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***o*-SEMIQUINOLATE COMPLEXES OF MANGANESE AND RHENIUM FORMED BY INTERACTION OF DECARBONYLS OF THESE ELEMENTS WITH HINDERED *o*-QUINONES**

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Summary

The influence of different solvents (oxygen-, sulfur-, and nitrogen-containing solvents, alkanes and aromatic hydrocarbons) and some donor ligands (triphenylphosphine, triphenylphosphite, cyclohexyl-isocyanide, triethylamine, cyclooctadiene) on ESR spectral parameters of manganese and rhenium *o*-semiquinolate complexes formed in the reactions of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ with hindered *o*-quinones (3,5- and 3,6-di-*tert*-butylbenzoquinones-1,2, perchloroxantrenquinone-2,3, tetrachlorobenzoquinone-1,2) have been investigated by the ESR method.

Introduction

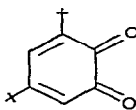
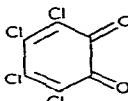
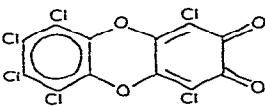
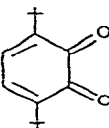
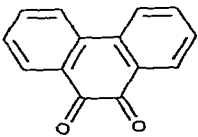
During the last years the reactions of manganese and rhenium decarbonyls with dicarbonyl compounds have been of interest. In spite of a number of publications in this field [1–6], some questions have not been studied and remain debatable. For example, in the paper of Posimeni [1] three ESR signals registered during the interaction of $\text{Mn}_2(\text{CO})_{10}$ with tetrachlorobenzoquinone-1,2 were discussed. If the fact of the formation of the mono-*o*-semiquinolate derivative is not doubtful, the attribution of the two other ESR signals observed to bis- and tris-*o*-semiquinolate complexes of manganese(I) is questionable and will be discussed below. Besides there are no data in the literature concerning the influence of the solvent, the nature and quantity of neutral ligands, and the nature of the *o*-semiquinolate fragment in the coordination sphere of the complexes on the ESR spectral parameters. The present work deals with these problems.

Results

Photochemical reaction of 3,5-di-*tert*-butylbenzoquinone-1,2 with $\text{Mn}_2(\text{CO})_{10}$ in organic solvents leads to the formation of paramagnetic adducts, the ESR spectra of which give information about the hyperfine interaction of unpaired electrons with the Mn^{55} nucleus and one proton (H^1) (in some spectra each component of the ESR spectrum has additional splitting with $a(\text{H}) = 0.6$ G). In the case of alkanes (pentane, hexane, heptane) and aromatic hydrocarbons (benzene, toluene) ESR spectra have been observed with g_i and $a(\text{Mn})$ parameters being equal for all named solvents. In oxygen-containing solvents (tetrahydrofuran, diethyl ether, dioxan, acetone) two different adducts (I and II)

TABLE 1

ESR SPECTRAL PARAMETERS OF THE PRODUCTS OF REACTIONS OF $\text{Mn}_2(\text{CO})_{10}$ WITH DIFFERENT *o*-QUINONES

Products of reaction $\text{Mn}_2(\text{CO})_{10} + \text{Q}$		g_i	$a(\text{Mn})$ (G)	$a(\text{H})$ (G)	Solvent
Q =					
	I ^a	2.0047	3.6	3.6	THF
	II ^b	2.0037	6.9	3.4	THF
	II	2.0036	7.0	3.5	toluene, hexane
	III	2.0034	3.9	—	THF
	IV	2.0036	8.8	$a(\text{Cl}) = 0.6$	toluene
	V	2.0030	6.6	—	toluene
	A	2.0028	6.7	—	toluene
	B ^c	2.0038	4.5	—	toluene
	C ^c	2.0028	6.2	—	toluene
	VI	2.0040	5.3	3.4	THF
	VII	2.0022	5.4	1.8 (4 H)	toluene

^a The ESR spectrum of this complex is shown in Fig. 1(b). ^b The ESR spectrum of this complex is shown in Fig. 1(a). ^c The products B and C were not identified.

