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Coordination and organometallic compounds based on the stable 1-hydroxy-2,4,6,8-tetrakis(t-butyl)phenoxazin-10-yl radical *

I.V. Karsanov, Ye.P. Ivakhnenko, V.S. Khandkarova, A.I. Prokof'ev, A.Z. Rubezhov * and M.I. Kabachnik

A.N. Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Vavilov Str. 28, Moscow (U.S.S.R.)

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Abstract

A new method for the preparation of a stable 1-hydroxy-2,4,6,8-tetrakis(t-butyl)phenoxazin-10-yl radical by oxidation of 3,5-di-t-butyl-*ortho*-aminophenol with 3,5-di-t-butyl-*ortho*-benzoquinone is reported. Interaction of the radical with the coordination or the organic compounds of various metals has been studied.

Introduction

Up to now a large number of complex and organometallic compounds bearing stable paramagnetic ligands or groups have been examined by ESR spectroscopy [1–3]. The distinctive feature of such compounds is the delocalization of the spin density of the unpaired electron over the entire molecule which results in hyperfine interaction of the unpaired electron with the most magnetic nuclei of the complex. Among the most studied of these compounds are those based on *ortho*-benzoquinone redox systems [1], compounds containing a sterically hindered phenoxyl group [2], and complexes with stable nitroxyl radicals [3]. Far less information is available on complexes and organometallic compounds containing magnetic nuclei (^{14}N, in particular) in the chelating moiety of a paramagnetic ligand. Here we present a brief account of investigations that we carried out on the coordination and the organometallic chemistry of a stable 1-hydroxy-2,4,6,8-tetrakis(t-butyl)phenoxazin-10-yl radical which fills the gap between an *ortho*-semiquinolate radical and ligands based on hindered phenoxyls.

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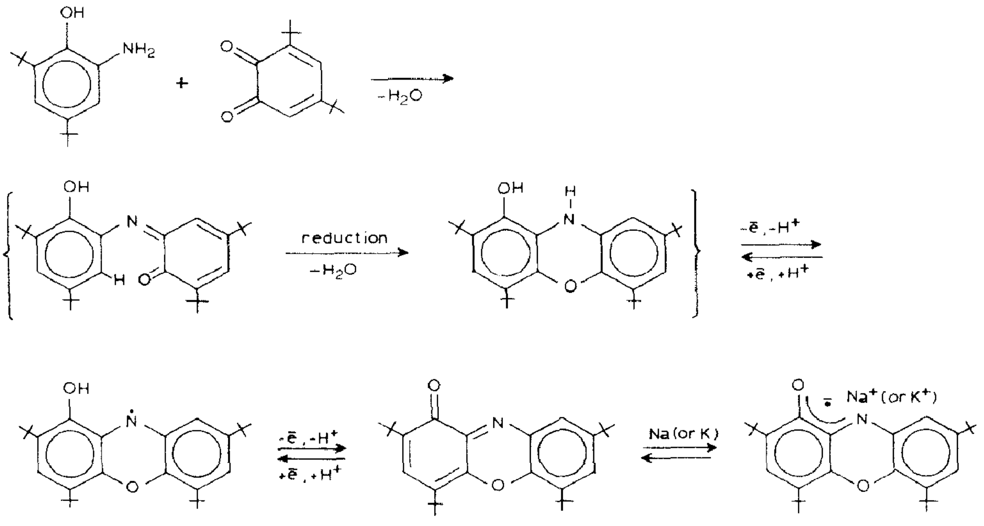
Results and discussion

Synthesis and properties of a stable 1-hydroxy-2,4,6,8-tetrakis(t-butyl)phenoxazin-10-yl radical (II)

The formation of II under the oxidation of 2-amino-4,6-di-t-butylphenol with oxygen in refluxing pyridine has previously been reported [4–7]. In addition to the radical, which was identified by ESR spectroscopy, the reaction also yields the oxidation product of II viz., -1H-1-oxo-2,4,6,8-tetrakis(t-butyl)phenoxazin (III). In order to obtain II on a preparative scale, we have studied oxidation of 2-amino-4,6-di-t-butylphenol with 3,5-di-t-butyl-*ortho*-benzoquinone in the presence of sodium ethylate as a base. The complexes formed, II and III, were separated by column chromatography on silica gel; the radical can be purified by sublimation in high vacuum. The reaction probably proceeds as follows:



(II) (III) (IV)

The reduction of III to II and further to the Schiff base I was studied electrochemically. It was found that conversion of compound III into radical II is completely reversible, whereas the second reduction step, that of the formation of I, is virtually irreversible.

Table 1

ESR data for derivatives of 1-hydroxy-2,4,6,8-tetrakis(t-butyl)phenoxazin-10-yl radical (II). Coupling constants are in mT [a]

NN	a_N	a_H^3	a_H^7	a_H^9	Other nuclei
II	0.767	0.381	0.417	0.263	–
IV	0.632	0.312	0.343	0.239	$a_{Na} = 0.07$
VI	0.776	0.350	0.350	0.156	$a_H^{NH} = 0.78$; $a_H^{OH} = 0.07$
VII	0.755	0.354	0.271	0.142	$a_D^{ND} = 0.120$
VIII	0.755	0.402	0.402	0.272	–
IX	0.731	0.392	0.392	0.260	$a_{^{31}P} = 0.39$

[a] Coupling constants are accurate to within ±0.0047 mT

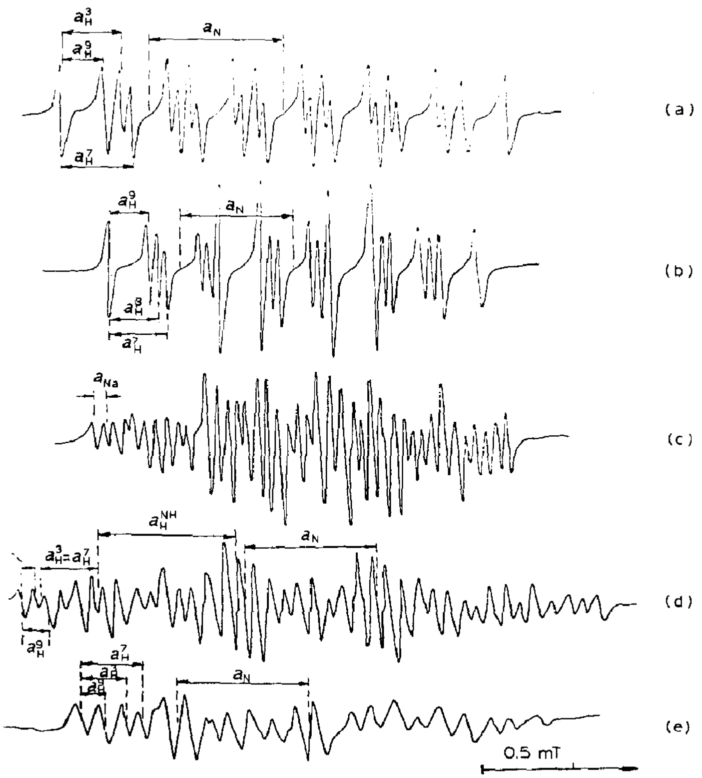
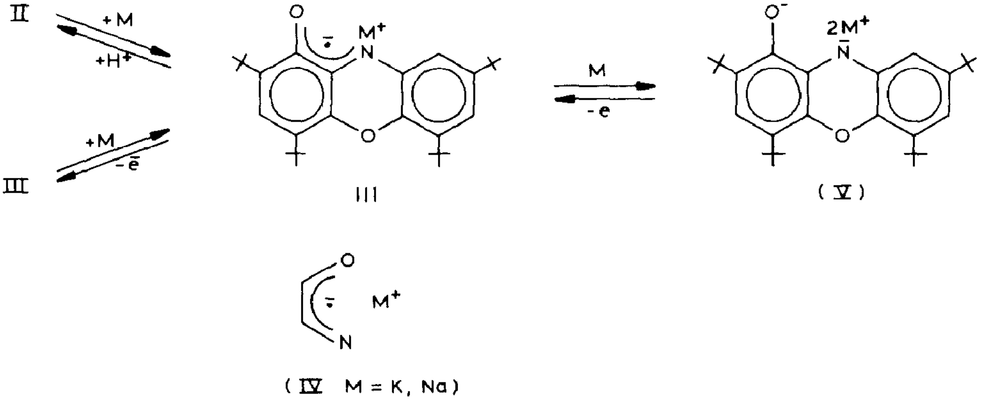


Fig. 1. ESR spectra of radicals of phenoxazine and its derivatives at 298 K: (a) radical II in toluene; (b) radical anion IV with K^+ as a cation in THF; (c) radical anion IV with Na^+ as a cation in THF; (d) radical cation VI in CH_3COOH/toluene; (e) radical cation VII in CD_3COOD/toluene.

The ESR spectrum of radical II is fully consistent with the structure proposed (Fig. 1 (a), Table 1). The IR spectrum of the radical both in solution and in the solid state shows a band in the 3610–3620 cm^{-1} range corresponding to stretching vibrations of the OH group in hindered phenols [8]. A concentration dependence study enabled us to assign the band to the free hydroxyl stretching vibrations that are not perturbed by the intramolecular hydrogen bonding with the N atom bearing the unpaired electron. However no hyperfine coupling to a hydroxyl proton was



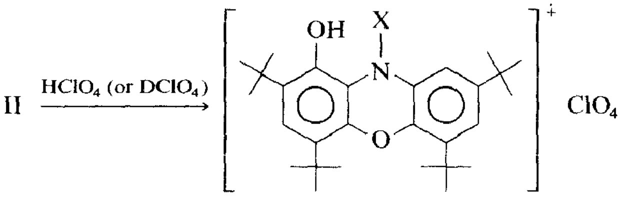
Scheme 1

observed, presumably because of the unpaired electron is largely attached to both the benzofragments of the radical.

