

Deprotonated *N*-phenyl-*o*-phenylenediimine as a bridging ligand

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Dedicated to Professor Oleg M. Nefedov for his outstanding contribution to organoelement chemistry

Abstract

The interaction of *N*-Ph-*o*-phenylenediamine with the trinuclear palladium complex $\text{Pd}_3(\mu\text{-OCCMe}_3)_6$ was investigated. The ionic complex obtained $[\text{K}\cdot\text{H}_2\text{O}]^+ \{\text{Pd}_3(\text{OCCMe}_3)_4(\mu\text{-OH})[\mu\text{-}N,N\text{-}\eta^2\text{-}N,N'\text{-}(\text{N})(\text{NPh})(\text{C}_6\text{H}_4)_2]\}^-$ has been structurally characterized by an X-ray diffraction study. It was found that the reaction of bis(*N*-phenyl-*o*-semiquinonediimine)platinum(+2) with $\text{Re}(\text{CO})_5\text{Cl}$, which has been preliminarily treated with silver triflate, afforded the heterometallic complex $(\text{CO})\text{Pt}[\mu\text{-}N,N\text{-}o\text{-}(\text{N})(\text{NPh})\text{C}_6\text{H}_4]_2\text{ReCl}[(\text{NH})(\text{NPh})\text{C}_6\text{H}_4]$. © 2001 Published by Elsevier Science B.V.

Keywords: Palladium; Rhenium; *o*-Phenylenediamine; Semiquinonediimine

1. Introduction

Metal binuclear complexes and clusters containing carbonyl and carbene bridging groups are widely distributed and well studied [1–5]. Much less studied are complexes with nitrene bridging groups [6–9].

Arguments for the nitrene intermediates formed by the reduction of nitrosoarenes with a palladium(+1) carbonyl complex, $\text{Pd}_4(\text{CO})_4(\text{OCCMe}_3)_4$ were adduced in Ref. [10]. An alternative way towards the formation of the nitrene species seems to be dehydrogenation of organic amines. In this context, we studied the reactivity of *N*-monosubstituted *o*-phenylenediamine and coordinated *N*-phenyl-*o*-semiquinonediimine anionic ligands under the conditions of oxidative dehydrogenation.

2. Results and discussion

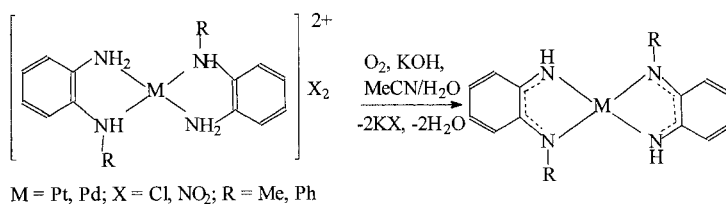
In polar media (H_2O , MeCN) platinum(II) and palladium(II) complexes with *N*-*R*-*o*-phenylenediamine

molecules ($\text{R} = \text{Me}, \text{Ph}$) as ligands are known to undergo oxidative dehydrogenation yielding complexes in which the central metal atom is bound to two chelate *N*-*R*-*o*-semiquinonediimine anionic ligands [11,12] (Scheme 1).