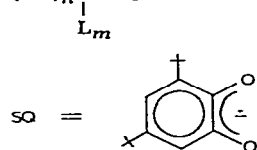
were formed as a result of photochemical reaction (Table 1). They differ from other in their g_i and $a(\text{Mn}^{55})$ values. The parameters of one of the observed ESR spectra (II) having in oxygen-containing solvents the lower intensity, are coincident with the corresponding parameters of the ESR spectrum observed in alkanes and aromatic solvents. However in oxygen-containing solvents it is not the major reaction product. The second signal registered in each oxygen-containing solvent (Table 2) has a considerably greater intensity and only this signal has been observed during longer irradiation. The distinctive characteristics of these ESR spectra are the result of hyperfine coupling with nucleus of Mn^{55} and the increase in g -factor (by 0.0030).

The dependence of ESR spectral parameters on solvent is also found in the case of reaction of $\text{Mn}_2(\text{CO})_{10}$ with tetrachlorobenzoquinone-1,2 (TCBQ) and with perchloroxantrenquinone-1,2 (PCQ) in THF and toluene. The interaction of TCBQ with $\text{Mn}_2(\text{CO})_{10}$ in THF leads to the adduct with $a(\text{Mn}^{55}) = 3.9$ G. In the case of toluene there are two ESR signals with different manganese hyperfine splitting constants ($a^{\text{I}}(\text{Mn}^{55}) = 8.8$ G, $a^{\text{II}}(\text{Mn}^{55}) = 6.6$ G), the signal with the smaller constant appearing after longer irradiation.

Three different ESR signals with the following spectral parameters: (1) $g_i = 2.0028$, $a(\text{Mn}^{55}) = 6.7$ G (A); (2) $g_i = 2.0038$, $a(\text{Mn}^{55}) = 4.5$ G (B); (3) $g_i = 2.0028$, $a(\text{Mn}^{55}) = 6.2$ G (C) (Table 1) are observed in the interaction of PCQ with $\text{Mn}_2(\text{CO})_{10}$.

TABLE 2

ESR SPECTRAL PARAMETERS OF MANGANESE *o*-SEMIQUINOLATE COMPLEXES OF THE TYPE $(\text{CO})_n\text{MnSQ}$



Complex	g_i	$a(\text{Mn})$ (G)	$a(\text{L})$ (G)	$a(\text{H}(\text{SQ}))$ (G)	Solvent
$\text{SQMn}(\text{CO})_3 \cdot \text{dioxan}$	2.0041	2.9	—	3.2	dioxan
$\text{SQMn}(\text{CO})_3 \cdot \text{Et}_2\text{O}$	2.0035	4.5	—	3.2	ether
$\text{SQMn}(\text{CO})_3 \cdot \text{acetone}$	2.0034	3.9	—	3.4	acetone
$\text{SQMn}(\text{CO})_3 \cdot \text{NCCH}_3$	2.0030	5.4	2.7(1N)	3.2	
$\text{SQMn}(\text{CO})_3 \cdot \text{EtSSnEt}_3$	2.0030	7.4	—	3.1	
$\text{SQMn}(\text{CO})_3 \cdot \text{THF}$	2.0045	3.6	—	3.6	THF
$\text{SQMn}(\text{CO})_3 \cdot \text{NEt}_3^a$	2.0032	7.2	2.7(1N)	2.9	THF, toluene
	2.0023	8.3	3.0(1N)	3.0	Et_3N
$\text{SQMn}(\text{CO})_3 \text{PPh}_3^b$	2.0029	9.9	33.6(P)	3.3	THF, toluene, hexane
$\text{SQMn}(\text{CO})_2(\text{PPh}_3)_2^c$	2.0015	18.3	42.1(2P)	3.3	THF, toluene
	2.0015	22.0	44.0(2P)	3.3	hexane
$\text{SQMn}(\text{CO})_3(\text{RNC})$	2.0038	8.7	—	3.0	toluene
$\text{SQMn}(\text{CO})_2(\text{RNC})_2$	2.0036	10.7	—	3.0	toluene
RNC =					
$\text{SQMn}(\text{CO})_2\text{P}(\text{OPh})_3$	2.0011	12.4	40.2	3.1	toluene

^a The ESR spectrum of this complex is shown in Fig. 4. ^b The ESR spectrum of this complex is shown in Fig. 2. ^c The ESR spectrum of this complex is shown in Fig. 3.

