LITERATURE CITED

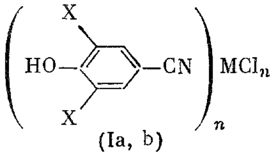
1. M. Gielen and Y. Tondeyr, J. Organomet. Chem., 169, 265 (1979).
2. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, Methods of Heteroorganic Chemistry. Germanium, Tin, Zinc [in Russian], Nauka, Moscow (1968).
3. E. R. Birnbaum and P. H. Javora, J. Organomet. Chem., 9, 379 (1967).
4. N. A. Bumagin, Yu. V. Gulevich, and I. P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2639 (1982).
5. N. A. Bumagin, I. G. Bumagina, A. N. Kashin, and I. P. Beletskaya, Dokl. Akad. Nauk SSSR, 261, 1141 (1981).
6. H. C. Clark, A. B. Goel, and C. J. Billard, J. Organomet. Chem., 182, 431 (1979).
7. M. F. Lappert and N. F. Travers, J. Chem. Soc. Chem. Communs., 1569 (1968).
8. A. N. Kashin, I. G. Bumagina, N. A. Bumagin, V. N. Bakunin, and I. P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2185 (1980).
9. I. G. Bumagina, Dissertation, Moscow (1981).
10. D. Azarian, S. S. Dua, C. Eaborn, and D. R. Walton, J. Organomet. Chem., 117, C55 (1976).
11. M. Kosugi, K. Shimizu, A. Ohtani, and T. Migita, Chem. Lett., 829 (1981).
12. H. Azizian, C. Eaborn, and A. Pidcock, J. Organomet. Chem., 215, 49 (1981).
13. J. F. Fauvarque, F. Pflüger, and M. Troupel, J. Organomet. Chem., 208, 419 (1981).
14. L. G. Volkova, I. Ya. Levitin, and M. E. Vol'pin, Usp. Khim., 44, 1217 (1975).
15. T. Kobayashi, and M. Tanaka, J. Organomet. Chem., 205, C27 (1981).

CONVERSION OF 4-HYDROXY-3,5-DI-tert-BUTYLBENZONITRILE TO PALLADIUM AND RHODIUM COMPLEXES

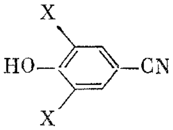
A. Z. Rubezhov, E. R. Milaeva, A. I. Prokof'ev,
I. V. Karsanov, and O. Yu. Okhlobystin

UDC 542.91:547.582.4:541.49:546.9

The stability of complexes of the platinum metals with paramagnetic ligands based on spatially-hindered phenoxyls depends essentially on the mode of bonding of the transition metal with the phenoxyl-containing ligand [1-3]. Whereas σ-phenoxyl complexes are unusually stable, compounds with 4-hydroxy-3,5-di-tert-butylazobenzene, in which the metal atom is bound to the ligand by σ-bonding through the N atom are very unstable. In the present work we have synthesized the complexes (I) of rhodium and palladium with an N-coordinated ligand—4-hydroxy-3,5-di-tert-butylbenzonitrile (II) [4] and have studied the stability of the paramagnetic derivatives formed when they are oxidized.



(Ia, b)



(II)

M = Pd, $n = 2$ (Ia); M = Rh, $n = 3$ (Ib); X = t-Bu.

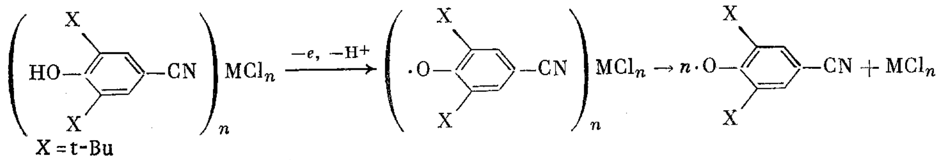
The starting diamagnetic compounds were prepared by the usual methods of synthesis for coordination compounds of the transition metals with nitriles [5]. Heating (II) with $RhCl_3 \cdot 3H_2O$ in alcohol at the boiling point for 2 days in an inert atmosphere (to prevent oxidation of the phenol) yielded the air-stable complex (Ib), soluble in benzene, chloroform, and alcohol and slightly soluble in ether and hydrocarbons. The direct method of synthesizing (Ia) from $PdCl_2$ proved unsuitable; to prepare the complex we utilized the well-developed tendency of $(PhCN)_2PdCl_2$ to undergo substitution of the PhCN by other ligands. Reaction of the complex with (II) in acetone at ∿20°C (3 h) gave (Ia), which was stable in air and was less soluble than the initial $(C_6H_5CN)_2PdCl_2$. The composition and structure of the prepared complexes were confirmed by means of elemental analysis and IR spectroscopy. The presence in the IR spectra of characteristic bands (ν_{OH} = 3520, ν_{CN} ∿ 2160 cm^{-1}) indicated that the phenol frag-

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimiya, No. 5, pp. 1143-1146, May, 1984. Original article submitted March 15, 1983.