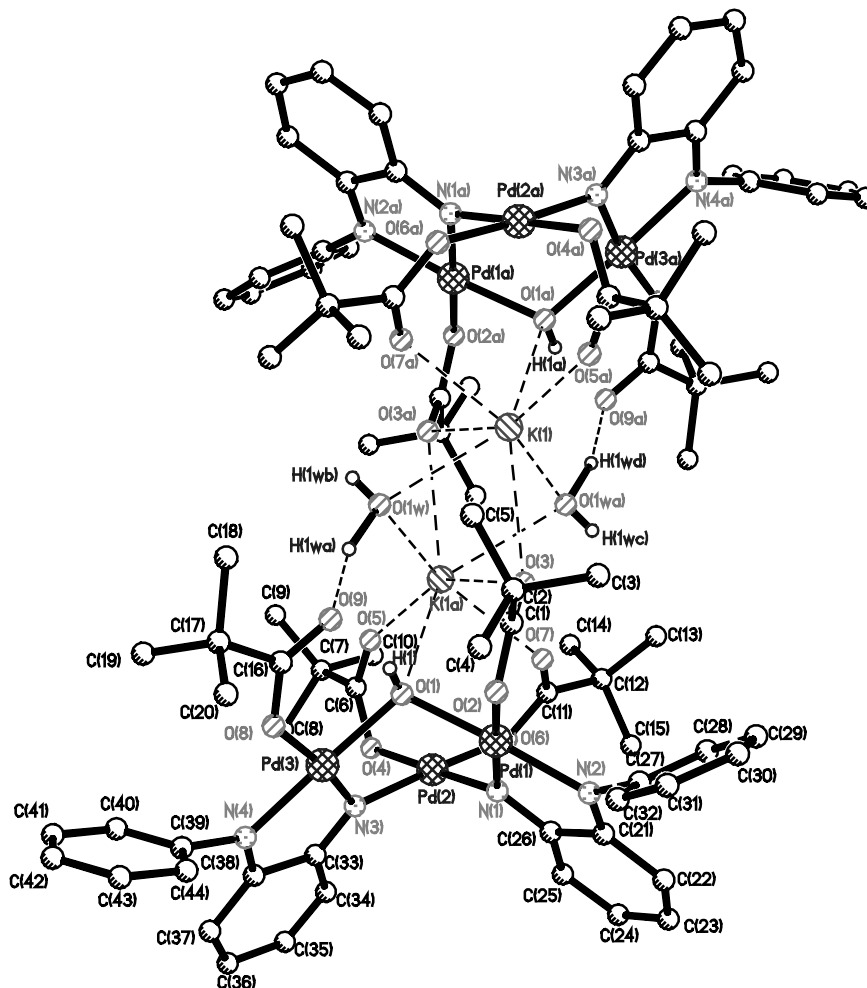
Oxidative dehydrogenation turned out to be sensitive towards the nature of the starting metal complex and the solvent. Thus we reacted *N*-phenyl-*o*-phenylenediamine (I) with trimeric palladium(+2) pivalate, $\text{Pd}_3(\mu\text{-OCCMe}_3)_6$ (II) in *m*-xylene solution. To avoid free ligand I oxidation, both reagents were allowed to react in the solution under an Ar atmosphere. Solid KOH was added to the solution after formation of the diamine complex was accomplished and the suspension of KOH and dissolved diamine complex was carefully treated with air. The product isolated was identified using X-ray techniques as anionic trinuclear palladium complex III (see Fig. 1, Table 1). Every palladium atom in the complex III has a square-planar environment, suggesting formal oxidation state of the Pd atoms to be +2. Hence, the organic *N*-donor ligands are monoanions as may be deduced from charge balance. The charge distribution within the *N*-donor organic ligand in complex III can be approximated by considering the possible resonance forms of the canonical nitrene (IVa) and imino (IVb) anionic structures (Scheme 2). Synthesis of complex III can be represented by Scheme 3.

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Scheme 1. Formation of the platinum and palladium semiquinonediimine derivatives.

Fig. 1. Structure of the complex $[\text{K}\cdot\text{H}_2\text{O}]^+ \{\text{Pd}_3(\text{OOCCMe}_3)_4(\mu\text{-OH})[\mu\text{-}N,N\text{-}\eta^2\text{-}N,N'\text{-}(\text{N})(\text{NPh})(\text{C}_6\text{H}_4)_2]\}^-$ (III) in the unit cell.

According to the X-ray diffraction study (Figs. 1 and 2, Table 1), three palladium atoms in diamagnetic triangle anion are separated by nonbonding distances (Pd(1)⋯Pd(2) 3.439(1), Pd(1)⋯Pd(3) 3.330(1) and Pd(2)⋯Pd(3) 3.459(1) Å).

Two trinuclear anions, two potassium atoms and two water molecules of two complexes III form a suprastructure in the unit cell (Fig. 1). In this supra-unit each of two potassium atoms is attached to a bridging water molecule (K–O(H₂O) 2.716(8) and 2.844(8) Å). The dipotassium fragment involving the K–O(OH) (2.860(7) Å) and K–O(OCO) (2.693(8)–2.772(7) Å) interactions joins two tripalladium anions.

The two pairs of palladium atoms, Pd(2)⋯Pd(1) and Pd(2)⋯Pd(3), within a tripalladium fragment are held together by the deprotonated and non-substituted imine nitrogen atom (Fig. 2) of the planar chelate-bridging *N*-phenyl-*o*-phenylenediimine anion (Pd(2)–N 1.964(7)–1.966(7), Pd(1)–N 1.971(7) and Pd(3)–N 1.969(7) Å, Pd(2)–N–Pd(1) 121.7(4) and Pd(2)–N–Pd(3) 123.2(4)°). The chelating function of the ligand towards the atoms Pd(1) and Pd(3) is effected by using the N atoms of the C=NPh group (Pd–N 2.016(7) and 2.001(7) Å, respectively) and the non-substituted N atom of the deprotonated diimine ligand. Remarkably, the phenyl rings of the C=N–Ph group are orthogonal

to the *N,N*,Pd-planes opening up the possibility for a conjugation between the nitrogen atom lone pair and the aromatic ring.

