Substituent Effects on Rhenium and Phosphorus Hyperfine Coupling Constants of Organometallic Rhenium(o) Radicals Spin Trapped by 9,10-Phenanthroquinone and its Derivatives

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A series of rhenium(o) radicals were spin trapped by 9,10-phenanthroquinone ($C_{14}H_8O_2$) and its derivatives, $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_4]$, $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_3(PPh_3)]$, and $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_2(PPh_3)_2]$ (n = 1, X = H, OMe-3, Cl-3, Br-3, Pr^i-3, CN-3, NO_2-2, or NO_2-4; n = 4, X_4 = Me_4-1,3,6,8 or -2,4,5,7), and were studied by e.s.r. spectroscopy. The rhenium hyperfine coupling constants, A_{Re}, for $[Re(^{\bullet}O_2C_{14}H_7X)(CO)_4]$ (X = H, OMe-3, Cl-3, Br-3, Pr^i-3, CN-3, NO_2-2, or NO_2-4) correlate very well with the Hammett parameter σ_p. Values of A_{Re} for $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_3(PPh_3)]$ and A_P for $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_3(PPh_3)]$ and $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_2(PPh_3)_2]$ also correlate with the A_{Re} values for $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_4]$. However, in the correlation of values of A_{Re} for bis(phosphine) and tetracarbonyl radicals, the data for radicals with a strong electron-withdrawing group attached to 9,10-phenanthroquinone are irregular. It is proposed that the irregularity is due to the stereochemical change of $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_3(PPh_3)_2]$ induced by the electron-withdrawing group.

Organometallic radicals which are reactive and unstable[1] have been proposed as intermediates in a large number of organometallic stocheiometric reactions,[2] as well as catalytic reactions.[3] To understand the chemical and spectroscopic properties of these radicals, it is convenient to stabilize them chemically. One approach is to stabilize the radicals sterically by introducing bulky ligands into the co-ordination sphere of the metal.[4] The other approach is to stabilize them electronically by spin trapping, with trapping agents such as nitroso compounds[5] and α,β-diketones.[6] The stabilized radicals can be studied by all conventional chemical and spectroscopic techniques, especially e.s.r. spectroscopy which can furnish information on electronic structure and reactivity.

The study of the influence of the electronic structure of spin-trapping agents on the properties of the trapped organometallic radical is vital to our understanding of the interaction of the radical with the organic substrate. This problem is especially important with regard to radical-catalyzed reactions. Hence, we have synthesized a series of substituted 9,10-phenanthroquinones ($C_{14}H_8O_2$) which can function as spin-trapping agents. The e.s.r. spectra of the rhenium carbonyl radicals trapped by substituted phenanthroquinones were studied in detail to understand the electronic factors controlling the properties of the spin-trapped radical.

Experimental

Measurements.—E.s.r. spectra were obtained using a Bruker ER 200D-SRC spectrometer equipped with a microwave frequency counter (Bruker model 371) and ERO35 n.m.r. gaussmeter. 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 was included in all subsequent g-value calculations. All spectra were measured at room temperature.

Synthesis of Substituted 9,10-*Phenanthroquinones.*—(i) Substituted *trans*-stilbenes were prepared by the Wittig reaction of *p*-substituted benzaldehyde and benzyl chloride in the presence of $P(OEt)_3$. The products were recrystallized from suitable solvents (benzene or n-hexane), and melting points (m.p.s) were compared with the literature values (see Table 1).

(ii) Substituted phenanthrenes were prepared from the corresponding *trans*-stilbenes by photochemical oxidative cyclizations.[7] Table 1 summarizes the products and the m.p.s, which were compared with the literature values.

(iii) Substituted 9,10-phenanthroquinones were prepared by oxidation of the corresponding phenanthrene with chromium trioxide[8] (see Table 1).

Besides the melting points, all synthesized compounds were confirmed by proton n.m.r. and i.r. spectroscopy.