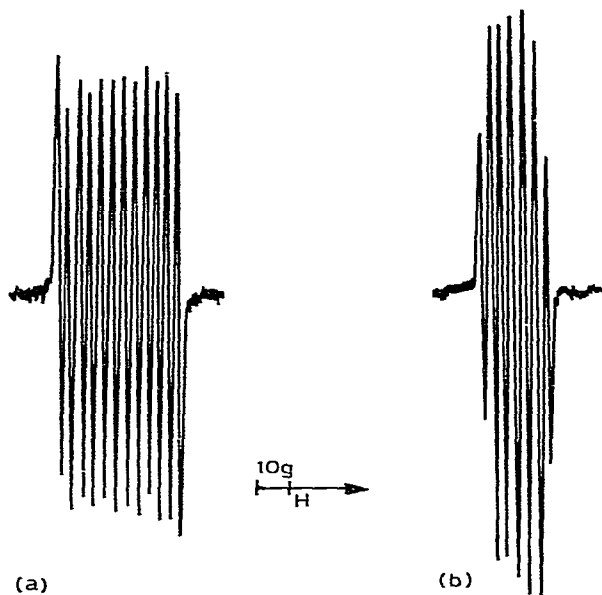


Fig. 1(a). The ESR spectrum of $(\text{CO})_4\text{MnSQ}$ in THF.

Fig. 1(b). The ESR spectrum of $(\text{CO})_3\text{Mn}(\text{SQ})(\text{THF})$ in THF.

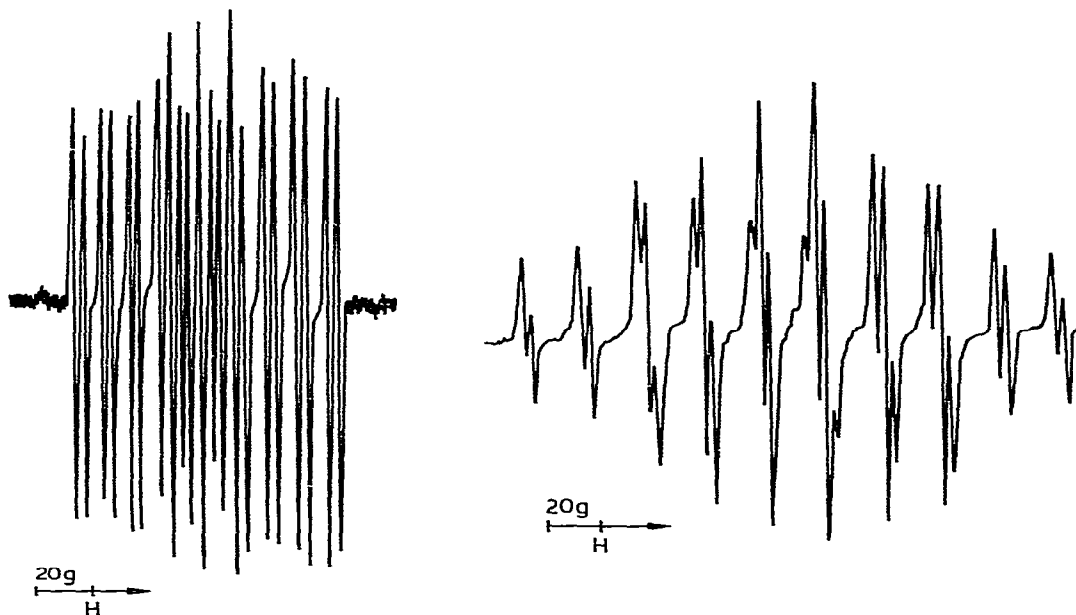
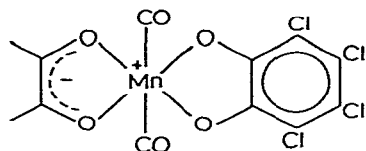