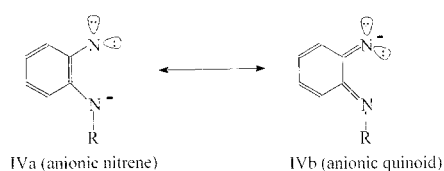
In addition, the Pd(1) and Pd(3) atoms are linked to a bridging hydroxo group (Pd(1)–O 2.021(6), Pd(3)–O

Table 1

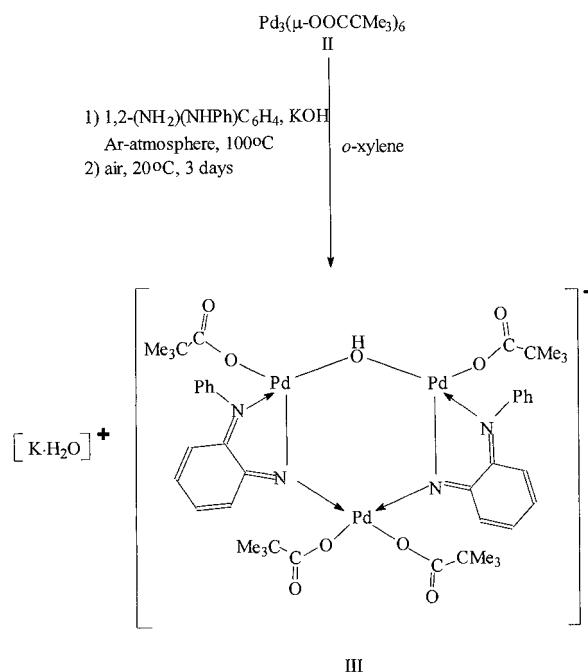
Selected bond lengths and angles for anion $\text{Pd}_3(\text{OCCMe}_3)_4(\mu\text{-OH})[\mu\text{-}N,N\text{-}\eta^2\text{-}N,N'\text{-}(\text{N}(\text{NPh})(\text{C}_6\text{H}_4))_2]$ in complex III

Bond lengths (Å)			
Pd(1)–N(1)	1.971(7)	Pd(1)–O(2)	2.014(6)
Pd(1)–N(2)	2.016(7)	Pd(1)–O(1)	2.021(6)
Pd(2)–N(3)	1.964(7)	Pd(2)–N(1)	1.966(7)
Pd(2)–O(6)	2.015(6)	Pd(2)–O(4)	2.021(6)
Pd(3)–N(3)	1.969(7)	Pd(3)–N(4)	2.001(7)
Pd(3)–O(1)	2.009(6)	Pd(3)–O(8)	2.025(6)
O(2)–C(1)	1.286(11)	O(3)–C(1)	1.227(11)
O(4)–C(6)	1.276(12)	O(5)–C(6)	1.251(11)
O(6)–C(11)	1.294(10)	O(7)–C(11)	1.234(10)
O(8)–C(16)	1.266(10)	O(9)–C(16)	1.224(10)
N(1)–C(26)	1.309(11)	N(2)–C(21)	1.305(11)
N(2)–C(27)	1.434(11)	N(3)–C(33)	1.299(11)
N(4)–C(38)	1.313(10)	N(4)–C(39)	1.445(11)
C(21)–C(22)	1.440(13)	C(21)–C(26)	1.488(12)
C(22)–C(23)	1.340(13)	C(23)–C(24)	1.442(14)
C(24)–C(25)	1.347(13)	C(25)–C(26)	1.436(11)
C(33)–C(34)	1.454(11)	C(33)–C(38)	1.476(11)
C(34)–C(35)	1.333(12)	C(35)–C(36)	1.437(13)
C(36)–C(37)	1.355(12)	C(37)–C(38)	1.438(12)