Sample Preparation for E.S.R. Study.—The substituted phenanthroquinone (2×10^{-3} mmol) and $[Re_2(CO)_{10}]$ (2×10^{-4} mmol) were weighed into a 5-mm e.s.r. quartz tube. Then benzene (2 cm^3), which was thoroughly dried by refluxing over sodium for 2 d, was introduced into the tube. The e.s.r. samples were prepared under nitrogen to avoid possible interference from oxygen.

After the e.s.r. sample tube was inserted into the cavity, the α,β-diketone trapped radical was generated *in situ* by photolysis inside the cavity using a 180-W medium-pressure mercury lamp. The duration of photolysis (*ca.* 10 min) was long enough to obtain e.s.r. spectra with a reasonable signal-to-noise ratio. The trapped rhenium carbonyl radicals were quite stable since there was no sign of decay in a 2 h period. After the e.s.r. measurement, excess triphenylphosphine was added to the sample tube to induce carbonyl substitution. The substitution of the first carbonyl group by triphenylphosphine was completed within 10 min at 25 °C. After heating at 70 °C for more than 24 h, no sign of the second carbonyl substitution was observed. However, under 180-W mercury lamp irradiation, the second substitution was completed within 10 min.

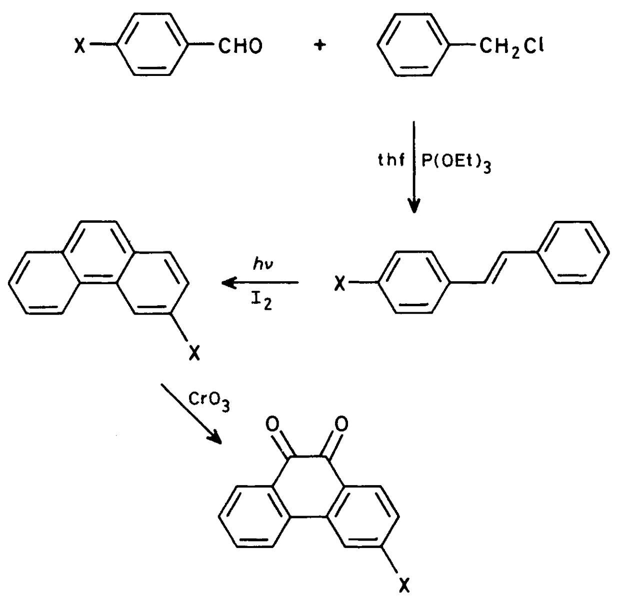
Results and Discussion

To study the substituent effect of spin-trapping agents on the electronic structure of spin adducts, we synthesized a series of substituted 9,10-phenanthroquinones. They were prepared by oxidation of the corresponding phenanthrenes. The synthesis of

Table 1. Yields and m.p.s for substituted products

Substituent(s)	Yield (%)	M.p. (°C)	Literature value (°C)	Ref.
(*a*) Substituted *trans*-stilbenes				
Me_4-2,2′:4,4′	72	107—109		
Me_4-3,3′:5,5′	80	139—141	140—141	9
Pr^i-3	85	90.5—91		
Cl-3	89	126—127	127	*a*
Br-3	82	141—142	139.5—140	*b*
OMe-3	80	134—135	135—136	*c*
Me-3	83	118—119	119.5—120	*c*
(*b*) Substituted phenanthrenes				
Me_4-2,4,5,7	70	112—114	111—113	10
Me_4-1,3,6,8	76	151—153	152.5—153.5	*d*
Me-3	81	61—62	62—63	8
Pr^i-3	74	Liquid		
OMe-3	56	56—57	59	*e*
Cl-3	86	80—81	80.5—81.5	*f*
Br-3	78	83—84	83—84	*f*
CN-3	62	78—79		
(*c*) Substituted 9,10-phenanthroquinones				
Me-3	71	205—206 (decomp.)	205—206 (decomp.)	8
OMe-3	63	209—211 (decomp.)	208 (decomp.)	*c*
Pr^i-3	65	164—165 (decomp.)		
Cl-3	86	262—264 (decomp.)	261 (decomp.)	*g*
Br-3	82	268—270 (decomp.)	268 (decomp.)	*h*
CN-3	80	256—257 (decomp.)		
Me_4-2,4,5,7	40	195—196 (decomp.)		
Me_4-1,3,6,8	42	205—206 (decomp.)		

