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Reactions of *N*-phenyl-*o*-semiquinonediimine complexes of nickel and platinum with carbonyl-containing low-valence iron and rhenium compounds

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The reactions of *o*-semiquinonediimine complexes $M[o\text{-}(NH)(NPh)C_6H_4]_2$ (M = Ni (**1**) or Pt (**2**)) with carbonyl-containing iron and rhenium compounds were studied. The reactions of complexes **1** or **2** with $Fe(CO)_5$ afforded the $Fe_2(CO)_6[\mu\text{-}(NH)(NPh)C_6H_4]$ complex (**3**) containing the bridging *N*-phenyl-*o*-phenylenediamide ligand in high yield. The reaction of the $Re(CO)_2(NO)Cl_2(thf)$ complex with complex **2** gave rise to the unusual mononuclear rhenium(III) complex, *viz.*, $Re(Ph)[\sigma\text{-}\eta^1\text{-}o\text{-}(NH)(NHPh)C_6H_4](CO)(NO)Cl_2$ (**4**), no changes in the geometry of *N*-phenyl-*o*-phenylenediamine bound to the $Re(NO)(CO)_2Cl_2$ fragment being observed. The reaction of complex **2** with the $Re(CO)_5Cl$ complex, which has been preliminarily treated with silver triflate, afforded the heterometallic complex $(CO)Pt[\mu\text{-}N,N\text{-}o\text{-}(N)(NPh)C_6H_4]_2ReCl[(NH)(NPh)C_6H_4]$. The structures of the resulting complexes were established by X-ray diffraction analysis.

Key words: redox transformations of coordinated ligands, *o*-semiquinonediimine nickel and platinum complexes, heterometallic compounds, synthesis, structure.

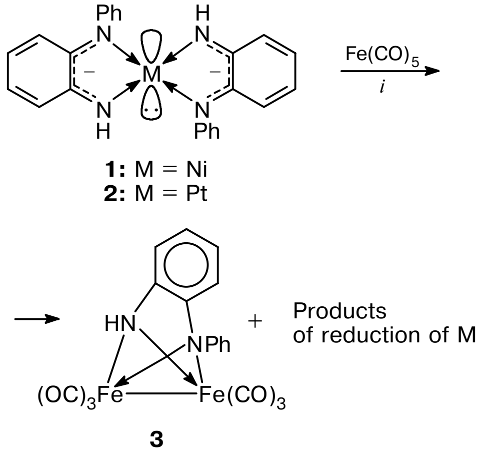
One of convenient procedures for the chemical design of heterometallic complexes and clusters of transition metals involves the use of metal-containing fragments as ligands with respect to other organometallic molecules. In this regard, the *o*-semiquinonediimine complexes of nickel(II) and platinum(II), *viz.*, $M[o\text{-}(NH)(NPh)C_6H_4]_2$ (M = Ni (**1**) or Pt (**2**)), which we have synthesized previously, may serve as promising starting blocks for the preparation of heterometallic complexes. We attempted to introduce these compounds into the reactions with moieties containing metal atoms in low oxidation states with the aim of preparing heterometallic compounds. The formation of the latter can also be accompanied by conversions of the coordinated semiquinonediimine ligand. In the present work, we report the reactions of complexes **1** and **2** with $Fe(CO)_5$, $Re(CO)_2(NO)Cl_2(thf)$, and $Re(CO)_5Cl$.

Results and Discussion

We found that refluxing of complexes **1** or **2** in the presence of $Fe(CO)_5$ in benzene resulted in the transfer of the *N*-phenyl-*o*-semiquinonediimine ligand to the iron atoms and its reduction, giving rise to the diamagnetic binuclear complex $Fe_2(CO)_6[\mu\text{-}(NH)(NPh)C_6H_4]$ (**3**) (Scheme 1).

According to the X-ray diffraction data, two $Fe(CO)_3$ fragments in complex **3** are held together by the Fe—Fe bond (2.372(2) Å) supplemented with the amide bridges formed by the nitrogen atoms of the *N*-phenyl-*o*-phenylenediamide ligand (Fe—N, 1.977(6)—2.022(6) Å). The reaction was accompanied by oxidation of the iron atoms and reduction of the coordinated *o*-semiquinonediimine ligand and the nickel(II) (to $Ni(CO)_4$) or platinum(II) atoms (platinum black was formed). It should be noted that complex **3** has been isolated previously[1] in the reaction of iron carbonyl with azobenzene. However, the reaction under study afforded complex **3** in higher yield (40% with respect to the ligand).*

Scheme 1



Conditions: *i*. Benzene, refluxing.