Bond angles (°)			
N(1)–Pd(1)–O(2)	176.3(3)	N(1)–Pd(1)–N(2)	81.8(3)
O(2)–Pd(1)–N(2)	95.4(3)	N(1)–Pd(1)–O(1)	93.1(3)
O(2)–Pd(1)–O(1)	89.6(2)	N(2)–Pd(1)–O(1)	174.9(3)
N(3)–Pd(2)–N(1)	91.2(3)	N(3)–Pd(2)–O(6)	175.4(3)
N(1)–Pd(2)–O(6)	91.2(3)	N(3)–Pd(2)–O(4)	90.5(3)
N(1)–Pd(2)–O(4)	178.3(3)	O(6)–Pd(2)–O(4)	87.1(2)
N(3)–Pd(3)–N(4)	81.9(3)	N(3)–Pd(3)–O(1)	92.4(3)
N(4)–Pd(3)–O(1)	174.1(2)	N(3)–Pd(3)–O(8)	172.3(3)
N(4)–Pd(3)–O(8)	90.9(3)	O(1)–Pd(3)–O(8)	94.7(2)
Pd(3)–O(1)–Pd(1)	111.4(3)	C(26)–N(1)–Pd(2)	123.8(6)
C(26)–N(1)–Pd(1)	114.0(6)	Pd(2)–N(1)–Pd(1)	121.7(4)
C(21)–N(2)–C(27)	122.6(8)	C(21)–N(2)–Pd(1)	113.2(6)
C(27)–N(2)–Pd(1)	124.0(6)	C(33)–N(3)–Pd(2)	123.4(5)
C(33)–N(3)–Pd(3)	113.2(5)	Pd(2)–N(3)–Pd(3)	123.2(4)
C(38)–N(4)–C(39)	120.3(7)	C(38)–N(4)–Pd(3)	113.8(5)
C(39)–N(4)–Pd(3)	125.9(5)	O(3)–C(1)–O(2)	125.0(8)
O(5)–C(6)–O(4)	125.6(9)	O(7)–C(11)–O(6)	123.4(8)
O(9)–C(16)–O(8)	125.2(7)	N(2)–C(21)–C(22)	126.4(9)
N(2)–C(21)–C(26)	115.0(8)	N(1)–C(26)–C(25)	126.1(8)
N(1)–C(26)–C(21)	116.0(7)	N(3)–C(33)–C(34)	125.8(8)
N(3)–C(33)–C(38)	117.5(7)	N(4)–C(38)–C(37)	126.4(8)
N(4)–C(38)–C(33)	113.6(7)		



Scheme 2. The nitrene (IVa) and quinoid (IVb) anionic resonance form descriptions of the *N*-donor anionic ligand IV in complex III.



Scheme 3. Synthesis of complex III.

2.009(6), O–H 0.72(5) Å, Pd(1)–O–Pd(3) 111.4(3)°. The hydrogen atom of this bridging group is involved in the formation of the hydrogen bonding with the oxygen atom of the terminal carboxylate ligand (O–H⋯OCO 1.99(5) Å) that is bound to Pd(3) atom (Pd(3)–O(8) 2.025(6) Å). All carboxylate groups are the terminal ligands. The atoms Pd(1) and Pd(3) have one carboxylate ligand (Pd(1)–O(OCO) 2.014(6) Å) and the atom Pd(2) has two carboxylate groups (Pd(2)–O(6) 2.015(6) and Pd(2)–O(4) 2.021(6) Å).

Both bridging *N*-donor ligands IV have a quinoid structure. Distances are close to that of regular N=C double bonds (N(1)–C(26) 1.309(11), N(2)–C(21) 1.305(11), N(3)–C(33) 1.299(11) and N(4)–C(38) 1.313(10) Å). Note that the distance for a single N–C(Ph) bond is normally within the range 1.434(11)–1.445(11) Å [13]. Two short and four long C–C bonds in the six-membered phenylene ring are also suggestive to the quinoid structure contributing to the electron distribution in ligand IV (see Table 1). However, though the geometry of *N*-donor ligands IV in complex III is close to that of the canonical structure (IVb) in Scheme 2, the contribution of nitrene form IVa to the structure of complex III cannot be excluded.

The data discussed above illustrate the propensity of ligand IV to bridge Pd(+2) atoms at a non-bonding distance. The capability of ligand IV to bridge short metal–metal contacts was demonstrated by synthesis of a Pt/Re complex.¹

¹ Preliminary short communication was published in *Russ. Chem. Bull.* [14].