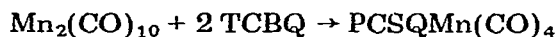
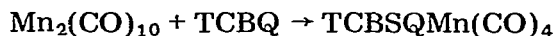
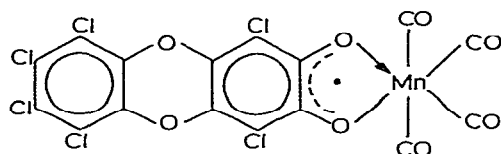
Fig. 2. The ESR spectrum of $\text{SQMn}(\text{CO})_3\text{PPh}_3$ in THF.

Fig. 3. The ESR spectrum of $\text{SQMn}(\text{CO})_2(\text{PPh}_3)_2$ in THF.

By comparison of spectral parameters, the adduct formed as a result of prolonged irradiation in the reaction of TCBQ with $\text{Mn}_2(\text{CO})_{10}$ is identified as being the same as complex A detected in the reaction between PCQ and $\text{Mn}_2(\text{CO})_{10}$ in toluene. This result and the data available [7] concerning the formation of perchloroxantrenquinone-2,3 from tetrachlorobenzoquinone-1,2 confirm that during prolonged irradiation two spin adducts with different *o*-semiquinolate fragments are formed in the reaction of TCBQ with $\text{Mn}_2(\text{CO})_{10}$: one with tetrachlorobenzosemiquinone-1,2 ($a(\text{Mn}^{55}) = 8.8 \text{ G}$) and the second with perchloroxantrensemiquinone-2,3 ($a(\text{Mn}^{55}) = 6.7 \text{ G}$). Thus the complex with the hyperfine splitting constant $a(\text{Mn}^{55}) = 6.8 \text{ G}$ described previously [1] and having the structure



actually represents the following derivative:

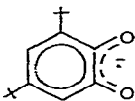


In the case of 3,6-di-*tert*-butylbenzoquinone-1,2 the reaction with $\text{Mn}_2(\text{CO})_{10}$ in THF leads to the formation of only the paramagnetic adduct with manganese constant equal to 5.7 G, unlike the unsymmetrical quinone.

The ESR spectral parameters of manganese *o*-semiquinolate complexes change significantly on addition of different *n*-donor ligands to the reaction mixture (π -ligands do not influence the spectral constants). It is of interest, that the values of HFS constants, $a(\text{Mn}^{55})$, of mono- and di-phosphine complexes differ by twice as much as the analogous derivatives with cyclohexylisocyanide ligands. The manganese constant of a dicyclohexylisocyanide complex is greater than $a(\text{Mn}^{55})$ of the corresponding monoligand derivative by a factor of 1.2. It should be noted that, unlike $\text{SQMn}(\text{CO})_n$, the solvent does not influence ESR spectral parameters of the $\text{SQMn}(\text{CO})_n\text{L}_m$ derivatives significantly. Triethylamine ($a(\text{Mn}^{55}) = 7.2 \text{ G}$ in THF, $a(\text{Mn}^{55}) = 8.9 \text{ G}$ in Et_3N) and diphosphine ($a(\text{Mn}^{55}) = 18.3 \text{ G}$ in toluene, $a(\text{Mn}^{55}) = 22.0 \text{ G}$ in hexane) complexes are an exception.

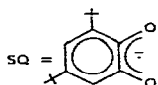
Rhenium decacarbonyl and pentacarbonyl rhenium chloride, like manganese decacarbonyl, react with *o*-quinones under irradiation. In this case, ESR spectral parameters of rhenium *o*-semiquinolate complexes differ slightly in various solvents (Table 3). Triethylamine, in which there is a decrease of the HFS constant $a(\text{Re})$ and a reduction of the *g*-factor (analogous to the behaviour of manganese *o*-semiquinolate in THF) is an exception.

