H = 0.0403$
	1	2.003 64	0.8020	2.597	$3A_H = 0.1529$, $4A_H = 0.0266$
	2	2.002 86	1.453	3.151	$3A_H = 0.1344$
3-Br	0	2.004 65	0.5625		$3A_H = 0.1642$, $4A_H = 0.0398$
	1	2.004 39	0.8125	2.565	$3A_H = 0.1504$, $4A_H = 0.0336$
	2	2.003 47	1.458	3.185	$3A_H = 0.1352$
3-OMe	0	2.003 92	0.5119		$3A_H = 0.1750$, $2A_H = 0.0515$, $2A_H = 0.0112$, $3A_H = 0.0255$
	1	2.003 41	0.7226	2.425	$3A_H = 0.1601$, $2A_H = 0.0388$, $5A_H = 0.0184$
	2	2.002 72	1.222	2.915	$3A_H = 0.1395$
3-Pr^i	0	2.003 84	0.5368		$3A_H = 0.1688$, $1A_H = 0.0765$ $10A_H = 0.0385$
	1	2.003 81	0.7558	2.498	$3A_H = 0.1560$, $4A_H = 0.0385$
	2	2.002 60	1.278	3.018	$3A_H = 0.1435$

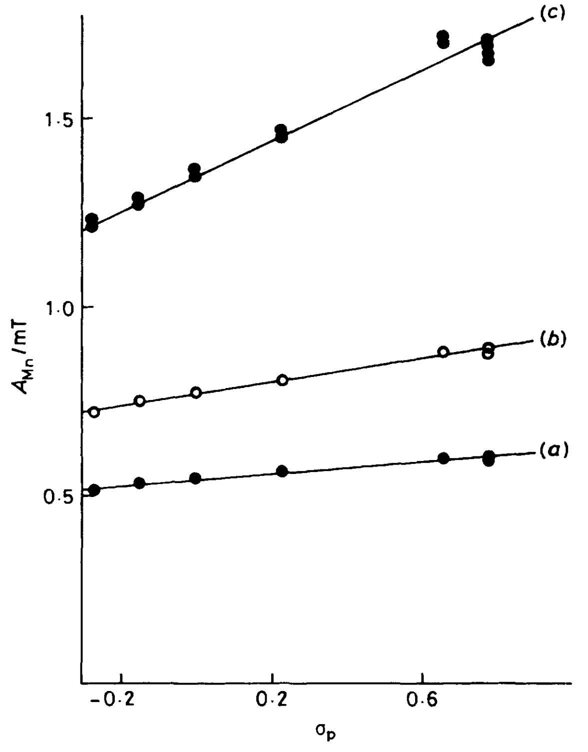


Figure 2. Correlation of A_{Mn} *vs.* Hammett parameter σ_p of substituent X in (*a*) $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_4]$, (*b*) $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_3(PPh_3)]$, and (*c*) $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_2(PPh_3)_2]$

$[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_3(PPh_3)]$, and $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_2(PPh_3)_2]$. In addition, the better the electron donating substituent X, the smaller the A_{Mn}. Linear relationships also exist between the phosphorus hyperfine coupling constants and the substituent Hammett parameters, as shown in Figure 3. Similarly to the trend observed for A_{Mn}, the better the electron withdrawing ability of X, the larger the A_P.

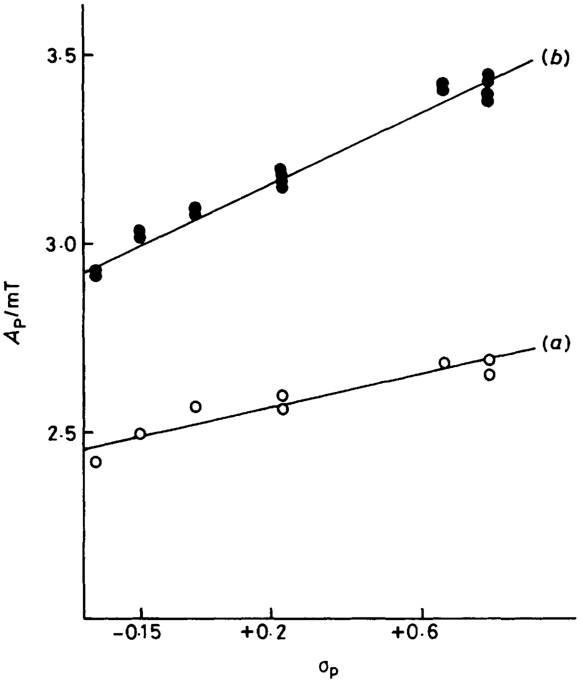


Figure 3. Correlation of A_P *vs.* Hammett parameter σ_p of substituent X in (*a*) $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_3(PPh_3)]$ and (*b*) $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_2(PPh_3)_2]$