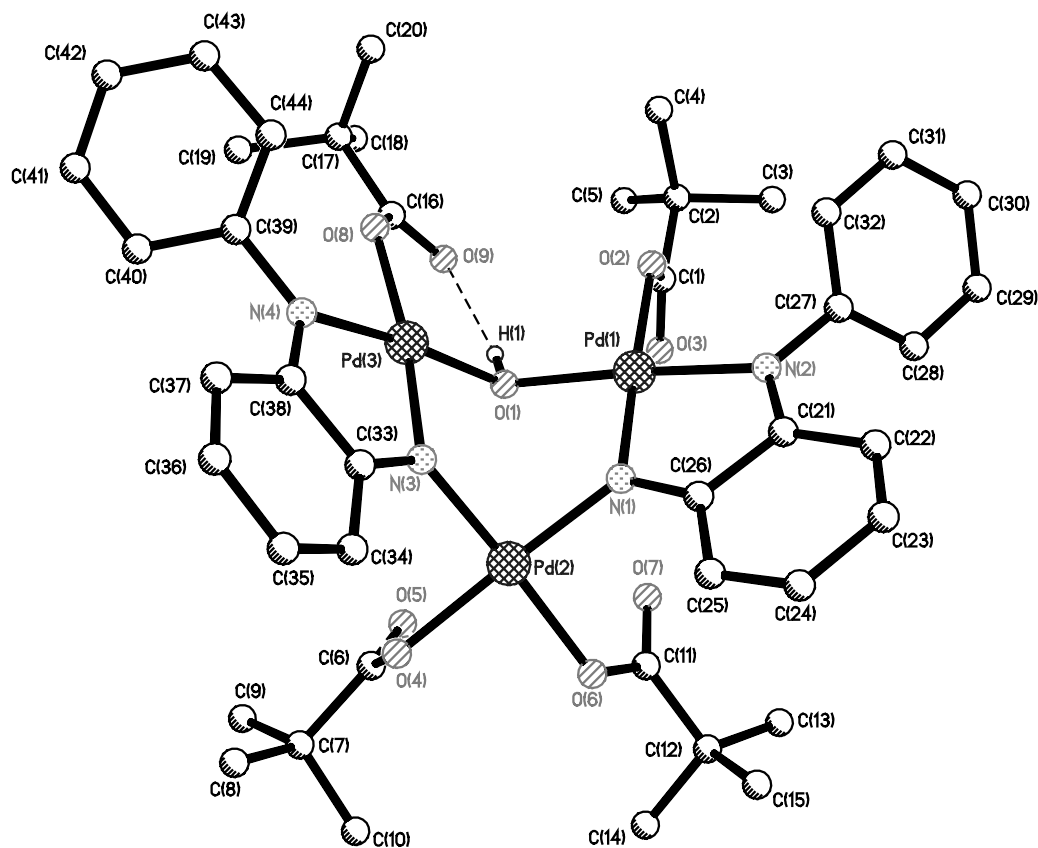


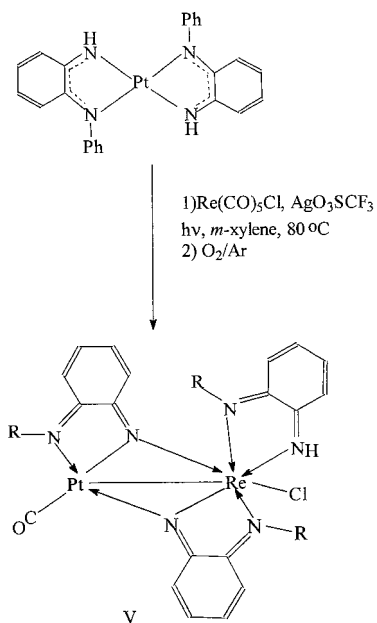
Fig. 2. Structure of the anion $\text{Pd}_3(\text{OOCCMe}_3)_4(\mu\text{-OH})[\mu\text{-}N,N\text{-}\eta^2\text{-}N,N'\text{-(N)(NPh)(C}_6\text{H}_4)_2]$.

Thus, UV-irradiation of bis(*N*-phenyl-*o*-semi-quinonediimine)platinum(+2) and $\text{Re}(\text{CO})_5\text{Cl}$ in the presence of AgO_3SCF_3 in *m*-xylene solution at 80 °C and subsequent careful air oxidation of the reaction mixture gives rise to the complex V, $(\text{OC})\text{Pt}[\mu\text{-}N,N\text{-}o\text{-(N)(NPh)C}_6\text{H}_4]_2\text{ReCl}[(\text{NH})(\text{NPh)C}_6\text{H}_4]$ (Scheme 4). According to the X-ray analysis data (Fig. 3, Table 2), the distances between the platinum and the rhenium atoms is remarkably short (3.057(1) Å), manifesting a Pt–Re bond (for example, the Pt–Re bonds are equal to 2.946(2) and 3.002(2) Å in the tetranuclear cation $[\text{Pt}_3\text{Re}(\text{CO})_3(\mu\text{-dppm})_3]^+$ [15] and are equal to 2.8815(8) Å (R = Ph) and 2.8673(4) Å (R = Cy) in the binuclear cations $[\text{Cp}(\text{NO})\text{Re}(\mu\text{-PR}_2)(\mu\text{-H})\text{Pt}(\text{PPh}_3)_2]^+$ [16]).

The platinum and rhenium atoms in the molecule are linked with two chelate-bridging *N*-phenyl-*o*-quinonediimine anions.

Two of the nitrogen atoms in these ligands are coordinated to both metal atoms (Pt–N(1) 1.96(2) and Pt–N(3) 2.01(1); Re–N(1) 1.81(2) and Re–N(3) 2.07(1); and N(1)–C(2) 1.36(2) and N(3)–C(14) 1.34(2) Å). The chelate coordination of the ligands to the rhenium and platinum atoms is achieved through the N atoms of the NPh group (Pt–N(2) 2.01(1); and Re–N(4) 2.13(1) Å). In spite of this mode of coordination, both bridging

ligands, like the third neutral *N*-phenyl-*o*-quinonediimine ligand, which is coordinated only to the Re atom



Scheme 4. Formation of the heterometallic binuclear platinum–rhenium complex V.