[a] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373. [b] J. I. G. Cadagom, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 1962, 4164. [c] L. Zeckmeister and W. H. McNeely, *J. Am. Chem. Soc.*, 1942, **64**, 1919. [d] A. Regnault and P. Cannonne, *Tetrahedron Lett.*, 1968, 355. [e] R. Pschorr, *Chem. Ber.*, 1901, **34**, 3998. [f] W. E. Beckman and C. H. Boatner, *J. Am. Chem. Soc.*, 1936, **58**, 2194. [g] H. Sandguist and A. Hagelin, *Chem. Ber.*, 1981, **51**, 1515. [h] J. Schmidt and O. Spond, *Chem. Ber.*, 1910, **43**, 1802.

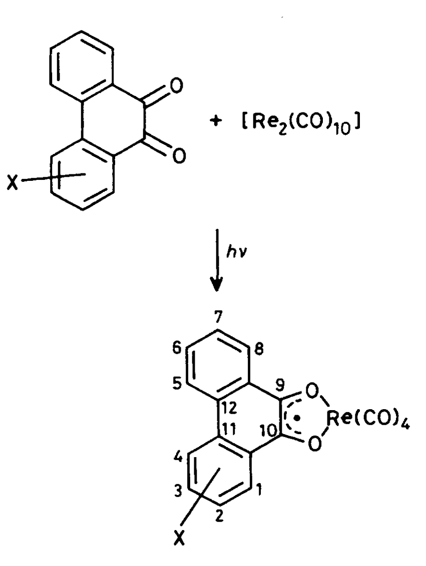


Scheme 1. X = OMe, Cl, Br, Pr^i, or CN; thf = tetrahydrofuran

substituted phenanthrenes was achieved by oxidative photocyclization of the corresponding stilbenes prepared by Wittig reaction of substituted benzaldehyde and benzyl chloride. The synthesis of 3-substituted 9,10-phenanthroquinones is described in Scheme 1.

1,3,6,8-Tetramethyl-9,10-phenanthroquinone and 2,4,5,7-tetramethyl-9,10-phenanthroquinone were prepared by oxidation (chromic acid in acetic acid) of 1,3,6,8- and 2,4,5,7-tetramethylphenanthrene respectively. 2,4,5,7-Tetramethylphenanthrene was prepared according to the literature procedure.[9,10] 1,3,6,8-Tetramethylphenanthrene was prepared by photochemical oxidative cyclization.[11]

The photochemical reaction between the phenanthroquinone derivative and $[Re_2(CO)_{10}]$ results in trapped radicals [equation (1)], $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_4]$ [n = 1, X = H (**1**),



(1)

OMe-3 (**2**), Cl-3 (**3**), Br-3 (**4**), Pr^i-3 (**5**), CN-3 (**6**), NO$_2$-2 (**7**), or NO$_2$-4 (**8**); n = 4, X$_4$ = Me$_4$-1,3,6,8 (**9**) or Me$_4$-2,4,5,7 (**10**)].

The rhenium pentacarbonyl radical $[\mathrm{Re(CO)_5}]^{\bullet}$, resulting from photochemical homolytic cleavage of the Re–Re bond in $[\mathrm{Re_2(CO)_{10}}]$ reacts rapidly with the phenanthroquinone derivative to form the relevant trapped radical denoted by $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]$,[6] with concomitant release of carbon monoxide. A typical e.s.r. spectrum of $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]$ is shown in Figure 1(*a*). It is noteworthy that the linewidth ΔH_{pp} is *ca* 0.7 mT and no hyperfine coupling with any nuclei in the phenanthroquinone derivative can be observed.