In the unsubstituted radical $[Mn(^{\cdot}O_2C_{14}H_7X)(CO)_4]$, when X = 3-CN or 3-OMe, two hyperfine proton coupling constants, *i.e.* $A_H(2,7)$ and $A_H(4,5)$ (values in parentheses indicate the

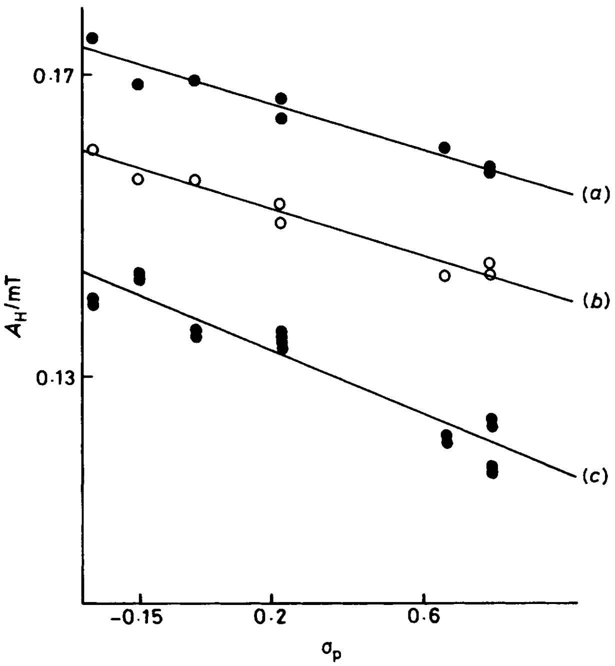


Figure 4. Correlation of A_H *vs.* Hammett parameter σ_p of substituent X in (*a*) [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_4$], (*b*) [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_3$(PPh$_3$)], and (*c*) [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_2$(PPh$_3$)$_2$]. The coupling constants are for protons at the 1, 3, 6, and 8 positions of $O_2C_{14}H_7X$

positions of protons), can be resolved, while no resolution can be detected for the others. The presence of triphenylphosphine in [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_3$(PPh$_3$)] and [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_2$(PPh$_3$)$_2$] results in a linewidth broadening which prevents the resolution of the small difference in A_H at positions 2, 4, 5, and 7. Because of the low A_H values and the complication of two values at positions 2, 4, 5, and 7, they will not be analysed further. However, it should be noted that A_H at 2, 4, 5, and 7 and A_H at 1, 3, 6, and 8 follow the same general trend. The hyperfine coupling constants of protons situated at positions available at 1, 3, 6, 8 are identical within experimental error for each radical. Values of A_H at positions 1, 3, 6, and 8 are plotted against σ_p in Figure 4. It is clear that reasonably straight lines can be drawn through the data. Contrary to the trend observed for A_{Mn} and A_P, it is observed that the better the donating ability of the substituent X the larger the A_H.

The bonding between $O_2C_{14}H_7X$ and Mn(CO)$_{n-4}$(PPh$_3$)$_n$ (n = 0—2) can be envisaged as follows. The manganese moiety loses an electron to $O_2C_{14}H_7X$ to become a Mn^I species. It then accepts four electrons from the charged semiquinone $^{\bullet}O_2C_{14}H_7X^-$ to comply with the 18-electron rule. Although this bonding scheme is very simple, it can satisfactorily account for the fact that the unpaired electron in the radical [M($^{\bullet}O_2C_{14}H_7X$)(CO)$_{4-n}$(PPh$_3$)$_n$] (M = Re or Mn, n = 0—2) resides mainly on the organic moiety.[11] The *X*-ray structure[16] of [Re(dtbq)(CO)$_3$(PPh$_3$)] also indicates that dtbq is actually a semiquinone. Thus, the unpaired electron occupies the π^* orbital of $O_2C_{14}H_7X$. This is further supported by the similarity in the values of proton hyperfine coupling constants between [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_4$] and the 9,10-phenanthroquinone radical anion.[17]