The reaction of radical II with alkali metals or the reduction of phenoxazine III by alkali metals gives the radical anion IV. The ESR spectrum of IV (Fig. 1 (b), (c), Table 1) exhibits hyperfine coupling with the ^{23}Na nucleus indicating contact ion pairs. Even after prolonged storage of solutions of IV over an alkali metal mirror, there are no signals to suggest that the reduction of IV to a paramagnetic dianion V occurs (Scheme 1).

The reduction of IV to V was found to be reversible; when treated with oxidants, such as $K_3Fe(CN)_6$, dianion V converts into the starting radical anion IV.

The protonation of radical II with $HClO_4$ gives a radical cation VI which is isolated as the perchlorate. Similarly the deuteroacid gives the radical deuterocation VII:



(VI X = H; VII X = D)

The ESR spectrum of the radical cation VI (Fig. 1 (d), Table 1) reveals the hyperfine coupling of the unpaired electron to the ring protons; the values are consistent with the relevant values for radical II and the radical anion IV. Furthermore substantial hyperfine interaction with the N-bonded proton is observed. The fact that protonation occurs at the nitrogen atom is confirmed by a comparison of the ESR spectra of the radical cation VI with that of its deuteroanalogue VII (Fig. 1 (e), Table 1).

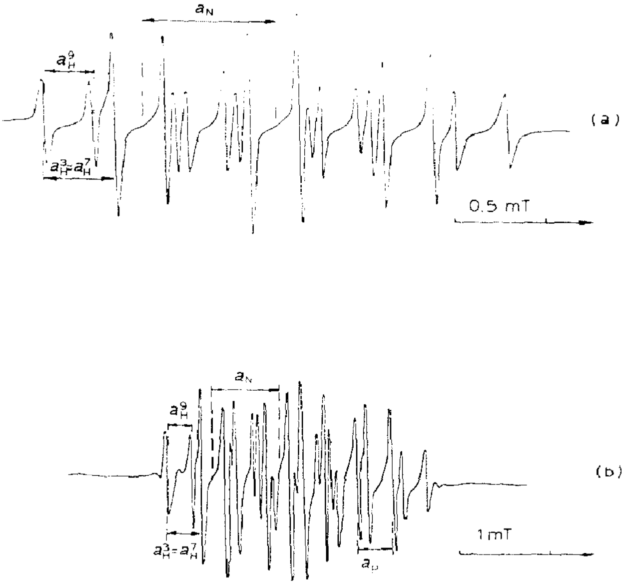
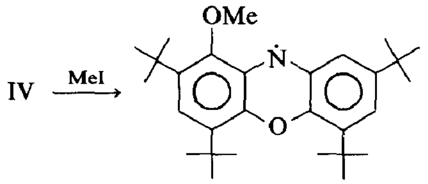


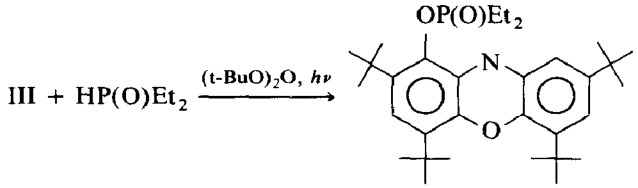
Fig. 2. ESR spectra of O-substituted phenoxazinyl radicals at 298 K: (a) methoxy derivative VIII in THF; (b) phosphoryl derivative IX in toluene.

The radical anion IV reacts with methyl iodide to afford the methoxy derivative VIII:



(VIII)

The radical VIII has been isolated pure and has been characterized by mass, IR and ESR spectra. The ESR spectrum does not reveal hyperfine coupling with methyl protons; the splitting pattern testifies to delocalization of the unpaired electron over the aromatic system (Fig. 2 (a), Table 1). The analogous *ortho*-diethylphosphoryl radical IX was obtained under UV irradiation of diethylphosphine oxide together with phenoxazine III in the presence of t-butyl peroxide:



(IX)

The equivalence of the hyperfine coupling to the protons at the 3- and 7- position and the slight hyperfine interaction with the nucleus of the ^{31}P is indicated by the ESR spectrum of IX (Fig. 2 (b), Table 1). These data also provide evidence that the spin density of the unpaired electron delocalizes mainly over the phenoxazinyl moiety.

Mono- and polyradical coordination compounds of 1H-1-oxo-2,4,6,8-tetrakis(t-butyl)-phenoxazine with the metals of groups 2–4

Reduction of III with thallium amalgam affords a monoradical salt X whose ESR spectrum is shown in Fig. 3 (a). The values of the hyperfine coupling constants of the unpaired electron to the magnetic nuclei of the phenoxazine moiety are of

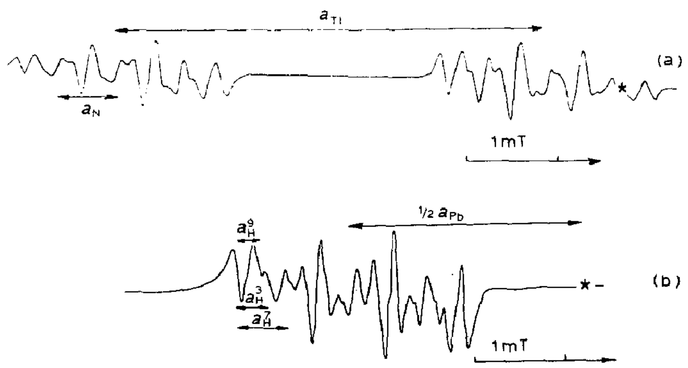


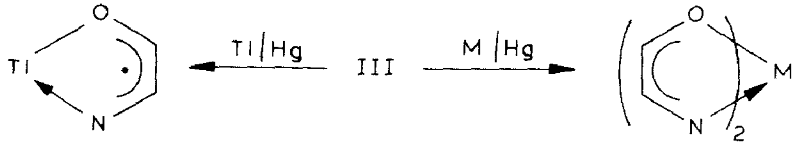
Fig. 3. ESR spectra of monoradical complexes in toluene at 298K: (a) X, Tl^+: (b) XVII, Pb^{2+} (doublet component downfield from the ^{207}Pb isotope is shown); ★ = centre of signal.

Table 2

ESR data for monoradical phenoxazinolate compounds of metals of groups II–IV. Coupling constan are given in mT.

NN	a_N	a_H^3	a_H^7	a_H^9	a_M	M
X	0.67	0.28	0.35	0.24	4.70	^{203,205}Tl
XIII	0.47	0.28	0.33	0.21	0.42	^{27}Al
XV	0.80	0.30	0.38	0.19	0.0	^{117,119}Sn
XVII	0.77	0.33	0.42	0.21	6.40	^{207}Pb

similar magnitude to those of the alkali metal phenoxazinolates of the type IV (s Table 2). The substantial coupling to the ^{203,205}Tl nuclei unequivocally indicates t "semiquinolate" nature of salt X (cf. refs. 9 and 10). Treatment of III with group



(X)

(XI:M = Zn;
XII:M = Cd)

metal amalgams (Zn, Cd) in organic solvents gives the biradical complexes XI an XII.

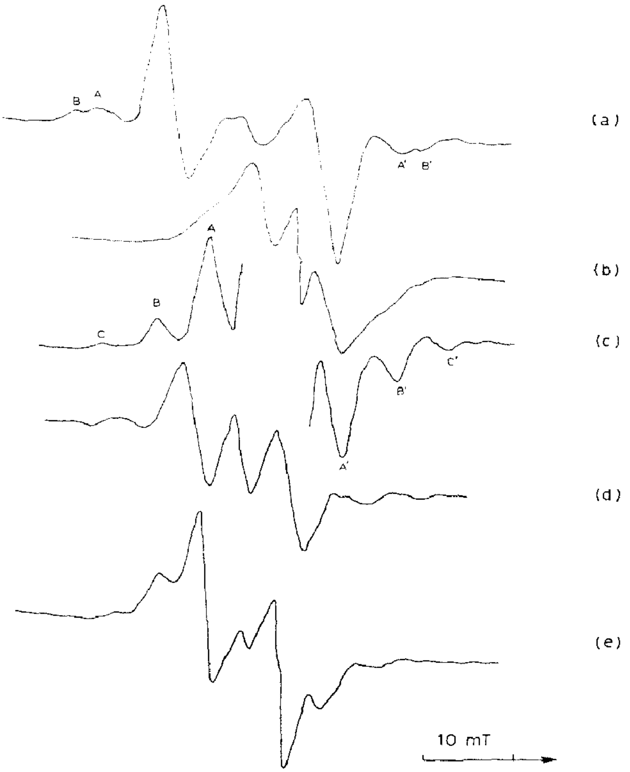


Fig. 4. ESR spectra of frozen solutions (77 K) for polyradical complexes of elements of groups II–IV: (a XI, Zn; (b) XII, Cd; (c) XIII, Al; (d) XIV, Ga; (e) XV, Sn.