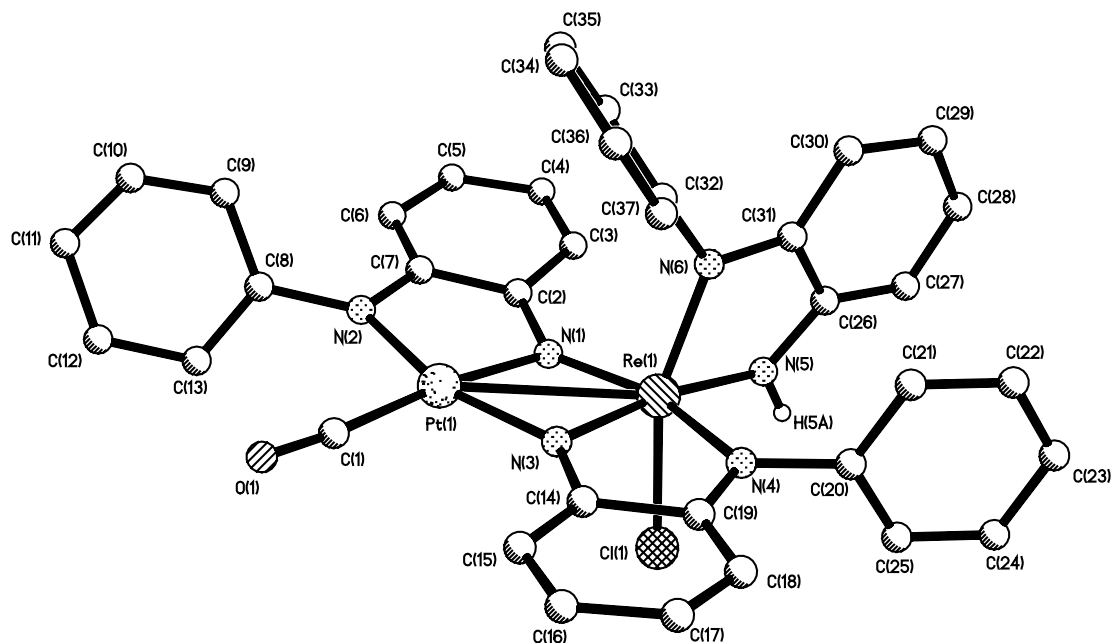


Fig. 3. Structure of heteronuclear complex $(OC)Pt[\mu-N,N'-o-(N)(NPh)C_6H_4]_2ReCl[(NH)(NPh)C_6H_4]$ (V).

(Re–N(5) 1.98(2) and Re–N(6) 2.01(1); N(5)–C(26) 1.35(2) and N(6)–C(31) 1.38(2); N(5)–H(5a) 0.78(6) Å, have the quinoid structure. As a result, the platinum atom is formally reduced to platinum(+1). The CO ligand (Pt–C(1) 1.884(9) Å; C(1)–O(1) 1.148(15) Å; and the Pt–C–O angle is $175.3(11)^\circ$) is coordinated to the Pt atom affording a pseudo square-planar ligand environment. The rhenium atom bearing the halide ligand (Re–Cl, 2.388(5) Å) is oxidized to rhenium(+2) and has a distorted octahedral environment.

3. Experimental

3.1. General comments

The synthesis of new compounds III and V was carried out with the use of anhydrous solvents prepared according to standard procedure. The starting trimers $Pd_3(\mu-OOCCMe_3)_6$ and $Pt[o-(NH)(NPh)C_6H_4]_2$ were prepared by known methods [17,12]. The reagents $Re(CO)_5Cl$, and AgO_3SCF_3 were purchased from Fluka. Column chromatography was carried out with the use of Kieselgel 60 (Fluka). The IR spectra were recorded on a Specord M80 instrument in KBr pellets.

3.2. Synthesis of $[K \cdot H_2O]^+ \{Pd_3(OOCCMe_3)_4(\mu-OH)-[\mu-N,N'-\eta^2-N,N'-(N)(NPh)(C_6H_4)]_2\}^-$ (III)

200 mg of complex $Pd_3(OOCCMe_3)_6$ (II, 0.22 mmol) and 120 mg of *N*-phenyl-*o*-phenylenediamine (I, 0.66