0568-5230/84/3305-1049$08.50

ment and the CN group, N-coordinated with the transition metal atom, had been retained. The complexes (Ia, b) were oxidized by PbO_2 in toluene in evacuated ampuls.

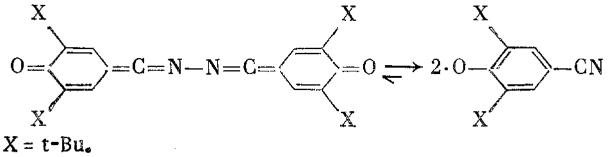


First of all the ESR spectrum corresponding to the free 2,6-di-tert-butyl-4-cyanophenoxyl radical was recorded [6]. The unpaired electron interacts with the two eqiivalent meta-protons of the phenoxyl ring (a_H = 2.2 Oe) and with the ^{14}N nucleus (a_N = 1.3 Oe). The absence of an interaction of the unpaired electron with the metal nucleus and the absence of any change in the hyperfine coupling (hfc) constants a_H, a_N confirmed the fact that during oxidation of the complex the generated radical leaves the coordination sphere, i.e., the ligand–metal bond is broken during conversion of the complex to the paramagnetic state.

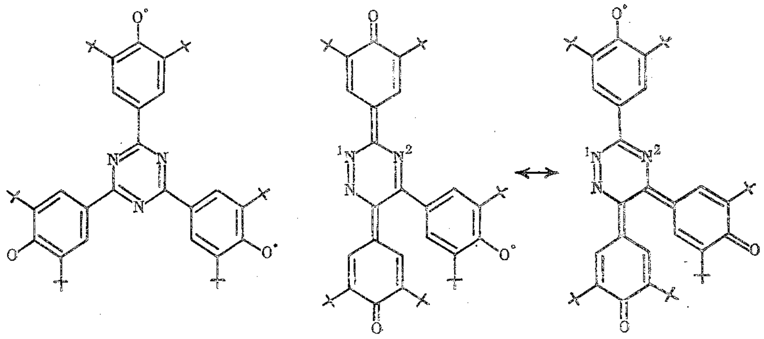
With time the spectral picture changes (Fig. 1). Analysis of the hyperfine structure of the ESR spectrum in the figure shows that in the paramagnetic species formed the unpaired electron interacts not only with two equivalent protons (a_H = 1.05 Oe), but also with two equivalent ^{14}N nuclei (a_N = 2.0 Oe).

The appearance of a new free radical species is explained by the possible cyclotrimerization derivatives of benzonitrile in the presence of salts and complexes of the transition metals [7]. In fact the spectral picture observed when the free nitrilophenoxyl radical was converted in the presence of $PdCl_2$, K_2PdCl_4, K_2PtCl_4, $RhCl_3 \cdot 3H_2O$ was the same in all cases and corresponded to the assumed trimer. In the absence of inorganic additives the free radical did not undergo change.

In order to verify this assumption we preparatively studied the reaction of $RhCl_3 \cdot 3H_2O$ with the 2,6-di-tert-butyl-4-cyanophenoxyl radical, which is a dimer in the solid state and which dissociates in solution according to the following scheme:



After mixing an alcoholic solution of the reagents in an inert atmosphere (5 h, 25°C) a bright blue colored substance was obtained the ESR spectrum of which in toluene was identical with the spectrum shown in Fig. 1. In the IR spectrum of the prepared compound the characteristic absorption of the OH group of spatially hindered phenols in the 3500-3650 cm^{-1} region was absent and it possessed the absorption characteristic of the cyclohexadiene fragment ($\nu_{C=O}$ = 1640 cm^{-1}). The data from the elemental analysis (empirical formula $C_{45}H_{60}O_3N_3$) and the mass spectrum (M^+ 690) indicated the trimeric structure of the product. It is known [7] that the cyclization of benzonitriles can lead to symmetrical (IIIa) and nonsymmetrical (IIIb ↔ IIIc) triazines.