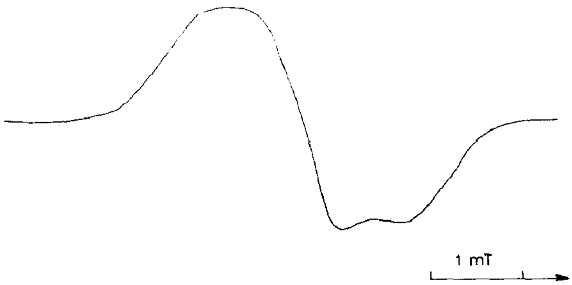
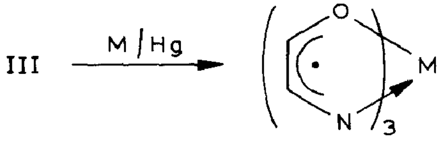


Fig. 5. ESR spectra of forbidden transitions $\Delta M_s = 2$ for the biradical complex XI.

At 77 K the ESR spectra of XI and XII exhibit zero-field splittings D (Fig. 4 (a), (b)); values, the average paramagnetic center distances R_{av} were estimated from the $D_\perp$ and $D_\parallel$ values [11]. From the data shown in Table 3 it follows that metal atom size is proportional to the R_{av} value.

The presence of a forbidden transition $\Delta M_s = 2$ (Fig. 5) clearly indicates a biradical structure for complexes XI and XII. The "forbidden" signal, $\Delta M_s = 2$, represents the sum of two signals which have different line widths. From these data, complex XI appears to exist in at least two conformations that have slightly differing D parameters and, hence, differing R_{av} as well. If a distorted tetrahedron structure is adopted for XI, then the difference in R_{av} values for both the conformations should be controlled by the differences in the mutual arrangement of the nitrogen atoms bearing the unpaired electron.

The triradical species has been detected after the reaction of III with group 3 metal amalgams (Al, Ga):



(XIII : M = Al;
XIV : M = Ga)

In solution at room temperature, the ESR spectra of XIII and XIV are wide single lines, whereas at 77 K there is an intense central transition (Fig. 4 (c), (d)). The signal with $\Delta M_s = 3$, however, could not be measured because of its low intensity. A noteworthy feature of the ESR spectrum of the gallium derivative XIV (Fig. 6) is the additional splitting on the $D_\perp$ and $D_\parallel$, as well as the relatively smaller width of the central line. A thorough study of the splittings (seven lines 1 : 3 : 6 : 7 : 6 : 3 : 1) on the $D_\perp$ component led us to conclude that the splitting is caused by hyperfine coupling of the unpaired electrons to three equivalent ^{14}N nuclei. Thus the system involves a rapid exchange process which results in the interaction of three unpaired electrons with the three nitrogen atoms of phenoxazinyl ligands.

The reaction of III with tin amalgam at room temperature yields a biradical complex XV. Its ESR spectrum is almost identical with that of the monoradical species IV (Table 2), whereas at 77 K the spectrum of XV shows a zero-field splitting parameter which points to a biradical structure of the organotin compound

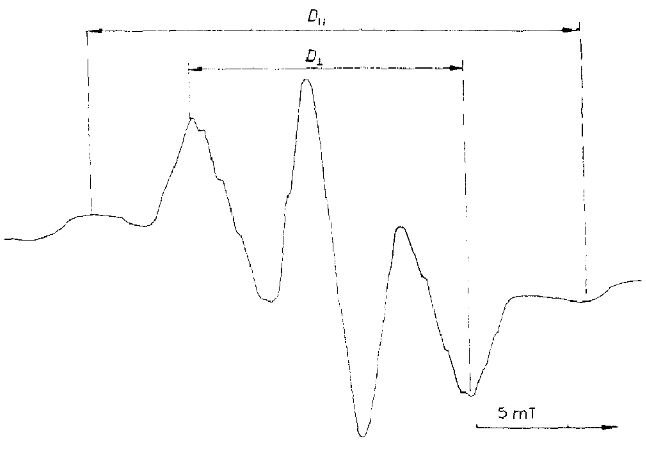
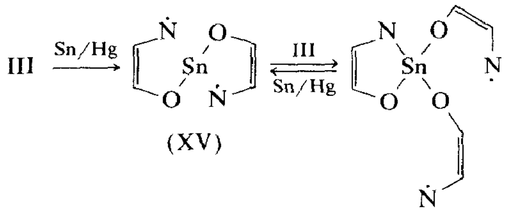


Fig. 6. ESR spectrum of the triradical complex XIV in toluene at 77 K.

(Fig. 4 (e)). The oxidation of XV with an excess of phenoxazine III gives the tetra-valent tin derivative XVI. Evidence for its biradical nature is obtained from the ESR spectra at room temperature (a single wide line) as well as at 77 K (Table 3). A triplet pattern is observed in the ESR spectrum of biradical XVI; a zero-field splitting parameter D is greater than that for XV because the Sn^{4+} radius is smaller than that of the Sn^{2+} ion. Complexes XV and XVI reversibly convert into each other either upon oxidation with phenoxazine III or upon reduction with tin amalgam. These interconversions may be depicted as follows:



(XV)

(XVI)

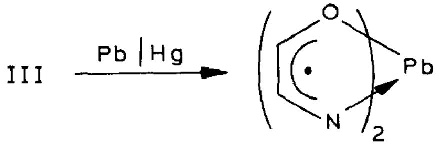
Table 3

Zero-field splittings for ESR spectra of polyradical compounds of groups II, III and IV metals containing phenoxazinolate ligands. Parameters D are in mT.

NN	D^a	D	M^+	R_{av} (Å)
XI	18.8	32.9	Zn	5.29 [b]
		37.8		5.53 [b]
XII	11.0	19.0	Cd	6.64
XIII	16.0	39.0	Al	5.23
XIV	15.5	30.0	Ga	5.71
XV	8.5	19.0	Sn	6.64 [c]
XVI	18.8	31.0	Sn	5.64 [c]

[a] Approximate values of D for XIII and XVI result from coincidence of signals of the corresponding species XIIIa and XV. [b] Two types of radical pairs are observed due to biradical XI existing in two conformations. [c] The radicals differ in oxidation states of the tin ion.

The coordination compound containing di-valent lead, XVII, was formed on reduction of phenoxazine III with lead amalgam:

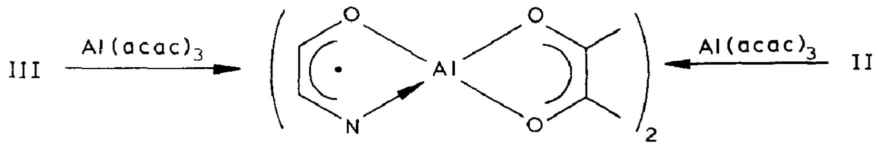


(XVII)

The structure of XVII is similar to that of the di-valent lead compound XV, but their respective ESR spectra are somewhat different. Namely, at room temperature the spectrum of XVII corresponds to a monoradical species (Fig. 3 (b)), the hyperfine structure shows the coupling to the ^{14}N nucleus and to the phenoxazinolate protons, thus indicating that the delocalization of the unpaired electron occurs mainly over the ligand. There is no interaction between the unpaired electrons owing to the large radius of the Pb^{2+} ion; the substantial coupling to the ^{207}Pb nucleus (Table 2) arises from polarization of the 5*s* orbital of the lead atom.

The complex and the organometallic phenoxazine radical

Radical II and phenoxazine III were found to react with aluminium acetylacetonate to yield a paramagnetic complex XVIII:



The ESR spectrum of XVIII (Fig. 7 (a), Table 4) is consistent with its structure; the chelate nature is confirmed by the hyperfine coupling of the unpaired electron with magnetic nuclei of phenoxazinyl radical (^{14}N, in particular) and magnetic ^{27}Al isotope.

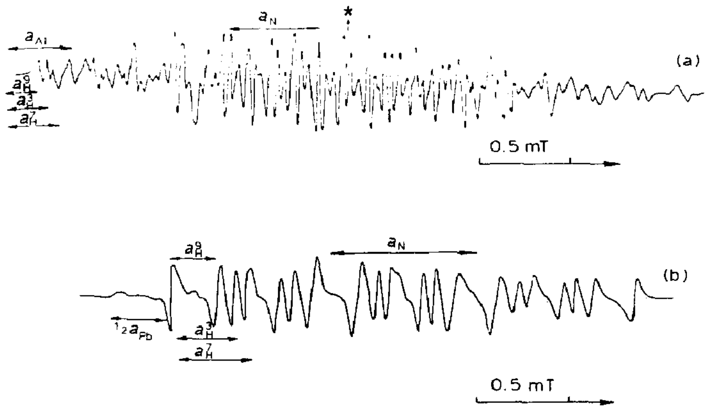


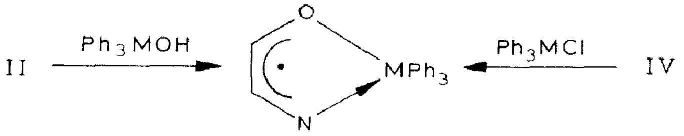
Fig. 7. ESR spectra of phenoxazinolate complexes in toluene at 298 K; (a) aluminum acetylacetonate XVIII; (b) triphenyllead XX.

Table 4

ESR data for coordination and organometallic compounds. Coupling constants are in mT.