The carbonyl group of the trapped radical can be readily substituted by triphenylphosphine according to equation (2). The thermal substitution reaction rates are fast at room temperature. For a PPh$_3$ concentration of the order 10^{-2} mol dm^{-3}, it took only 10 min to complete the substitution reaction. The reaction rate was observed to be quite independent of the PPh$_3$ concentration. The substitution mechanism is likely to be dissociative.[6c,6d] A typical e.s.r. spectrum of the monosubstituted radical is shown in Figure 1(*b*).

$$\underset{\mathbf{(1)-(10)}}{[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]} + \mathrm{PPh_3} \xrightarrow{\text{heat}} \underset{\mathbf{(11)-(20)}}{[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_3(PPh_3)}]} + \mathrm{CO} \tag{2}$$

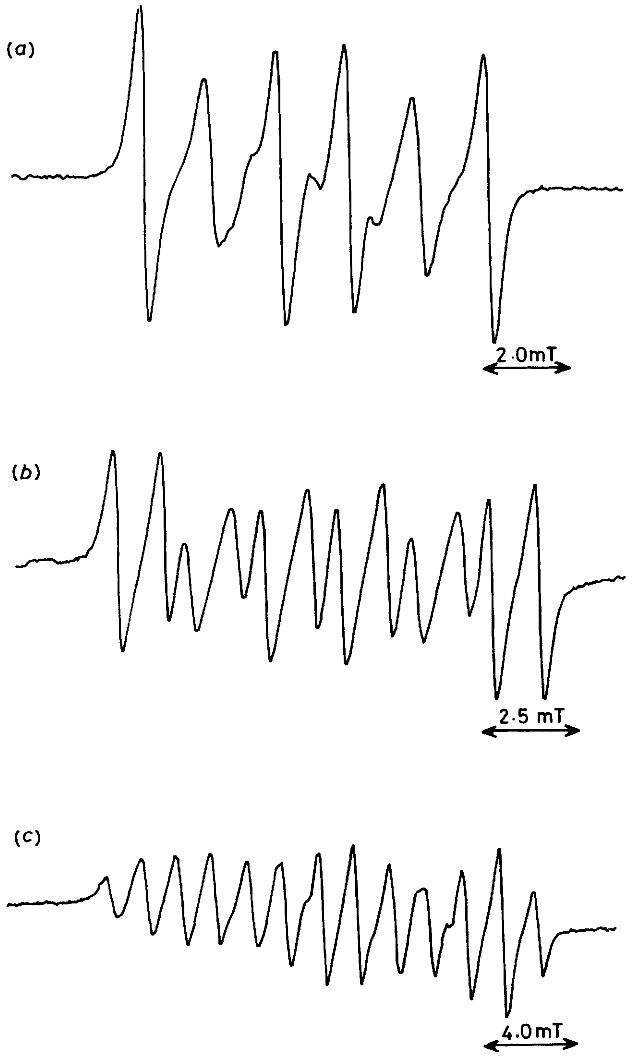


Figure 1. Solution e.s.r. spectra of the 3-chlorophenanthroquinone trapped rhenium radicals: (*a*) $[\mathrm{Re(^{\bullet}O_2C_{14}H_7Cl\text{-}3)(CO)_4}]$; (*b*) $[\mathrm{Re(^{\bullet}O_2C_{14}H_7Cl\text{-}3)(CO)_3(PPh_3)}]$; and (*c*) $[\mathrm{Re(^{\bullet}O_2C_{14}H_7Cl\text{-}3)(CO)_2(PPh_3)_2}]$