mmol) were dissolved in Ar atmosphere in 25 ml of *o*-xylene with the formation of brown solution. Solid KOH (2 g) was added to this solution and reaction mixture formed was stirred for 1 h at 100 °C. Solution was cooled to room temperature, filtered and stored for 3 days under an Ar–air (~1:1) atmosphere until the formation of black prismatic crystals of III as a solvate with 0.5 xylene molecule and 1 water molecule (40 mg, 20%), which were suitable for X-ray investigation. Anal. Found: C, 46.5; H, 6.0; N, 4.65. Calc. for $KPd_3(OOCCMe_3)_4(OH)[(N)(NPh)(C_6H_4)]_2 \cdot 2H_2O \cdot 0.5C_6H_4Me_2$: C, 46.74; H, 6.00; N, 4.54%. IR, ν cm^{-1} : 3440s, 3344s, 2928m, 2856w, 1664w, 1576vs, 1528m, 1488s, 1440vs, 1336s, 1272m, 1216m, 1136m, 1072w, 968w, 928w, 912w, 864m, 736m, 680m, 584m, 560w, 432w.

3.3. Synthesis of bis($\mu-N',N'-\eta^2-(N-phenyl-o-benzoquinonediimine)carbonyl$)platinum(+1)- $\eta^2-(N-phenyl-o-benzoquinonediimine)chlororhenium(+2)$, $(OC)Pt[\mu-N,N'-o-(N)(NPh)C_6H_4]_2ReCl[(NH)(NPh)C_6H_4]$ (V)

A solution of CF_3SO_3Ag (0.25 g, 1 mmol) in *m*-xylene (10 ml) was added to a solution of $Re(CO)_5Cl$ (0.36 g, 1 mmol) in *m*-xylene (10 ml). The reaction mixture was stirred for 0.5 h until a precipitate formed. A solution of complex $Pt[o-(NH)(NPh)C_6H_4]_2$ (0.55 g, 1 mmol) in *m*-xylene (10 ml) was added to the resulting suspension and the reaction mixture was irradiated with UV light at 80 °C for 3 h. The reaction mixture was stored under an Ar–air (~1:1) atmosphere for 12 h. The resulting solution was filtered and

concentrated to dryness at 70 °C (0.1 Torr). Hexane (5 ml) was added to the residue, and the resulting suspension was applied to a column (5 × 30 cm) with Kieselgel 60. The dark-brown zone was eluted with benzene (50 ml; R_f 0.60). The solution thus obtained was concentrated to 10 ml at 70 °C (0.1 Torr) and kept at 20 °C for 1 day. The dark-brown prismatic crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried in air. Complex V was obtained in a yield of 0.28 g (28%). Anal. Found: C, 45.2; H, 3.3; N, 8.3. Calc. for (OC)Pt[(N)(NPh)C₆H₄]₂ReCl[(NH)(NPh)C₆H₄]: C, 44.91; H, 2.85; N, 8.49%. IR, ν cm⁻¹: 3033w, 2920w, 2032w, 1704w, 1656w, 1624w, 1568w, 1464m, 1384w, 1256s, 1096s, 1032s, 872w, 808s, 616w, 464w.

Table 2
The main geometric parameters for structure V

Bond lengths (Å)			
Pt(1)–Re(1)	3.057(1)	Re(1)–Cl(1)	2.388(5)
Pt(1)–C(1)	1.89(2)	Pt(1)–N(1)	1.96(2)
Pt(1)–N(3)	2.01(1)	Pt(1)–N(2)	2.01(1)
Re(1)–N(1)	1.81(2)	Re(1)–N(5)	1.98(2)
Re(1)–N(6)	2.01(1)	Re(1)–N(3)	2.07(1)
Re(1)–N(4)	2.13(1)	O(1)–C(1)	1.11(2)
N(1)–C(2)	1.36(3)	N(2)–C(7)	1.38(2)
N(2)–C(8)	1.48(2)	N(3)–C(14)	1.34(2)
N(4)–C(19)	1.36(2)	N(4)–C(20)	1.45(2)
N(5)–C(26)	1.35(2)	N(6)–C(31)	1.38(2)
N(6)–C(32)	1.49(2)	C(2)–C(7)	1.47(2)
C(2)–C(3)	1.52(3)	C(3)–C(4)	1.39(2)
C(4)–C(5)	1.40(2)	C(5)–C(6)	1.43(3)
C(6)–C(7)	1.42(2)	C(14)–C(15)	1.33(2)
C(14)–C(19)	1.52(3)	C(15)–C(16)	1.33(3)
C(16)–C(17)	1.42(3)	C(17)–C(18)	1.26(2)
C(18)–C(19)	1.34(3)	C(26)–C(31)	1.38(2)
C(27)–C(28)	1.38(2)	C(28)–C(29)	1.39(3)
C(29)–C(30)	1.41(2)	C(30)–C(31)	1.43(2)
Bond angles (°)			
C(1)–Pt(1)–N(1)	173.4(8)	C(1)–Pt(1)–N(3)	98.7(7)
N(1)–Pt(1)–N(3)	76.2(7)	C(1)–Pt(1)–N(2)	98.2(7)
N(1)–Pt(1)–N(2)	87.2(7)	N(3)–Pt(1)–N(2)	162.4(5)
C(1)–Pt(1)–Re(1)	140.8(5)	N(1)–Pt(1)–Re(1)	34.1(6)
N(3)–Pt(1)–Re(1)	42.2(4)	N(2)–Pt(1)–Re(1)	121.0(4)
N(1)–Re(1)–N(5)	110.8(6)	N(1)–Re(1)–N(6)	96.1(6)
N(5)–Re(1)–N(6)	75.5(6)	N(1)–Re(1)–N(3)	78.1(6)
N(5)–Re(1)–N(3)	170.4(6)	N(6)–Re(1)–N(3)	107.8(5)
N(1)–Re(1)–N(4)	150.1(6)	N(5)–Re(1)–N(4)	99.0(6)
N(6)–Re(1)–N(4)	89.5(5)	N(3)–Re(1)–N(4)	72.2(5)
N(1)–Re(1)–Cl(1)	97.4(6)	N(5)–Re(1)–Cl(1)	84.3(5)
N(6)–Re(1)–Cl(1)	158.6(4)	N(3)–Re(1)–Cl(1)	91.2(4)
N(4)–Re(1)–Cl(1)	86.9(4)	N(1)–Re(1)–Pt(1)	37.4(5)
N(5)–Re(1)–Pt(1)	148.1(5)	N(6)–Re(1)–Pt(1)	104.5(3)
N(3)–Re(1)–Pt(1)	40.8(4)	N(4)–Re(1)–Pt(1)	112.9(4)
Cl(1)–Re(1)–Pt(1)	96.23(11)	Re(1)–N(1)–Pt(1)	108.6(8)
Pt(1)–N(3)–Re(1)	97.0(7)	O(1)–C(1)–Pt(1)	172.5(17)