NN	a_N	a_H^3	a_H^7	a_H^9	a_M	M	(I)
XVIII	0.52	0.27	0.31	0.21	0.39	^{27}Al	(5/2)
XIX	0.79	0.35	0.41	0.24	0.165	^{117}Sn	(1/2)
XX	0.79	0.34	0.41	0.24	0.66	^{207}Pb	(1/2)
XXI	0.72	0.31	0.39	0.21	0.21	^{201}Hg	(3/2)
XXII	0.90	0.30	0.34	0.21	0.78	^{55}Mn	(5/2)
XXIII	0.85	–	–	–	–	^{185}Re	(5/2)
XXIV	0.77	0.22	0.22	0.18	0.85	^{95}Mo	(5/2)

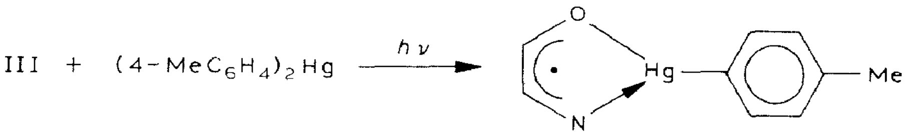
Exchange reactions of radical II with the corresponding triphenyl hydroxides or the reaction of the radical anions IV with either triphenylstannyl chloride or triphenylchloroplumbane were used to obtain paramagnetic triphenyltin and triphenyllead phenoxazinolates:



(XIX: M = Sn;
XX : M = Pb)

The ESR spectra of complexes XIX and XX are fully in accord with the structures proposed. The satellite lines observed in the spectra may be assigned to interaction of the unpaired electron with nuclei of ^{117,119}Sn and ^{207}Pb, $I = 1/2$; the intensities of the lines reflect the natural occurrence of the different isotopes (Fig. 7 (b), Table 4). A comparison of the ESR spectral parameters for radicals XIX and XX reveals the nature of their electronic structures. The hyperfine coupling to the nitrogen nucleus provides evidence for this conclusion; the nature of the metal atom brings about the difference in the coupling constants with magnetic isotopes of the central atom (Table 4).

Exposure of phenoxazine III to UV light in the presence of bis(*p*-tolyl)mercury, produces a paramagnetic complex, XXI, as detected by ESR spectroscopy:

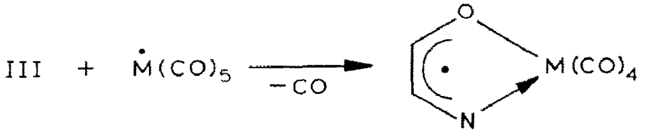


(XXI)

The ESR spectral parameters, and specifically the values of hyperfine coupling constants with the ^{14}N and ^{201}Hg nuclei, confirm the structure of XXI (Table 4).

The reaction of phenoxazine III with dimeric manganese and rhenium decacarbonyls as well as with bis(tricarbonylcyclopentadienylmolybdenum) was examined directly in the ESR spectrometer resonator under UV irradiation. The photolysis of the dimeric carbonyls is attended with the formation of the corresponding metal-centred free radicals which react further with III to give the paramagnetic complexes XXII and XXIII:

$$M_2(CO)_{10} \xrightarrow{h\nu} 2\ \dot{M}(CO)_5$$



(XXII: M = Mn;
XXIII: M = Re)

An analysis of the ESR spectra of manganese- and rhenium-containing complexes (Fig. 8 (a), (b)) enabled the coupling constants to be determined (Table 4). The similarity of these constants to those of the corresponding semiquinolate compounds [12–16] unequivocally indicates a chelate structure for XXII and XXIII since the values of hyperfine coupling constants to the ^{55}Mn and ^{185,187}Re nuclei are close to those of the secondary orthobenzoquinones. All attempts to detect primary complexes containing the $M(CO)_5$ moiety were unsuccessful even at low tempera-

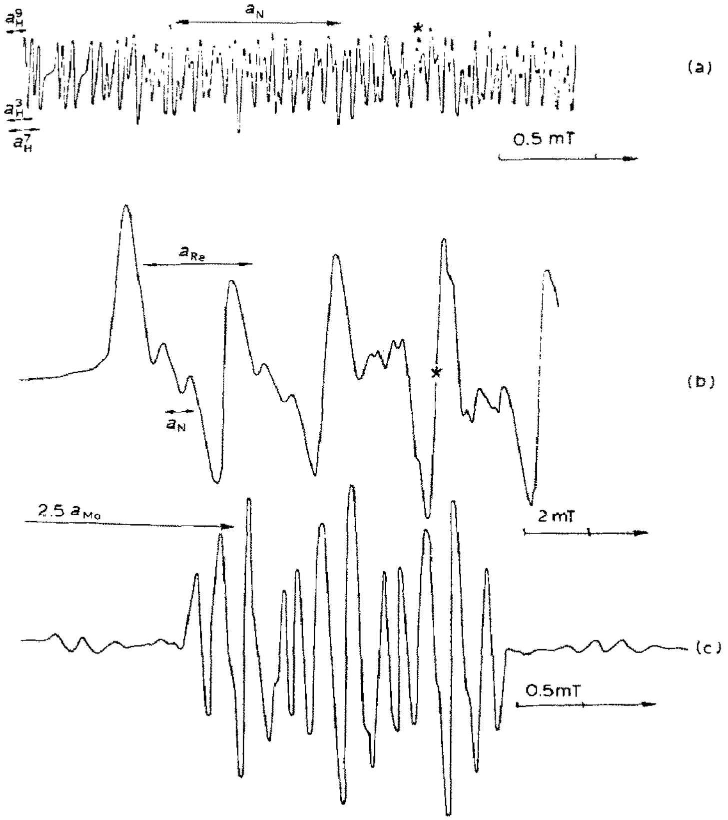
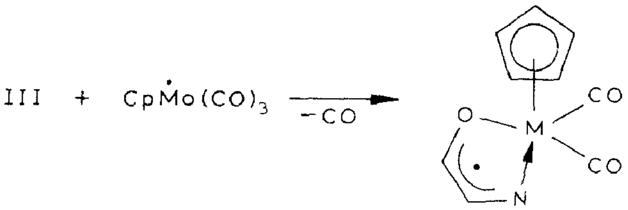


Fig. 8. ESR spectra of paramagnetic carbonyl complexes in toluene at 298 K: (a) manganese complex XXII; (b) rhenium complex XXIII; (c) molybdenum complex XXIV. ★ = centre of signal.

tures, and points to a strong chelating ability of phenoxazinolate ligand; the formation of a coordinate metal–nitrogen bond, removes a carbonyl ligand from the metal coordination sphere.

The formation of a molybdenum phenoxazinolate complex XXIV occurs likewise. Its structure was confirmed from a comparison of the ESR spectral data (Fig. 8 (c), Table 4) for XXIV with those for its *ortho*-semiquinolate analogue [17], though no hyperfine coupling with the ^{95,97}Mo magnetic isotopes was revealed:

$$\left[CpMo(CO)_3\right]_2 \xrightarrow{h\nu} 2\ Cp\dot{M}o(CO)_3$$



(XXIV)

Ion-radical complexes of metal carbonyls

The photochemical reaction of phenoxazine III with chromium hexacarbonyl in THF in the presence of metallic iodine leads to the formation of a radical cation XXV. On the basis of the ESR spectral data (Fig. 9 (a), (b), Table 5) this was assigned a structure having two chelate moieties, viz. phenoxazine and pheno-

Table 5

ESR data for ion-radical complexes of chromium, molybdenum, and tungsten with phenoxazinolate ligands. Coupling constants are given in mT.

NN	a_N	a_H^3	a_H^7	a_H^9	a_M	g-factor	M
IV	0.63	0.31	0.37	0.24	–	2.0030	K
X	0.67	0.28	0.35	0.24	4.70	2.0040	Tl
XXV	0.61	–	–	–	2.45	1.9730	Cr
XXVI	0.47	0.07	0.07	0.07	2.45	1.9660	Cr
XXVII	0.79	0.27	0.27	0.22	0.24	2.0034	Cr
XXVIII	0.73	0.21	0.21	0.21	– [a]	2.0040	Cr
XXIX	0.78	0.28	0.28	0.22	0.38	2.0045	Mo
XXX	0.78	0.24	0.24	0.24	0.76 [a]	2.0005	Mo
XXXI	0.17	–	–	–	2.93	1.9580	Mo
XXXII	0.80	0.24	0.24	0.24	0.24	2.0080	W
XXXIII	0.20	–	–	–	–	1.9590	W

[a] Additional hyperfine interaction with nuclei of ^{31}P for complexes XXVIII ($a_P = 5.67$ mT) and XXX ($a_P = 3.78$ mT) is recorded.

