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Preliminary communication

PALLADIUM- AND PLATINUM-CONTAINING FREE RADICALS

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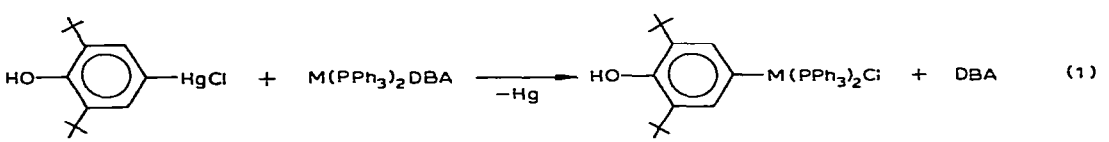
Summary

The synthesis and ESR-spectra of the novel paramagnetic σ-phenoxyl derivates $L_2M[C_6H_2$-t-$Bu_2O^{\cdot}]X$ (M = Pd, Pt; L = PPh_3; X = Cl) are reported.

Previously, we have described platinum metal complexes with redox ligands based on hindered phenols with the metal atom conjugated with the paramagnetic fragment [1,2]. However, directly ring-metalated phenoxyl derivatives have not yet been characterised.

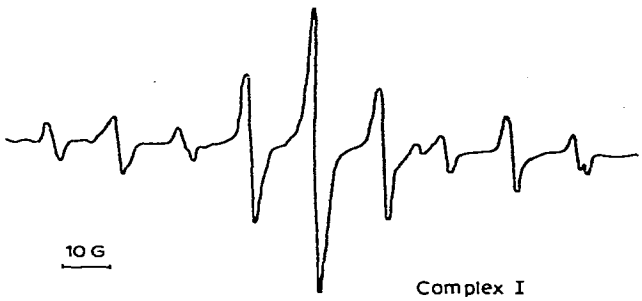
We now report the synthesis of σ-bonded derivatives of the transition metals by interaction of Pd^0 and Pt^0 complexes with 4-hydroxy-3,5-di-t-butylphenylmercuric chloride [4] in benzene as solvent. This method has been developed by Reutov et al. [3] and it is a very efficient and simple way to σ-alkyl and σ-aryl derivatives of Pd and Pt.



(I, M = Pt ; II, M = Pd ; DBA = dibenzylideneacetone ; † = t-butyl)

All compounds obtained are colourless crystalline substances stable in air and in solution; melting point: I, 247—248°C (benzene); II, 132—133°C(acetone). The structure of the complexes has been confirmed by elemental analysis and by IR and NMR spectroscopy.

Oxidation of the compounds obtained by anhydrous plumbic compounds ($-e, -H^+$) in toluene as solvent leads to the corresponding free organometallic radicals (equation 2); ESR spectra of the radicals generated are shown in Fig. 1.



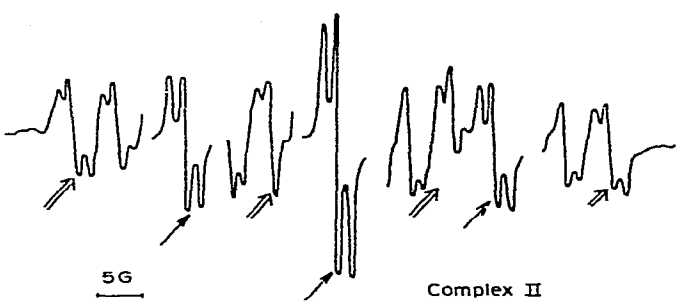
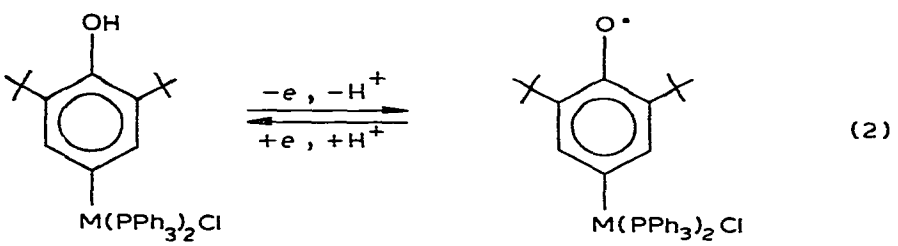


Fig. 1. ESR spectra for complexes I and II. Solvent-toluene. Temperature +40°C. For II, common signal is split, satellites from ^{105}Pd nuclei were detected upon gain increase by a factor of twenty.



(2)

(I, M = Pt ; II, M = Pd)

The hyperfine structure of the ESR spectra indicated interaction of the unpaired electron with the *m*-protons of the phenoxyl ring, two equivalent phosphorous nuclei and the metal nuclei. The intensity of the lines from the paramagnetic isotopes ^{105}Pd and ^{195}Pt completely corresponds to their natural abundances; spectra multiplicity arises from the nuclei spin differences (Table 1).

TABLE 1

ESR DATA FOR COMPLEXES I AND II

Metal	Natural content of paramagnetic isotope	I	$a(m\text{-H})$ (G)	$a(^{31}P)$ (G)	$a(M)$ (G)	g-factor
^{195}Pt	33.7	1/2	1.2	16	94	2.0079
^{105}Pd	22.2	5/2	1.5	18.7	5.45	2.0051

The type of ESR spectra remains invariable within the temperature range −70—+70°C; at room temperature and under airless conditions the character of the signal is maintained for a long time, indicating extremely high stability of the generated organometallic radicals.

References

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