TABLE 3
ESR SPECTRAL PARAMETERS OF RHENIUM *o*-SEMIQUINOLATE COMPLEXES

Complex	g_i	$a(\text{Re})$ (G)	$a(\text{L})$ (G)	$a(\text{H}(\text{SQ}))$ (G)	Solvent
$\text{SQ} = $ 					
$\text{SQRe}(\text{CO})_3\text{THF}$	1.9961	28.0		3.4	THF
$\text{SQRe}(\text{CO})_4$	2.0011	28.6		3.0	Hexane, toluene
$\text{SQRe}(\text{CO})_3\text{Et}_3\text{N}$	2.0013	24.0			Et_3N
$\text{SQRe}(\text{CO})_3\text{PPh}_3$	1.9987	39.0	26.0	3.0	THF
	2.0002	38.8	25.6		Hexane
	1.9998	38.7	25.7		Toluene
	2.0025	26.7			Et_3N
$\text{SQRe}(\text{CO})_2(\text{PPh}_3)_2^a$	1.9977	58.8	29.4		Toluene

^a The ESR spectrum of this complex is shown in Fig. 5.

It is well to point out the considerably greater stability of carbonylrhenium *o*-semiquinolates as compared with the corresponding manganese derivatives; because of this the complexes $\text{SQRe}(\text{CO})_3\text{THF}$ and $\text{SQRe}(\text{CO})_3\text{PPh}_3$

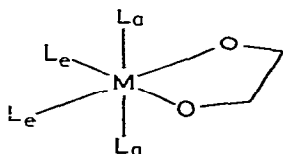


have been isolated and characterized by elemental analysis. The distinctive characteristic of *o*-semiquinolaterhenium complex reactions with donor ligands is consecutive formation of mono- and di-ligand derivatives according to the quantity of the initial donor, whereas manganese *o*-semiquinolates are in equilibrium with the same derivatives. This makes the isolation of the manganese complexes impossible.

Discussion

Relationship between ESR spectral parameters of Mn(I) and Re(I) o-semiquinolate complexes and their structure

The geometry of six-coordinative *o*-semiquinolate complexes is close to octahedral



In these complexes the semiquinolate ligand occupies two coordination places in the equatorial plane; due to the molecule symmetry the four other coordination places in pairs (two equatorial and two axial), are equivalent to the orbital of the SQ ligand occupied by an unpaired electron. The interaction of the unpaired

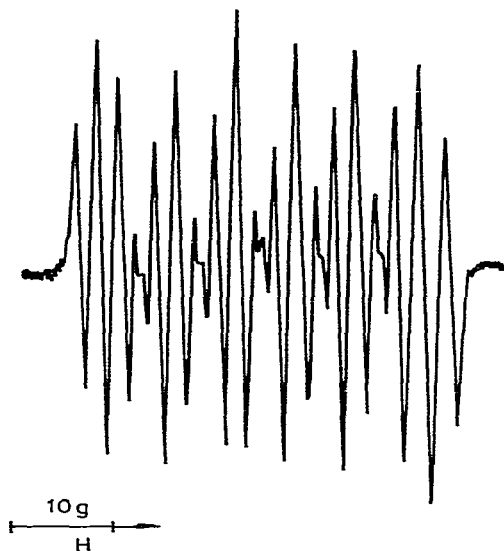


Fig. 4. The ESR spectrum of $\text{SQMn(CO)}_3(\text{NEt}_3)$ in THF.