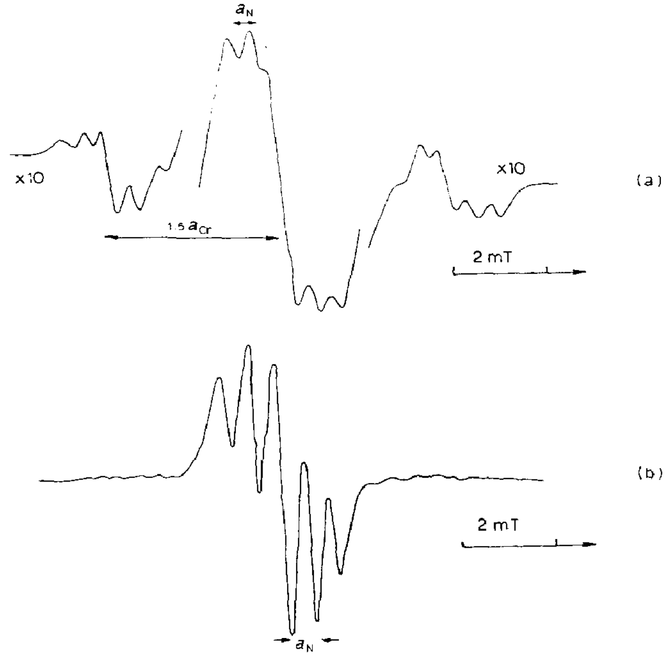
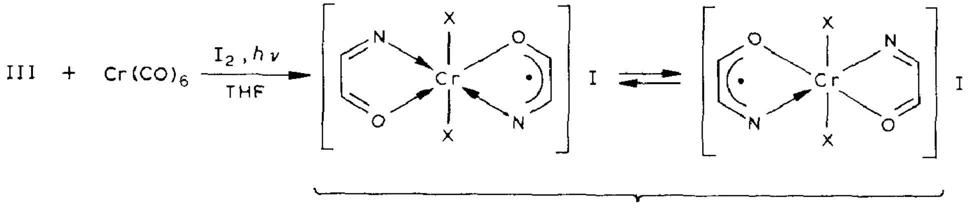


Fig. 9. ESR spectra of a cation-radical complex XXV (a, b) in THF at 298 K. At the high gain level satellites from ^{53}Cr nuclei are detected.

xazinolate; both the ligands are magnetically equivalent because of rapid exchange processes:



XXV

Such a structure gives rise to a quintuplet pattern in the spectrum corresponding to interaction of the unpaired electron with two equivalent ^{14}N nuclei. Moreover, hyperfine coupling to the magnetic isotope, ^{53}Cr, can be observed, whereas isotropy of the *g*-factor suggests that the complex is metal-centered. XXV is formed by replacement of carbonyl ligands; with regard to the ligands designated as “X”, the question remains unsettled since in the complex obtained the solvent molecules (THF) can successfully compete with carbonyl ligands in XXV.

Reaction of III with $Cr(CO)_6$ in THF in the presence of metallic potassium, i.e. under conditions of a radical anion IV formation, produces a paramagnetic species which has been characterised by ESR spectroscopy (Fig. 10 (a), (b)). The hyperfine couplings of the unpaired electron with the magnetic nuclei were calculated from the ESR spectrum (Table 5). From the values obtained it follows that the central metal atom is coordinated to two equivalent chelate ligands (the signal from two equivalent ^{14}N nuclei and six equivalent protons); the *g*-factor and the coupling

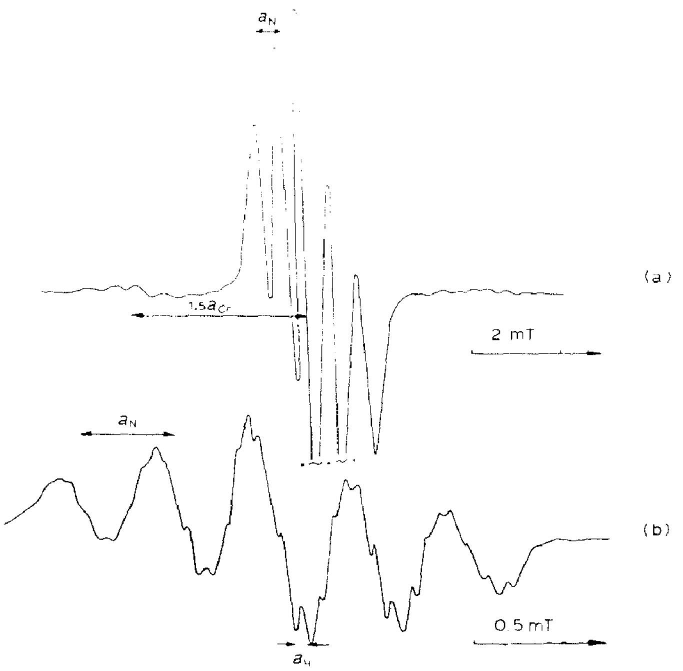
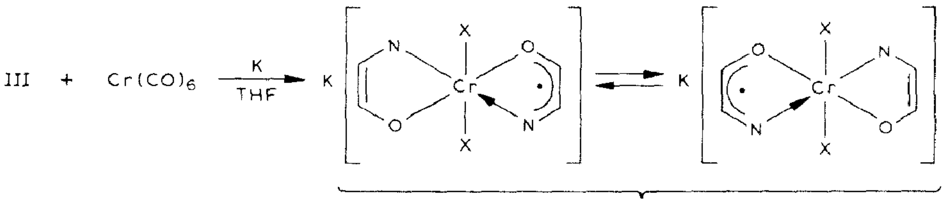


Fig. 10. ESR spectra of anion-radical complex XXVI in THF at 298K: (a) the entire spectrum with satellites from the nuclei of ^{53}Cr; (b) central part of the spectrum recorded at small field scanning (hyperfine coupling to phenoxazinolate protons is observed).

constant to the nucleus of ^{53}Cr are virtually isotropic indicating that, as in XXV, the radical complex XXVI is ligand-centred:

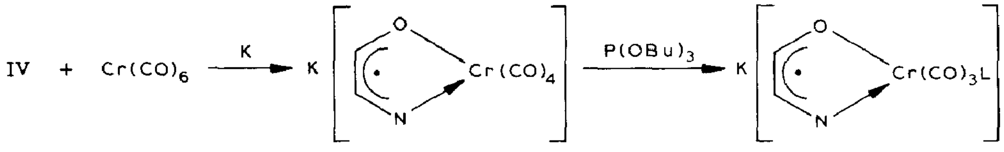


XXVI

As in the case of XXV, there remains uncertainty as to of the nature of the "X" ligands.

It is of interest to compare the redistribution of the spin density of the unpaired electron in the free radical anion IV with that of the chromium complex. Comparison of the spin densities on one nitrogen atom and on the hydrogen atom at the 9-position in XXVI with the corresponding data for IV gave the following relations: $2a_N$ (XXVI)$/a_N$(IV) = 1.5 $2a_H$(XXVI)$/a_H$(IV) = 0.6. Thus a decrease in the coupling to the proton is accompanied by a proportional rise in the coupling to the nitrogen nucleus which indicates that the spin density is displaced from aromatic nuclei to the nitrogen nuclei of the chelate metallacycle. A similar injection of spin density into the cyclic chelate by the phenoxazinolate system is also observed for XXV as compared with radical II (relation $2a_N$(XXV)$/a_N$(II) = 1.9).

The formation of the radical anion XXVI proceeds stepwise. We have found that a monochelate radical anion XXVII is formed in the first stage of interaction of IV with chromium carbonyl:



XXVII XXVIII

The ESR spectrum of XXVII is shown in Fig. 11 (a).

The displacement of spin density towards the chromium atom points to coordina-

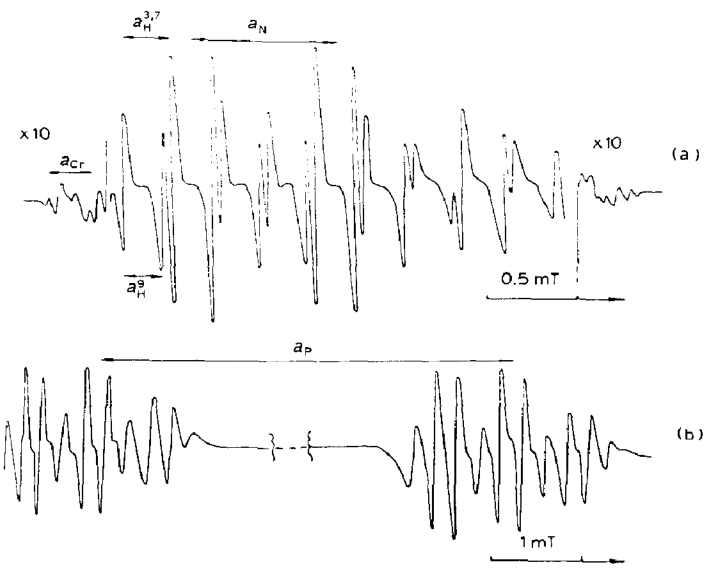


Fig. 11. ESR spectra of anion-radical complexes XXVII (a) and XXVIII (b) in THF at 298K (at the high gain level satellites from the nucleus of ^{53}Cr are observed).

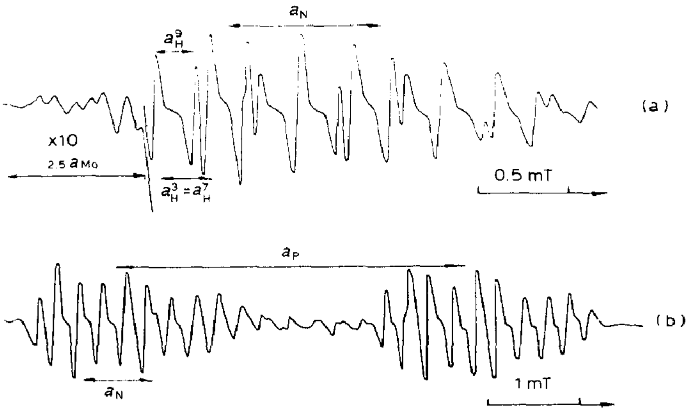
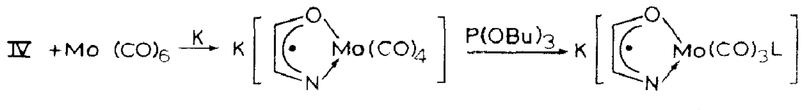


Fig. 12. ESR spectra of anion-radical complexes XXIX (a) and XXX (b) in THF at 298 K. Satellites from the ^{95,97}Mo nuclei are observed.

tion of the radical-anion ligand (see Table 5 for the coupling constants).