(IIIa) (IIIb) (IIIc)

The triradical structure (IIIa) does not correspond to the observed spectrum (see Fig. 1). Study of frozen solutions (−180°) did not reveal the characteristic lines corresponding

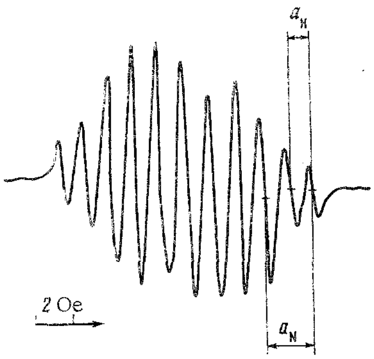


Fig. 1. ESR spectrum of the radical (IIIb, c), toluene, 20°.

to spin–spin coupling of unpaired electrons typical of bi- and polyradical systems of similar type [8]. Hence the observed spectra relate to the mesomeric structures (IIIb, c). The equivalent N nuclei are denoted by the indices 1 and 2.

In order to confirm the structure (IIIb, c) the reaction product was reduced by means of $K_4Fe(CN)_6$ to a diamagnetic derivative which was characterized by the PMR and mass spectra (M^+ 691). In the PMR spectrum three singlets were observed due to the protons of three nonequivalent sets of tert-butyl groups (δ 1.101; 1.156; 1.201 ppm), a singlet due to the proton of HO (δ 3.176 ppm), a singlet due to two aromatic meta-protons (δ 6.664 ppm) and four doublets ($J \simeq 1.5$ Hz) of the pour protons of two cyclohexadiene rings (δ 6.87; 6.70; 6.412, and 5.985 ppm). The weak splitting of the singlets indicates a transannular interaction of the protons.

The PMR spectroscopic data were in good agreement with the structure (IIIb, c). Formation is most probably represented by a 1,4-addition of the 4-cyanophenoxyl radical by a Diels–Alder type reaction to the diamagnetic dimer of 4-cyano-2,6-di-tert-butylphenoxyl present in the solution.

Thus during oxidation of complexes of 4-hydroxy-3,5-di-tert-butylbenzonitrile with rhodium (III) and palladium (II) cleavage of the transition metal—ligand bond occurs, and then the ligand under the action of the metal salt undergoes a cyclic trimerization with formation of the nonsymmetrical 1,2,4-triazine.

EXPERIMENTAL

2,6-Di-tert-butylcyanophenol was prepared by a published method [4] from 2,6-di-tert-butyl-4-formylphenol and $NH_2OH \cdot HCl$ in the presence of pyridine with subsequent dehydration with acetic anhydride. The 2,6-di-tert-butylcyanophenoxyl radical was synthesized by oxidation of 2,6-di-tert-butylcyanophenol by means of $K_3Fe(CN)_6$ [4, 6]. Bis(benzonitrile)-palladium dichloride was obtained by the published method [5], $RhCl_3 \cdot 3H_2O$ (commercial preparation) was used without prior purification. The IR spectra of the substances in KBr tablets were recorded on a UR-20 spectrometer, the NMR spectra on the Brucker WP200 instrument, and the ESR spectra on a Varian E-12A spectrometer.

Bis(4-hydroxy-3,5-di-tert-butylbenzonitrile)palladium Dichloride. To a solution of 0.35 g (0.001 mole) dibenzonitrilepalladium dichloride in 15 ml acetone was added 0.5 g (0.002 mole) 4-hydroxy-3,5-di-tert-butylbenzonitrile in 15 ml acetone. The reaction mixture was stirred for 3 h at ∿20°; the resulting yellow precipitate was filtered off, washed with acetone and hexane and recrystallized from a benzene–hexane mixture (1:1). A light yellow crystalline product was obtained. Yield 0.52 g (81%), mp (with dec.) 194°C. Found: C 55.30; H 6.58; N 4.36; Pd 18.92%. $C_{30}H_{42}Cl_2N_2PdO_2$. Calculated: C 56.25; H 6.58; N 4.38; Pd 18.81%.

Tris(4-hydroxy-3,5-di-tert-butylbenzonitrile)rhodium Dichloride. To a solution of 0.75 g (0.003 mole) 4-hydroxy-3,5-di-tert-butylbenzonitrile in 50 ml alcohol was added a solution of 0.26 g (0.001 mole) $RhCl_3 \cdot 3H_2O$ in alcohol. The reaction mixture was maintained at boiling for 2 days in an Ar atmosphere, cooled, evaporated to small volume and chromatographed on silica gel. Benzene eluted unreacted 4-hydroxy-3,5-di-tert-butylbenzonitrile; alcohol eluted an orange substance which was recrystallized from a benzene–hexane (1:1) mixture. Yield 0.12 g (14%), mp (with dec.) 260-261°C. Found: C 59.71; H 6.77; N 4.52; Ph 11.40%. $C_{45}H_{63}Cl_3N_3O_3Rh$. Calculated: C 59.85; H 6.98; N 4.66; Ph 11.41%.