A second triphenylphosphine substitution of the carbonyl group in the trapped radical proceeds only slowly [equation (3)]. After heating the reaction mixture containing excess triphenylphosphine for 2 d, only small amounts of the monosubstituted radical were converted into the disubstituted radical. However, this reaction proceeds rapidly under photolysis. A typical e.s.r. spectrum of a disubstituted radical is shown in Figure 1(*c*).

$$[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_3(PPh_3)}] + \mathrm{PPh_3} \xrightarrow[\text{benzene}]{} \underset{\mathbf{(21)-(30)}}{[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_2(PPh_3)_2}]} + \mathrm{CO} \tag{3}$$

The e.s.r. parameters of all the radicals $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]$, $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_3(PPh_3)}]$, and $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_2(PPh_3)_2}]$, are collected in Table 2. The hyperfine coupling constants, A_{Re} and A_{P}, were carefully checked with spectral simulations to avoid error caused by spectral overlapping. The *g* values for unsubstituted, mono-, and di-substituted radicals have ranges of 2.0039—2.0029, 2.0024—2.0014, and 2.0006—1.9982, respectively. All the *g* values are close to the free electron *g* value (2.0023). This indicates that the unpaired electron resides mainly on a molecular fragment not containing the heavy rhenium atom, which has a large spin–orbit coupling constant and may cause the *g* value to deviate substantially away from the free electron value. Upon substituting CO by triphenylphosphine, the *g* value decreases. The second phosphine substitution causes even more dramatic reduction in *g* values. However, no obvious correlation between *g* values and electronic properties of the substituent, X, on phenanthroquinone can be found.

In the $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]$ series, the hyperfine coupling constants with rhenium ($I = \frac{5}{2}$), A_{Re}, correlate very well with the Hammett substituent parameters, σ_{P}.[12] The relationship is given in equation (4). The tetramethyl substituted radicals (**9**) and (**10**) were omitted. To rationalize the linear correlation, the closely related radical $[\mathrm{Re(dtbq)(CO)_4}]^{\bullet}$,[6c] where dtbq is 3,5-di-t-butyl-*o*-benzoquinone, was considered. A large hyperfine coupling constant with the proton at position 4 can be observed. On the other hand, coupling with the proton at position 6 is negligibly small. The same coupling pattern with protons is also observed in $[\mathrm{Mn(dtbq)(CO)_4}]$,[13] where the coupling to protons in the 5-t-butyl group can also be resolved. Thus, there are high spin densities at carbons 4 and 5 in dtbq. By analogy, at carbons 11 and 12 of $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_4}]$, there are high spin densities which can be efficiently transferred to carbons at 1, 3, 6, and 8 through resonance. Hence, one could expect the substituent effect of X at position 3 to be accounted for by the Hammett parameters, σ_{p}.

$$A_{\mathrm{Re}}\,[\mathbf{(1)}-\mathbf{(8)}] = 0.32\,(\pm 0.04)\,\sigma_{\mathrm{p}} + 2.20\,(\pm 0.02) \tag{4}$$

In the monosubstituted radicals $[\mathrm{Re(^{\bullet}O_2C_{14}H_{8-\mathit{n}}X_\mathit{n})(CO)_3(PPh_3)}]$, the rhenium hyperfine coupling constants are larger than those of the unsubstituted radicals. Furthermore, there is a linear relationship as shown in equation (5), between the A_{Re}

$$A_{\mathrm{Re}}\,[\mathbf{(11)}-\mathbf{(20)}] = 1.58\,(\pm 0.06)\,A_{\mathrm{Re}}\,[\mathbf{(1)}-\mathbf{(10)}] - 0.51\,(\pm 0.13) \tag{5}$$

Table 2. Table of e.s.r. parameters of trapped phenanthroquinone derivatives of rhenium(0) radicals