In complex XXVII one of the carbonyl ligands can be replaced by tributylphosphite to yield the paramagnetic compound XXVIII whose ESR spectrum shows coupling of the unpaired electron not only to the magnetic nuclei of the phenoxazinyl fragment but also to the ^{31}P nucleus (Table 5, Fig. 11b).

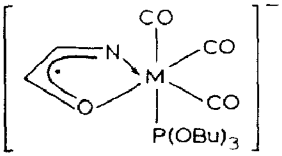
The interaction of the radical anion IV with molybdenum hexacarbonyl proceeds likewise; the first stage gives a monophenoxazinolate complex XXIX whose ESR spectral parameters (Fig. 12 (a), Table 5) are identical with those of complex XXVII. Similarly, XXIX reacts with tributylphosphite to afford compound XXX; its ESR spectrum (Fig. 12 (b), Table 5) also resembles that of XXVIII.



(XXIX) (XXX)

The ESR spectra of the Cr and Mo phosphite derivatives, XXVIII and XXX, reveal the coupling to ^{31}P nuclei thus indicating that the phosphite ligands lie out of that phenoxazinolate plane involving the unpaired electron (Table 5); the spin density transfer is attributable to σ_{M-P},π conjugation.

Taking into consideration that substitution of a carbonyl ligand occurs preferentially in the position *cis* to the O–M bond of the phenoxazinolate ligand [18,19], the coordination geometry in the complexes XXVIII and XXX may be depicted as follows:



The reaction of the monochelate radical anions XXVII, XXIX, or XXXII with an excess of phenoxazine III results in further replacement of carbonyl groups to give the bis-chelates XXVI, XXXI or XXXIII, respectively:

(XXVII M=Cr; XXIX M=Mo; XXXII M=W) (XXVI M=Cr; XXXI M=Mo; XXXIII M=W)

The ESR spectra of complexes XXVI and XXXI are depicted in Figure 10 (a), (b) and 13, respectively; spectral parameters are listed in Table 5. A comparison of the coupling constants to the ^{53}Cr and $^{95,97}Mo$ nuclei for these complexes with those for the monophenoxazinolate derivatives suggests that the spin density is displaced towards the metal atom because of the change in the oxidation state of the metal as the type of complex varies. The ESR spectrum of the chromium complex XXVI shows isotropic parameters whereas those of molybdenum and tungsten are char-

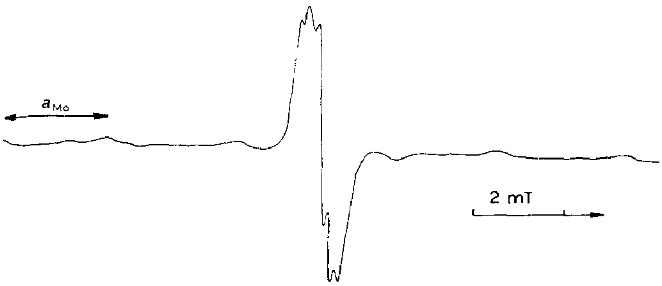
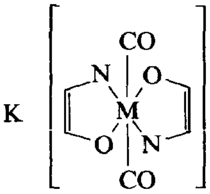


Fig. 13. ESR spectrum of anion-radical complex XXXI.

acterized by substantional anisotropy of the *g*-factor (Table 5) and appear to be typical examples of the metal-centred free radical in which the unpaired electron is largely based on metal orbitals:



(XXXI M = Mo;
XXXIIa M = W)

The values of the hyperfine coupling constants to the ^{15}N nuclei, which are lower than those of the starting radical anions, support our interpretations of the ESR spectral parameters for complexes XXVI and XXXIII.

Paramagnetic phenoxazinolate complexes of platinum group metals

The reaction of a radical anion IV with $PdCl_2$ affords a complex whose ESR

Table 6

ESR data for phenoxazinolate complexes of platinum group metals. Coupling constants are given in mT.

NN	a_N	a_H^3	a_H^7	a_H^9	a_M	M	*g*-factor
XXXIV	0.92	0.31	0.31	0.21	0.50	Pd	2.0020
XXXV	0.83	0.26	0.26	0.19	0.54	Pd	2.0075 [a]
XXXVI	0.92	0.33	0.33	0.21	0.55	Pd	2.0020
XXXVII	0.80	0.28	0.38	0.22	0.35	Pd	2.0040 [b]
XXXVIII	0.78	0.27	0.27	0.21	0.52	Pd	2.0060 [c]
XXXIX	0.94	–	–	–	4.70	Pt	2.0000
XL	0.90	0.28	0.28	0.21	5.20	Pt	2.0070 [c]
XLI	0.65	0.28	0.33	0.24	0.06	Os	2.0040
XLII	0.93	0.30	0.30	0.23	0.71	Ru	2.0025
XLIII	0.89	0.28	0.28	0.28	0.28	Rh	2.0040

[a] Addition hyperfine interaction with two equivalent phosphorus nuclei ($a_P = 12.3$ mT) is observed. [b] Two non-equivalent *anti*-protons of the allyl ligand are distinguishable in the spectrum: $a_H^{13.1} = 0.09$ mT and $a_H^{11.1} = 0.06$ mT. [c] Coupling constants to phosphorus nuclei of complexes XXXVIII ($a_P = 1.01$ mT) and XL ($a_P = 1.75$ mT) were detected.

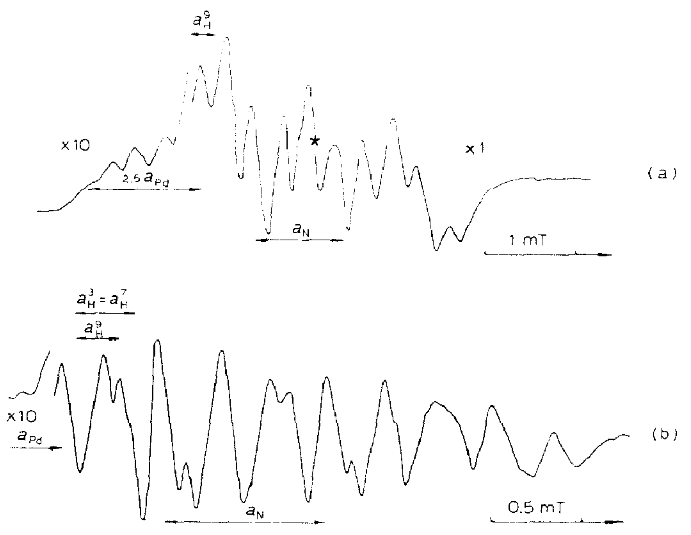
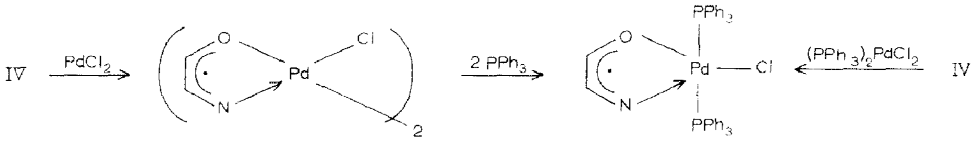


Fig. 14. ESR spectrum (THF, 298 K) of paramagnetic complexes formed upon interaction of IV with: (a) palladium dichloride (XXXIV); (b) palladium hexafluoroacetylacetonate (XXXVI). Satellites from ^{105}Pd nuclei are detected at the high gain level. * = centre of signal.

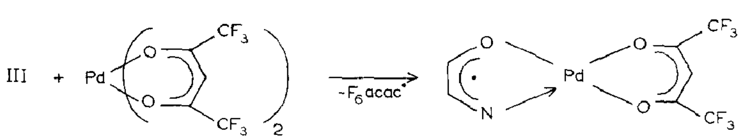
spectrum (Fig. 14 (a), Table 6) reveals the interaction of the unpaired electron with the magnetic nuclei of the phenoxazinolate ligand. Moreover, the spectrum exhibits hyperfine coupling to the isotope of ^{105}Pd, the intensity of the lines being fully in accord with its natural abundance (22.2%). We suggest that this complex has the dimeric, μ-bridged structure XXXIV; however, the phenoxazinolate ligands are far removed from each other, thus the complex has the properties of a monoradical species. The addition of two triphenylphosphine ligands to XXXIV cleaves the bridges to give the paramagnetic compound XXXV. The latter can also be obtained by reaction of either a radical anion IV or a monoradical salt X with bis(triphenylphosphine)palladium chloride:



(XXXIV) (XXXV)

The values of hyperfine coupling constants to ^{31}P nuclei (Table 6) fix the triphenylphosphine ligands as being axial in a trigonal bipyramidal coordination. In addition, a decrease in the value of the coupling constant to the nitrogen nucleus can safely be attributed to the increase in polarity of the bond between the phenoxazinolate ligand and the palladium atom, compared to that in complex XXXIV.

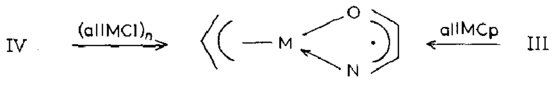
The paramagnetic complex XXXVI is produced by reaction of bis(hexafluoroacetylacetonato)palladium with phenoxazine III. Its ESR spectrum (Fig. 14b, Table 6) is virtually identical with that of XXXIV.