Reaction of 2,6-Di-tert-butyl-4-nitrilophenoxyl Radical with $RhCl_3 \cdot 3H_2O$. To a solution of 0.7 g (0.003 mole) 2,6-di-tert-butyl-4-nitrilophenoxyl radical in alcohol was added dropwise an alcoholic solution of 0.26 g (0.001 mole) $RhCl_3 \cdot 3H_2O$. The reaction mixture was stirred 5 h in an Ar atmosphere at ∿20°, then decomposed with an equal volume of water and extracted with benzene. After the usual treatment a bright blue powdery substance was obtained, which was recrystallized from a benzene—hexane (1:1) mixture. Yield 0.33 g (47%), mp (with dec.) 232°C. Found: C 78.00; H 8.70; N 6.13%. $C_{45}H_{60}N_3O_3$. Calculated: C 78.25; H 8.74; N 6.10%. M^+ 690.

0.3 g of the prepared blue substance was dissolved in acetone and an excess of an aqueous solution of $K_4Fe(CN_6)$ added. The reaction mixture was stirred for 4 h at ∿20° then stood overnight. After extraction with ether and removal of the solvent a yellow colored residue was obtained, which was recrystallized from hexane. Yield 100%, mp 134-136°C. Found: C 78.15; H 8.78; N 6.07%. $C_{45}H_{61}N_3O_3$. Calculated: C 78.16; H 8.83; N 6.08%. M^+ 691.

CONCLUSIONS

Complexes of palladium (II) and rhodium (III) with 4-hydroxy-3,5-di-tert-butylbenzonitrile have been synthesized and it has been found that during their oxidation the metal—ligand bond is broken to yield the free nitrilophenoxyl radical in solution which under the action of the transition metal salt undergoes cyclotrimerization with formation of the nonsymmetrical triazine.

LITERATURE CITED

1. E. R. Milaeva, L. Yu. Ukhin, V. B. Panov, A. Z. Rubezhov, A. I. Prokof'ev, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 242, 125 (1978).
2. E. R. Milaeva, A. Z. Rubezhov, A. I. Prokoph'ev, and O. Yu. Okhlobystin, J. Organomet. Chem., 193, 135 (1980).
3. E. R. Milaeva, A. Z. Rubezhov, A. I. Prokoph'ev, A. G. Milaev, and O. Yu. Okhlobystin, J. Organomet. Chem., 188, C43 (1980).
4. E. Muller, K. Ley, K. Scheffler, and R. Mayer, Chem. Ber., 91, 2691 (1958).
5. L. Malatesta and C. Cariello, J. Chem. Soc., 2323 (1958).
6. E. Muller, K. Ley, K. Scheffler, R. Mayer, and A. Rieker, Chem. Ber., 92, 2278 (1959).
7. W. Z. Held, J. Organomet. Chem., 6, 292 (1966).
8. N. Yang and A. Castro, J. Am. Chem. Soc., 82, 6208 (1960).

CHEMISTRY OF VINYLIDENE COMPLEXES.

COMMUNICATION 2.* CONVERSIONS OF PHENYLVINYLIDENE IN POLYNUCLEAR COMPLEXES OF OSMIUM AND MANGANESE

A. B. Antonova, S. V. Kovalenko, E. D. Korniets,
I. Yu. Efremova, A. A. Ioganson, and S. P. Gubin

UDC 542.91:541.49:547.1'13:546.94

The most significant features of mononuclear vinylidene complexes of transition metals are the presence of the unsaturated M=C=C metalloallene grouping and the deficiency of electron density on the α-carbon atom [1]. The M=C=C group can take part in very diverse processes: the addition of carbenoid metal-complex fragments containing Mn, Re, Fe, or Pt across the M=C bond, the addition of nucleophilic reagents (CO, phosphites) to the α-carbon atom, hydrogenation, etc. [1-7].

In this communication we shall report the conversions of phenylvinylidene in a heteronuclear system of four metal atoms formed during the reaction between the phenylvinylidene complex of manganese $Cp(CO)_2Mn{=}C{=}CHPh$ (I) and the unsaturated carboyl hydride cluster of osmium $H_2Os_3(CO)_{10}$. As far as we know, reactions of mononuclear vinylidene complexes with clusters of metals have not previously been reported.

---

*For Communication 1, see [1].

Institute of Chemistry and Chemical Engineering, Academy of Sciences of the USSR, Siberian Branch, Krasnoyarsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1146-1152, May, 1984. Original article submitted March 9, 1983.

0568-5230/84/3305-1052$08.50