The opposite trends observed for the dependence of A_H and A_{Mn} or A_P on σ_p can be rationalized by considering the orbital interaction between the unpaired π^* electron orbital of $O_2C_{14}H_7X$ and the orbital on the Mn(CO)$_{4-n}$(PPh$_3$)$_n$ fragment with appropriate symmetry. An electron donating substituent X on $O_2C_{14}H_8$ tends to raise the π^* orbital energy of $O_2C_{14}H_7X$. This results in less orbital mixing between π^* and Mn(CO)$_{4-n}$(PPh$_3$)$_n$ orbitals based on energy considerations because the orbitals of the organometallic moiety have less energy than the π^* of $O_2C_{14}H_8$. Thus, with a stronger electron donating substituent, the unpaired electron is localized more on $O_2C_{14}H_7X$ consistent with the experimentally observed trend. This leads to a larger A_H and smaller A_{Mn} and A_P for [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_{4-n}$(PPh$_3$)$_n$] with an electron donating substituent X. The simple bonding picture described above can also be used to explain the variation in A_{Mn}, A_P and A_H due to the different degree of phosphine substitution. Since triphenylphosphine is known to be a better electron donor and poorer π acceptor in comparison with CO, substituting CO by PPh$_3$ raises the energy of the orbital of Mn(CO)$_{4-n}$(PPh$_3$)$_n$ and favours the mixing with the π^* orbital of $O_2C_{14}H_7X$. Consequently, more unpaired electron spin density is transferred to the Mn(CO)$_{4-n}$(PPh$_3$)$_n$ moiety and hence A_{Mn} and A_P increase and the A_H decreases upon phosphine substitution. The relationship between the metal coupling constant and ligand π donating ability is also apparent in [Co^{III}L(dtbq)],[18] where L is a N_2O_2-donor type of ligand. When the π donating ability of L increases, A_{Co} also increases.

From the spin density on $O_2C_{14}H_7X$ in [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_{4-n}$(PPh$_3$)$_n$], it is possible to estimate the degree of $p\pi$–$d\pi$ orbital mixing. It is reasonable to assume that A_H of the protons at positions 1, 3, 6, and 8 is roughly 0.18 mT if an unpaired spin is localized on $O_2C_{14}H_7X$. This assumed value is slightly larger than that of $^{\bullet}O_2C_{14}H_8^-$ since the A_H values for most [Mn($^{\bullet}O_2C_{14}H_7X$)(CO)$_4$] radicals are also larger than that of $^{\bullet}O_2C_{14}H_8^-$ presumably because of the perturbation caused by complexation. Taking [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_{4-n}$(PPh$_3$)$_n$] as an example, the other radical systems can be evaluated accordingly and the qualitative results are the same. Comparing [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_3$(PPh$_3$)] and [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_4$], A_H is reduced by 0.0129 mT and the spin density on $O_2C_{14}H_8$ is therefore reduced by 7.2%. The corresponding A_{Mn} is increased by 0.2274 mT. Hence in [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_4$], the A_{Mn} value of 0.5501 mT roughly indicates a 17.4% spin transfer from $^{\bullet}O_2C_{14}H_8^-$ to the Mn(CO)$_4$ fragment. In [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_3$(PPh$_3$)] and [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_2$(PPh$_3$)$_2$], the transferred spin densities are 24.6 and 43.4% respectively. From symmetry considerations, the isotropic coupling constants A_{Mn} and A_P most likely arise from spin polarization. This is reflected in the transferred spin densities in [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_{4-n}$(PPh$_3$)$_n$]. Since an electron in a Mn 4*s* atomic orbital will give A_{Mn} = 179.7 mT, the spin densities calculated from A_{Mn} are 3.06×10^{-3}, 4.37×10^{-3}, and 7.56×10^{-3} for [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_4$], [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_3$(PPh$_3$)], and [Mn($^{\bullet}O_2C_{14}H_8$)(CO)$_2$(PPh$_3$)$_2$] respectively. These values are only 17% of those transferred spin densities calculated based on A_H. The phosphorus coupling constants indicate a negligibly small participation of the phosphorus 4*s* orbital. Thus, the majority of spin density transferred from $^{\bullet}O_2C_{14}H_8^-$ to Mn(CO)$_{4-n}$(PPh$_3$)$_n$ resides mainly on the π-type orbitals of the Mn(CO)$_{4-n}$(PPh$_3$)$_n$ fragment. It further indicates that spin polarization may be responsible for the coupling between an unpaired electron and manganese.

In our attempts to prepare single crystals of dtbq or 9,10-phenanthroquinone complexes with low-valent organometallic moieties, such as [Re(CO)$_4$], it is observed that if carbonyl is substituted by PPh$_3$, then the radical stability is increased. This phenomenon can be explained by the gain of stabilization energy because of the better mixing between the π^* orbital of dtbq and the $d\pi$ orbital of [Re(CO)$_3$(PPh$_3$)]. In studying the chemistry of [Re($^{\bullet}O_2C_{14}H_7X$)(CO)$_4$], we have also found[11] that the better the electron withdrawing ability of substituent X, the better the stability of the radical. These two observations point the way for the preparation of stable α,β-diketone complexes of organometallic radicals.

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