XXXVI

A hexafluoroacetylacetonate radical was expected as the other product of the reaction, however, it was not detected. It is noteworthy that bis(acetylacetonato)palladium does not undergo a similar conversion probably because of its lower electron affinity compared with that of the fluorinated analogue.

The allyl complexes of Pd and Pt react with the radical anions IV or with the phenoxazine III to afford paramagnetic π-allyl complexes:



(XXXVII M=Pd; XXXIX M=Pt)

Apart from the coupling to the magnetic nuclei of the phenoxazinolate fragment (viz. nuclei of ^{14}N and the ring protons) and to the magnetic isotope of ^{105}Pd, the ESR spectrum of XXXVII (Fig. 15 (a)) also shows an additional doublet-doublet structure with small coupling constants which is attributable to the splittings on the *anti*-protons of the allyl ligand. The doublet-doublet structure indicates non-equivalence of the *anti*-protons of the allyl ligand (Table 6) owing to its non-symmetric orientation towards the phenoxazinolate fragment bearing the unpaired electron

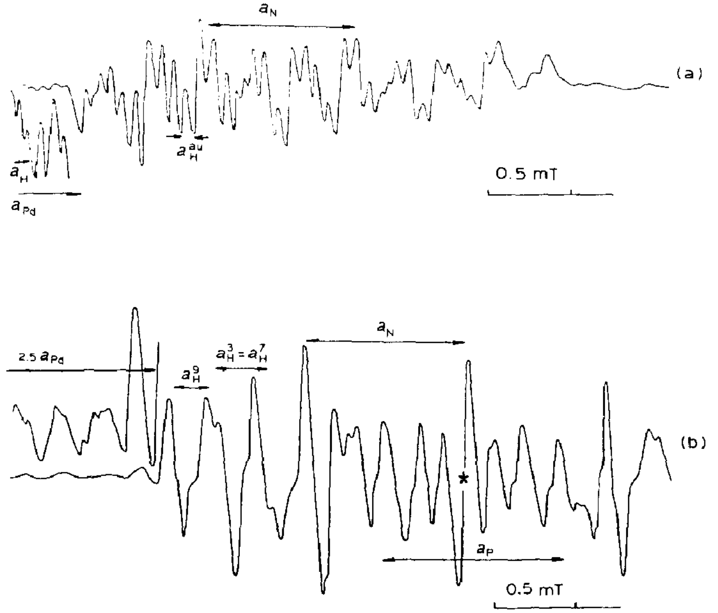


Fig. 15. ESR spectra of allyl palladium phenoxazinolate complexes in THF at 298 K: a) XXXVII; b) a penta-coordinate complex XXXVIII. Satellites from nuclei of ^{105}Pd are observed. ★ = centre of signal.

[20]. The transfer of spin density onto the protons of the terminal allylic groups is direct; in this case the value of the hyperfine coupling constant is inversely proportional to the cube of the distance between the unpaired electron and the interacting nucleus, thus coupling only to the *anti*-protons of the allyl ligand is observed. Hyperfine interaction with the four protons of terminal methylene groups and also with the proton on the central carbon atom, would be observed if the unpaired electron is located on the allyl moiety. However, experimental data have proved this suggestion to be wrong.

The ESR spectrum of a platinum complex XXXIX (Fig. 16 (a)) exhibits hyperfine coupling to the ^{14}N nucleus and magnetic platinum isotope, ^{195}Pt, whereas no interaction with phenoxazinolate and allyl ligand protons could be detected owing to the large line widths of the hyperfine spectral structure (Table 6).

The ESR spectral parameters of complexes XXXVII and XXXIX provide evidence for the chelate coordination of the phenoxazinolate ligand which is manifested in the spin density shift towards the chelate metallacycle and the associated increase in the coupling to the ^{14}N nuclei (Table 6) as opposed to that for the starting radical anion. Such a spin density redistribution gives rise to additional hyperfine coupling to the ^{105}Pd and to the ^{195}Pt nuclei (Table 6). Similar values of the coupling constants have been reported for allyl palladium complexes involving a 3,6-bis(t-butyl)-*ortho*-benzosemiquinolate ligand [21–24].

The spectral pattern (Fig. 15 (b)) is different when the paramagnetic palladium complexes XXXVII are treated with donor ligands such as triphenylphosphine: additional hyperfine coupling to the nucleus of ^{31}P indicates that the phosphine is coordinated to the palladium stom. The values of the coupling constant with magnetic nuclei of the phenoxazinolate fragment in XXXVIII indicate that the chelate metallacycle remains unchanged. On the other hand, the value of the

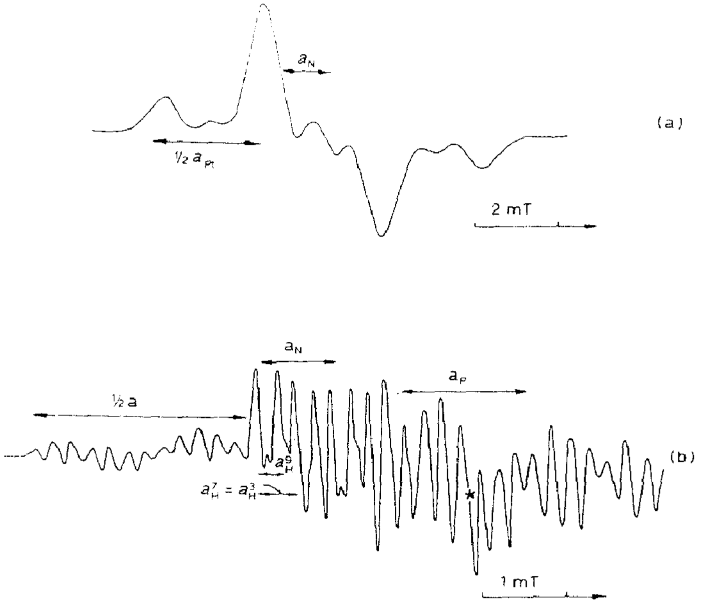
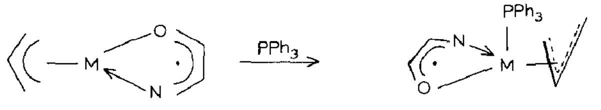


Fig. 16. ESR spectra of allyl platinum phenoxazinolate complexes at 298 K in THF: (a) XXXIX; (b) the penta-coordinate complex XL. Satellites from ^{195}Pt nuclei are observed. ★ = centre of signal.

coupling constant to the phosphorus nucleus suggests that the phosphine ligand occupies the fifth coordinate position outside the plane of the phenoxazinolate cycle, thus completing the coordination node structure to trigonal pyramidal or square pyramidal [25–30]:

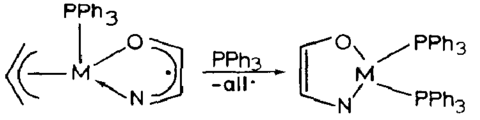


(XXXVIII M=Pd; XLM=Pt)

If an equimolar amount of triphenylphosphine is added to the platinum complex XXXIX, less line broadening is observed in the ESR spectrum (Fig. 16 (b)); as a consequence, the couplings to the phenoxazinolate protons are revealed, and an additional hyperfine interaction with the ^{31}P nucleus comes into existence (Table 6). The structure of the resultant 5-coordinate platinum complex XL is analogous to that of the palladium derivative XXXVIII. The values of the coupling constants to the ^{31}P nuclei in the complexes XXXVIII and XL, suggest that the transfer of spin density onto the phosphorus nuclei is by σ_{M-P}, π-conjugation.

A similar spectral pattern was observed for the reaction of π-allylpalladium *ortho*-semiquinolate with PPh_3 [24]. Here the pattern was interpreted in terms of the formation of a square planar π-allyl complex; penta-coordinate compounds of the types XXXVIII and XL were not detected.

The formation of penta-coordinate complexes of Pd and Pt increases the metal–nitrogen bond polarity and results in enhanced coupling to the magnetic isotopes of ^{105}Pd and ^{195}Pt and a weakened interaction with the nitrogen nuclei of phenoxazinolate ligands. The penta-coordinate compounds XXXVIII and XL readily undergo dissociation with the loss of the phosphine ligand to afford the starting square planar complexes XXXVII and XXXIX. However, in the presence of an excess of triphenylphosphine, solutions of XXXVIII or XL lose their paramagnetic properties, to yield the diamagnetic derivatives XXXVIIIa or XLa, respectively:



(XXXVIIIa M=Pd;
XLa M=Pt)

A similar reaction, reported for *ortho*-semiquinolate complexes [22,26], has been found to involve electron transfer from the allyl ligand to the phenoxazinolate via the central metal atom with the loss of the allyl moiety.

The products of the reactions of the radical anions, IV or X, with π-allyl-π-benzeneosmium chloride (XLI) bis(π-benzeneruthenium dichloride) (XLII), and bis(diallylrhodium chloride) (XLIII), have been studied by ESR spectroscopy.

Figure 17 (a), (b) and Table 6 illustrate the results obtained. The values of the coupling constants to the nuclei of ^{14}N, $^{99,101}Ru$, ^{103}Rh and ^{189}Os suggest that in all instances a chelate metallacycle is formed. With regard to other ligands in the complexes under consideration it is impossible to cover all structural details within the framework of this investigation.