	Radical	g Value	A_{Re}/mT	A_{P}/mT
(1)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_8})(\mathrm{CO})_4]$	2.0033	2.24	
(11)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_8})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0018	3.00	1.90
(21)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_8})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9991	4.48	2.23
(2)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7OMe\text{-}3})(\mathrm{CO})_4]$	2.0032	2.07	
(12)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7OMe\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0018	2.76	1.81
(22)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7OMe\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9993	4.07	2.09
(3)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_4]$	2.0031	2.27	
(13)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0020	3.08	1.94
(23)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Cl\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9990	4.703	2.25
(4)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Br\text{-}3})(\mathrm{CO})_4]$	2.0039	2.28	
(14)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Br\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0024	3.07	1.91
(24)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Br\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9990	4.48	2.23
(5)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Pr^i\text{-}3})(\mathrm{CO})_4]$	2.0030	2.17	
(15)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Pr^i\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0018	2.89	1.88
(25)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7Pr^i\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9994	4.28	2.20
(6)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7CN\text{-}3})(\mathrm{CO})_4]$	2.0030	2.45	
(16)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7CN\text{-}3})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0015	3.36	1.99
(26)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7CN\text{-}3})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9982	4.50	2.33
(7)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}4})(\mathrm{CO})_4]$	2.0030	2.41	
(17)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}4})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0014	3.33	2.02
(27)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}4})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9986	4.30	2.23
(8)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}2})(\mathrm{CO})_4]$	2.0029	2.45	
(18)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}2})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0014	3.36	1.98
(28)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_7NO_2\text{-}2})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9994	4.24	2.25
(9)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}1,3,6,8})(\mathrm{CO})_4]$	2.0033	2.03	
(19)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}1,3,6,8})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0020	2.73	2.04
(29)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}1,3,6,8})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	1.9979	3.96	2.42
(10)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}2,4,5,7})(\mathrm{CO})_4]$	2.0034	2.01	
(20)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}2,4,5,7})(\mathrm{CO})_3(\mathrm{PPh_3})]$	2.0023	2.65	1.81
(30)	$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}2,4,5,7})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$	2.0006	3.82	2.04

values for all ten radical systems. The fact that the slope is 1.58 indicates that $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_3(\mathrm{PPh_3})]$ are more responsive than $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_4]$ to substituent X. This can be easily rationalized because $\mathrm{PPh_3}$ is a better σ donor and poorer π acceptor than CO. It is noteworthy that the phosphorus hyperfine coupling constants in $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_3(\mathrm{PPh_3})]$ increase as A_{Re} increases. Indeed, there is a linear correlation as shown in equation (6), where A_{Re} values for

$$A_{\mathrm{P}}\ [\mathbf{(11)}\text{—}\mathbf{(18)}, \mathbf{(20)}] = 0.47\ (\pm 0.06)\ A_{\mathrm{Re}}\ [\mathbf{(1)}\text{—}\mathbf{(8)}, \mathbf{(10)}] + 0.84\ (\pm 0.14) \quad (6)$$

$[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_4]$ are used in place of A_{Re} values for $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_3(\mathrm{PPh_3})]$. $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_4Me_4\text{-}1,3,6,8})(\mathrm{CO})_3(\mathrm{PPh_3})]$ is the only exception to the above correlation. We do not know why this particular radical behaves differently.