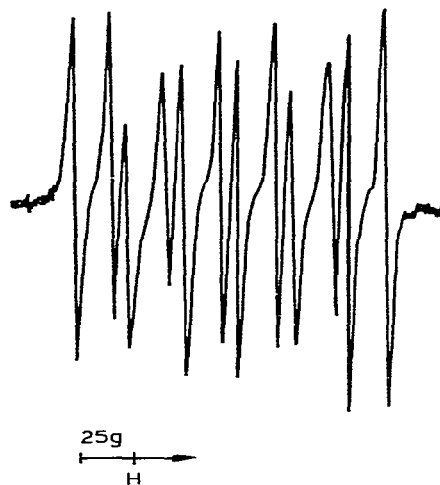


Fig. 5. The ESR spectrum of $\text{SQRe(CO)}_2(\text{PPh}_3)_2$ in toluene.

electron with axial ligands is more effective than that with equatorial ones, consequently the hyperfine coupling constants with magnetic nuclei of axial ligands $a(L_a)$ are considerably greater than $a(L_e)$. All Mn^{I} and Re^{I} *o*-semiquinolate complexes of the type L(SQ)M(CO)_3 studied in the present work are the products of substitution of one axial CO ligand. In the case of PPh_3 and Bu^tNC , substitution of the second axial ligand also takes place.

The distinctive characteristics of Mn^{I} and Re^{I} *o*-semiquinolate complexes are the great dependence of the hyperfine coupling constant with the central atom on the nature of the axial ligands. In a number of $(\text{CO})_2\text{L}^1\text{L}^2\text{MnSQ}$ complexes $a(\text{Mn}^{55})$ changes in the range from 2.9 ($\text{L}^1 = \text{CO}$, $\text{L}^2 = \text{dioxane}$) to 22.0 G ($\text{L}^1 = \text{L}^2 = \text{PPh}_3$). The dependence observed points to the fact that spin density of the unpaired electron appears on the ^{55}Mn nucleus at the expense of the interaction of the SQ ligand π -orbital occupied by the unpaired electron with the MO orbital of corresponding symmetry of the $(\text{CO})_2\text{L}^2\text{M}$ moiety, including atomic orbitals of the central atom and other ligands. The effectiveness of this interaction is determined by the symmetry and energy of the atomic orbitals of the axial ligands. The change of unpaired electron orbital energy (when substituting *o*-semiquinolate ligands) also influences the effectiveness of spin density transfer. The latter is expressed in the change of HFS constants, $a(\text{Mn})$, in a number of complexes $(\text{CO})_3(\text{PPh}_3)\text{MnSQ}$ (Table 1).

Mechanism of the interaction of manganese and rhenium decacarbonyls with o-quinones

The mechanism of the interaction of $\text{Mn}_2(\text{CO})_{10}$ with carbonyl derivatives has been discussed repeatedly [1–3,7]. However, such an important question as the influence of solvent has not been studied. We suggest a reaction scheme

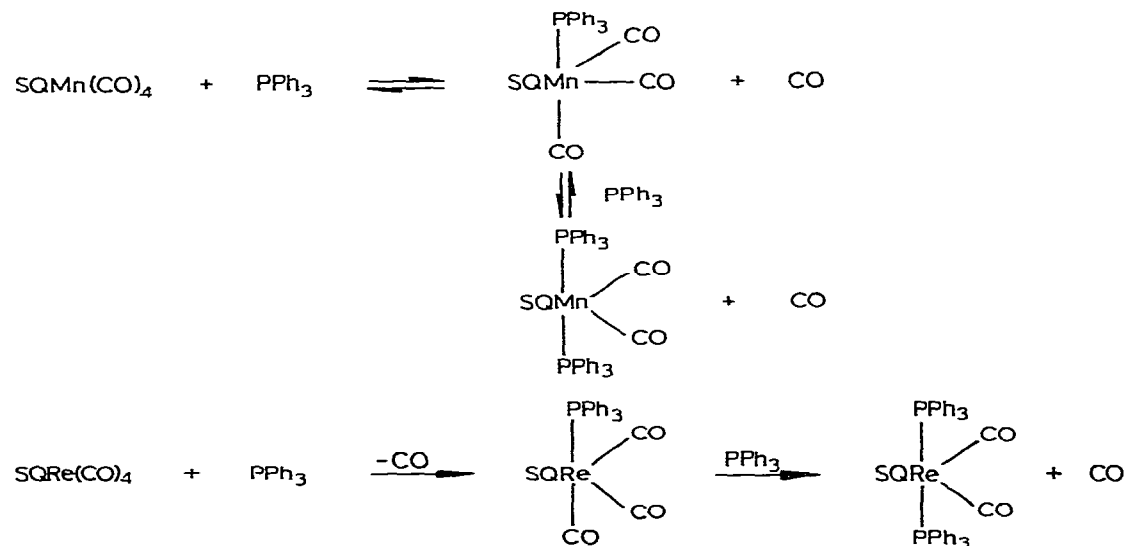
on the basis of the investigation of $\text{Mn}_2(\text{CO})_{10}$ interaction with *o*-quinones in different solvents.