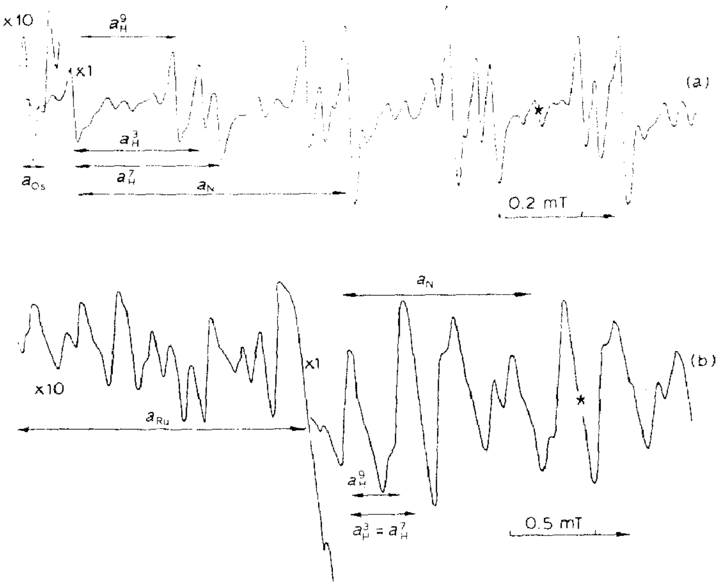
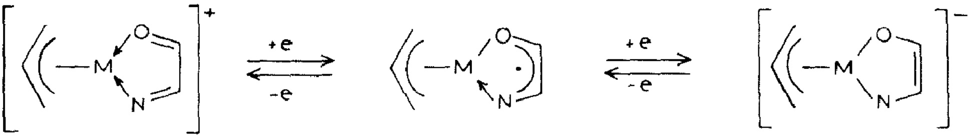


Fig. 17. ESR spectra of organometallic phenoxazinolate complexes at 298 K in THF: (a) osmium complex XLI; (b) ruthenium complex XLII. At the high gain level satellites from magnetic isotopes of ^{189}Os and ^{99,101}Ru are observed. ★ = centre of signal.

The redox properties of the paramagnetic complexes XXXVII and XXXIX were examined by cyclic voltammetry (Table 7). For these compounds, the redox processes are limited by diffusion because the maximal currents are proportional to the square root of potential scan rate.



(XXXVII : M = Pd ;
XXXIX : M = Pt)

Reduction of the complexes gives rise to the stable diamagnetic anions which undergo reversible oxidation to the starting compounds and diamagnetic cations.

Table 7

The redox potentials of phenoxazine III, palladium complex XXXVII, and platinum complex XXXIX

NN	Reduction				Oxidation			
	$-E_{pc}$	I_{pc}	$-E_{pa}$	I_{pa}	E_{pa}	I_{pa}	E_{pc}	I_{pc}
III	0.74	9.2	0.56	7.6	–	–	–	–
	1.56	4.4	1.26	3.2	–	–	–	–
XXXVII	0.45	7.0	0.39	7.0	0.44	7.6	0.35	7.0
XXXIX	0.56	7.8	0.45	7.2	0.57	7.0	0.53	6.0
Cp_2Fe	–	–	–	–	0.56	8.0	0.45	8.0

[a] Versus a saturated calomel electrode, recorded for 5.10^{-3} M THF solution with $[NBu_4][ClO_4]$ as base electrolyte.

We have used ferrocene as an example to show that the reduction of complexes XXXVII and XXXIX proceeds by a one-electron reduction.

Experimental

All experiments were carried out under dry purified argon in degassed absolute solvents. The electrochemical measurements were performed by use of a Pt disk electrode with the potentiostat Λ-5827M under using triangular impulses at a frequency of 0.1–1.0 Hz. The reference electrode was a SCE. Polarography of complexes was carried out with a UP-9 TESLA instrument. The IR spectra were recorded on a Specord-751R instrument in 5.10^{-2} M CH_2Cl_2 solutions or in Nujol. The NMR spectra were recorded on a Bruker-WP200 instrument in deuterochloroform as solvent with TMS as internal standard. The ESR spectra were recorded on a Varian-E12A instrument equipped with temperature control. The sample solutions were prepared as follows:
(a) The phenoxazine derivatives II or III were used to generate the radical anions IV, X–XVII, and XXV–XXXIII in ESR hook-ended ampoules by metal mirrors or by reduction with amalgams of metals of groups 2–4. The radical anions of metal carbonyls of types XXV–XXXV were generated from the relevant carbonyl in situ.
(b) The paramagnetic compounds XIII and XXI–XXXIII were prepared by direct UV irradiation of an ESR ampoule containing the precursor.
(c) The paramagnetic platinum metal complexes were prepared from the anion-radical salts and an excess of the corresponding halogen-containing diamagnetic platinum metal complexes.

g-Factors were determined relative to an external standard from the following relation:
$g = g_{st}(1 \pm \Delta H/H_0)$, where $g_{st} = 2.0028$; H_0 is field strength; ΔH is the shift of a signal relative to the standard, ΔH was regarded as positive when the standard signal was left of the sample signal. g-Factors are accurate to within ±0.0004.

Preparation of II and III. A mixture of 3,5-di-t-butyl-*ortho*-benzoquinone (2.2 g, 10 mmole) and 3,5-di-t-butyl-*ortho*-aminophenol (2.2 g, 10 mmole) were heated in ethanol (350 ml) under reflux for 2 hours in the presence of equimolar amount of sodium ethylate. After cooling, the mixture was quenched with cold water (150 ml) and the resulting dark blue precipitate was chromatographed on silica gel to give the following fractions:
(i) Elution with hexane, removal of solvent on a rotary evaporator, and sublimation of the residue ($100\,^\circ C/5 \cdot 10^{-2}$ mmHg), gave complex II (1.14 g, 27%), m.p. 148 °C. Found: C, 79.41; H, 9.56; N, 3.29. $C_{28}H_{40}NO_2$ calcd.: C, 79.62; H, 9.47; N, 4.22%.
(ii) Elution with a benzene/hexane mixture (3 : 10), and removal of solvent, gave complex III (1.9g, 46%), m.p. 208 °C. Found: C, 79.62; H, 9.18; N, 3.28. $C_{18}H_{39}NO_2$ calcd.: C, 79.81; H, 9.26; N, 3.32%. Mass spectrum: M^+ 421.

Preparation of perchlorate VI. The radical II (0.85 g) was ground with an excess of $HClO_4$ in an agate mortar. The reaction mixture was filtered on a glass filter, washed with hexane, and dried in vacuum. A red solid was obtained (1.01 g, 97%), decomp. temp. 116 °C. Found: C, 64.21; H, 7.89. $C_{28}H_{41}ClNO_6$ calcd.: C, 64.37; H, 7.85%.

Preparation of methoxy derivative VIII. The dark-blue solution of III (10 mmole) in THF (150 ml) was treated with finely divided sodium until the solution became colourless. Then methyl iodide (9 ml, 12 mmole) was added and the reaction mixture was stirred at room temperature for one hour. The solvent was evaporated and the residue was chromatographed on silica gel. The first fraction (benzene/hexane (3 : 10)) contained unchanged starting material (III); elution with benzene/hexane (10 : 3) after removal of solvent, gave compound VIII as a red solid (4.05 g, 93%), m.p. 179 °C. Found: C, 79.91; H, 9.87; N, 3.06. $C_{29}H_{42}NO_2$ calcd.: C, 79.82; H, 9.63; N, 3.20. Mass spectrum: M^+ 436.

Preparation of XXXVII. To a solution of bis(allylpalladium chloride) (0.1 g, 0.3 mmole) in THF (30 ml) was added a solution of IV prepared from III (0.2 g, 0.47 mmole) in THF (50 ml) and sodium. The reaction mixture was stirred for an hour, then evaporated, and the residue was chromatographed on silica gel. Elution with hexane gave the starting II; elution with benzene, removal of the solvent, and crystallization of the residue from hexane on cooling to −45 °C, gave XXXIX as brown crystals (0.14 g, 52%), decomp. temp. 187 °C. Found: C, 65.45; H, 7.74; Pd, 18.72. $C_{41}H_{44}NO_2Pd$ calcd.: C, 66.15; H, 8.37; Pd, 18.06%.

Preparation of XXXIX. To a solution of the amino-radical IV (prepared as described above) was added a suspension of tetrakis(allylplatinum chloride) (0.27 g, 0.25 mmole) in THF (30 ml) was added. The mixture was stirred at room temperature for 1.5 hour and filtered. The filtrate was evaporated and the residue was chromatographed on silica gel. Hexane was used to elute radical II; elution with benzene/acetone (10 : 3) after removal of solvent and crystallization from pentane at −45 °, gave XXXIX as dark violet crystals (0,245 g, 78%), decomp. temp. 284 °C. Found: C, 56.87; H, 6.92; Pt, 29.97. $C_{41}H_{44}NO_2Pt$ calcd.: C, 56.61; H, 6.60; Pt, 29.74%.

Preparation of XXXIXa. Complex XXXIX (0.2 g, 0.3 mmole) and triphenylphosphine (0.24 g, 0.9 mmole) were stirred together at 25 °C for an hour till the mixture became completely colourless. The resulting precipitate was filtered off, washed with hexane and crystallized from a benzene/hexane (5 : 3) mixture to give XXXIXa (0.33 g, 96%), decomp. temp. 277 °C. Found: C, 67.11; H, 6.43; Pt, 17.81. $C_{64}H_{69}NO_2P_2Pt$ calcd.: C, 67.36; H, 6.05; Pt, 17.13%.

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