In the disubstituted radicals, $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$, the hyperfine coupling constants A_{P} also correlate with A_{Re} of $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_4]$ with the exception of radical **(29)**. However, the behaviour of the A_{Re} values, as indicated in Figure 2, is different from those of $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_3(\mathrm{PPh_3})]$. There are three data points which are ostensibly far off the straight line with an expected large slope of 2.5 ($\pm$0.4). These three radical systems have strong electron-withdrawing groups cyanide and nitro, attached to phenanthroquinone. We propose that the deviation may be caused by the formation of different geometrical isomers for bis(phosphine) substituted radicals **(26)**, **(27)**, and **(28)**. Wan and co-workers[6c] have established that the phosphites in $[\mathrm{Re(dtbq)(CO)_2\{P(OPh)_3\}_2}]$ are in axial *trans* positions. For most of the disubstituted radicals the two triphenylphosphines may be assumed to be at the axial *trans* positions. For the radical systems with strong electron-withdrawing groups attached, the two phosphines may assume the axial–equatorial *cis* positions. This proposition is substantiated by the observation that the substituted radical $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_6Br_2\text{-}3,6})(\mathrm{CO})_3\mathrm{L}]$ [L = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane][14] was formed initially with L at the axial position, but the L ligand slowly rearranges into the equatorial position. This indicates that the phosphine ligand has a tendency to occupy the equatorial position, which is presumably energetically more stable, when a strong electron-withdrawing group is attached to the phenanthroquinone. Another driving force is that the electronically unfavourable axial-*trans* arrangement of the phosphines is released by transforming into the more favourable axial–equatorial *cis* arrangement.

In conclusion, the substituent at position 3 in phenanthroquinone in the spin-trapped radical behaves as a *para*-substituent in phenyl compounds. The substituent acts to enhance or reduce the back donation from the rhenium centre to the phenanthroquinone π^* orbital. This behaviour can be described quantitatively by the Hammett parameter σ_{p}. It is also reflected in the slopes of the correlation between A_{Re} values of $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_4]$, $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_3(\mathrm{PPh_3})]$, and $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$. The electron-withdrawing substituent at position 3 of phenanthroquinone tends to facilitate back donation from rhenium to the phenanthroquinone. With a strong electron-withdrawing substituent such as a cyano group, the *cis* isomer of $[\mathrm{Re}(^{\bullet}\mathrm{O_2C_{14}H_{8-n}X_n})(\mathrm{CO})_2(\mathrm{PPh_3})_2]$ may become more stable than the *trans* isomer. Consistent with the back donation pic-

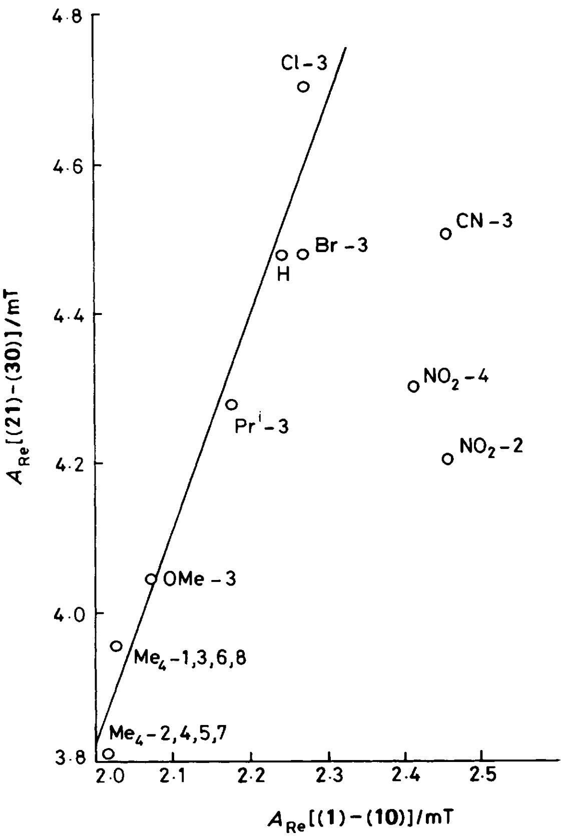


Figure 2. Linear correlation between the rhenium hyperfine coupling constants, A_{Re}, of $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_4]$ and $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_2(PPh_3)_2]$. Each point is indicated by the relevant substituent. Three points are far off the linear correlation; for details see text

ture, we have observed that the radical $[Re(^{\bullet}O_2C_{14}H_{8-n}X_n)(CO)_{4-m}(PPh_3)_m]$ (m = 0, 1, or 2) is more stable with an electron-withdrawing substituent, X.

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