Crystals of the solvate V·THF suitable for X-ray investigation were prepared by slow evaporation of the solution of V in THF.

3.4. Crystal structure determinations

Crystals of solvates III·0.5C₆H₄Me₂·H₂O and V·THF suitable for study by X-ray diffraction were prepared as described above. The X-ray intensity data set for III was collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 100 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure [18]. The semiempirical absorption correction was applied [19]. The X-ray diffraction data set for V was collected according to a standard procedure on a four-circle automated Siemens R3v/m diffractometer (λ Mo–K α radiation, $\lambda = 0.71074$ Å, $T = 22$ °C). The crystallographic parameters and selected details of the refinement of structures are given in Table 3. The structures of III and V were solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands in III, phenyl and phenylene rings of *N*-donor ligands in III and V were calculated geometrically and refined using the riding model. The positions of the hydrogen atoms of the bridging OH group and one water molecule connected with the potassium cation in III were found from the difference Fourier map and refined isotropically. The hydrogen atoms for the second solvate water molecule in structure III were not located. The hydrogen atom of the NH fragment of neutral diimine ligand in V was located from difference Fourier synthesis and refined isotropically. Solvate xylene molecule in III was found and refined to occupancy of 0.5. All calculations were carried out with the use of the SHELX97 program package [20]. The main geometric parameters for compounds III and V are given in Tables 1 and 2.

X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow).

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Table 3
Data collection and processing parameters for investigated compounds III and V

Compound	III	V
Empirical formula	C ₄₄ H ₅₅ KN ₄ O ₉ Pd ₃ ·0.5Me ₂ C ₆ H ₄ ·2H ₂ O	C ₃₇ H ₂₈ ClN ₆ OPtReC ₄ H ₈ O
Formula weight	1232.3	1061.5
Color and habit	Brown prism	Brown prism
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.851(11)	11.290(3)
<i>b</i> (Å)	15.033(7)	12.191(3)
<i>c</i> (Å)	15.177(19)	14.627(4)
α (°)	62.21(5)	83.98(2)
β (°)	63.55(7)	73.69(2)
γ (°)	82.61(9)	82.67(2)
<i>V</i> (Å ³)	2670(4)	1911.3(10)
<i>Z</i>	2	2
ρ_{calc} (g cm ⁻³)	1.522	1.844
Absorption coefficient (cm ⁻¹)	11.35	69.33
Theta range for data collection (°)	1.68–31.43	1.45–26.06
Unique data	7321	7953
Reflections observed	6147 $F_o > 4\sigma(F_o)$	7550 $F_o > 4\sigma(F_o)$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0931P)^2 + 0.0000P]$; $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.0000P]$; $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.038	0.855
R_1	0.0606	0.0458
wR_2	0.1508	0.0977
Residual extrema in final diff. Map (e Å ⁻³)	2.188–1.070	1.359–2.043

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