In nonpolar or weakly polar solvents, such as hexane and toluene, the organometallic radical formed as a result of photodissociation reacts with *o*-quinone to form $(\text{CO})_4\text{MnSQ}$ (eq. 3). In polar (oxygen-, nitrogen- and sulfur-containing) solvents $\cdot\text{Mn}(\text{CO})_5$ forms reversibly with solvent a six-coordinative complex (eq. 2). Thus two radicals exist simultaneously in solution: $\cdot\text{Mn}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5(\text{S})$. Their interaction with *o*-quinones leads to the formation of two different *o*-semiquinolate adducts: $\text{SQMn}(\text{CO})_4$ and $\text{SQMn}(\text{CO})_3(\text{S})$. *o*-Semiquinolate complexes with a coordinated molecule of solvent may be obtained according to the exchange reaction of $\text{SQMn}(\text{CO})_4$ with corresponding solvent (eq. 4). The dependence of ESR spectral parameters on the solvent nature confirms also the existence of the complex of type $\text{SQ}(\text{S})\text{Mn}(\text{CO})_3$. Thus, in the range of oxygen-containing solvents $a(\text{Mn})$ changes from 2.9 to 4.5 G. In the case of nitrogen-containing solvents an interaction of unpaired electron with nitrogen nucleus takes place (Table 2).

The detailed analysis of the influence of the solvent on the mechanism of reactions of $\text{Re}_2(\text{CO})_{10}$ with *o*-quinones is difficult owing to the low sensitivity of ESR spectra of *o*-semiquinolate complexes to the nature of the ligands in the coordination sphere and owing to the great (as compared with manganese) component line-width. However, the isolation of $\text{SQRe}(\text{CO})_3(\text{THF})$ points to the fact that both $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ react with *o*-quinones analogously.

The addition of PPh_3 , AsR_3 and isocyanides to $\text{SQM}(\text{CO})_n\text{L}$ leads also to the substitution of one or two CO molecules situated in axial positions to give correspondingly mono- or di-ligand derivatives.

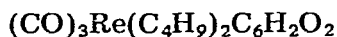


It should be noted that addition of triphenylphosphine ligands occurs in the trans positions, as demonstrated by the equal $a(P^{31})$ coupling constants.

Experimental

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were kindly supplied by Doctor V.G. Syrkin (Moskow). 3,5-Di-tert-butylbenzoquinone-1,2, tetrachlorobenzoquinone-1,2 and perchloroxantrenquinone-2,3 were correspondingly obtained by known procedures [8–10]. Samples were prepared using standard vacuum techniques. Irradiation was performed with a mercury lamp, DRT-375.

The ESR spectra were recorded with a RE-1301 instrument. Manganese *o*-semiquinolate complexes were studied in solutions; some rhenium derivatives were isolated as individual compound.



Found: C, 44.76; H, 5.32; Re, 32.85. Calcd. for $C_{21}H_{28}O_6Re$: C, 44.84; H, 4.98; Re, 33.09%.



Found: C, 55.54; H, 4.84; Re, 24.54. Calcd. for $C_{35}H_{35}O_5PRe$: C, 55.78, H, 4.64; Re, 24.70%.

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