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* The crystallographic and geometric parameters of complex **3** correspond to those reported previously.[1]

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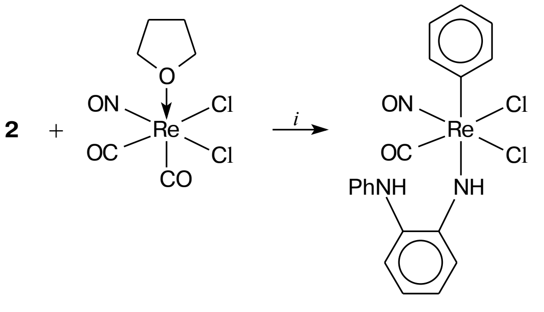
More profound conversions of the coordinated *N*-phenyl-*o*-semiquinonediimine ligand occurred in the reaction of complex **2** with the nitrosyl carbonyl chloride rhenium(I) complex $Re(CO)_2(NO)Cl_2(thf)$ in boiling toluene containing 2—3% of water to form the diamagnetic complex $Re(Ph)[(\sigma\text{-}\eta^1\text{-}o\text{-}(NH)(NHPh)C_6H_4](CO)(NO)Cl_2$ (**4**) in 48% yield:



4

Conditions: *i.* toluene, 2—3% H_2O.

According to the X-ray diffraction data (Fig. 1), the rhenium atom in complex **4** is coordinated by two chlorine atoms (Re—Cl, 2.426(5) and 2.431(5) Å), the nitrosyl group (Re—N, 1.789(17) Å), and the carbonyl group (Re—C, 1.787(17) Å). The environment about the rhenium atom is completed to an octahedron with two atoms occupying axial positions, *viz.*, with the nitrogen atom (Re—N, 2.184(11) Å) involved in the reduced *N*-phenyl-*o*-phenyleneaminoamide ligand and the carbon atom (Re—C, 2.155(11) Å) of the σ-bound phenyl fragment, which was, apparently, formed as a result of the cleavage of the N—Ph bond in the initial coordinated *o*-semiquinonediimine ligand.

It should be noted that no conversions of free *N*-phenyl-*o*-phenylenediamine occurred when it was introduced into the direct reaction with the dimeric carbonyl nitrosyl chloride rhenium complex; instead, only the complex $Re[\eta^1\text{-}(NH_2)(NHPh)C_6H_4](CO)_2(NO)Cl_2$ (**5**) was obtained in high yield (Scheme 2).

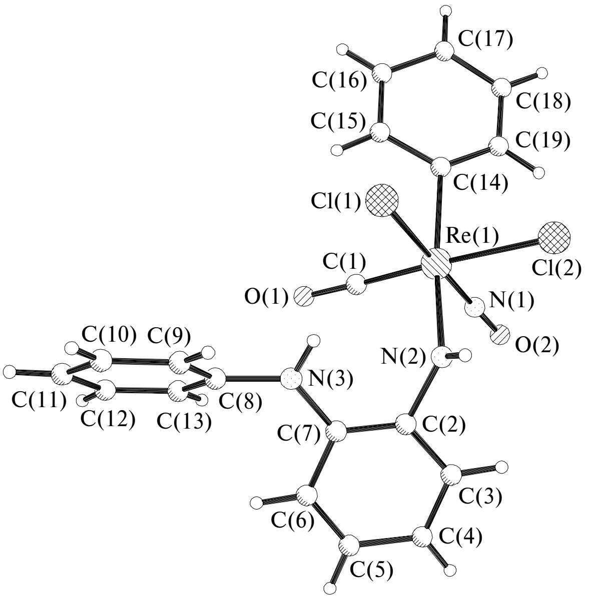
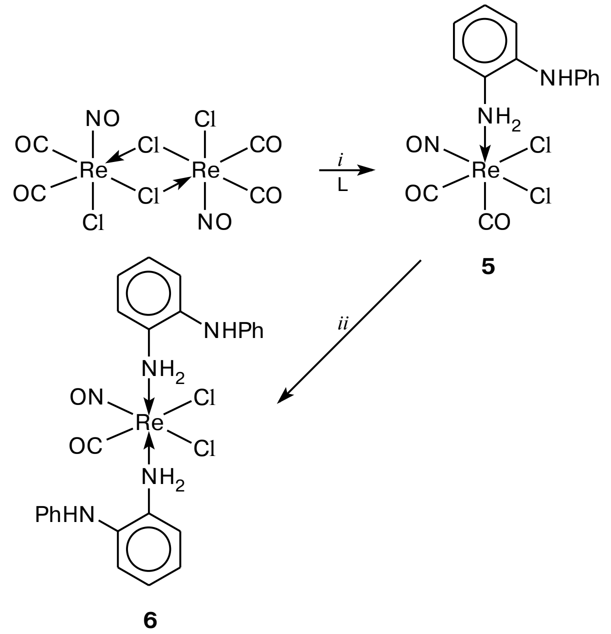


Fig. 1. Structure of complex **4**.

Scheme 2



L = *N*-phenyl-o-phenylenediamine.

Conditions: *i.* toluene, 20 °C; *ii.* toluene, 120 °C.

According to the X-ray diffraction data (Fig. 2), the rhenium atom in complex **5** is coordinated by two chlorine atoms (Re—Cl, 2.399(3) and 2.419(3) Å), the nitrosyl group (Re—N, 1.831(11) Å), two carbonyl groups (Re—C, 1.912(10) and 2.036(13) Å), and the nitrogen atom of the amino group of *N*-phenyl-*o*-phenylenedi-

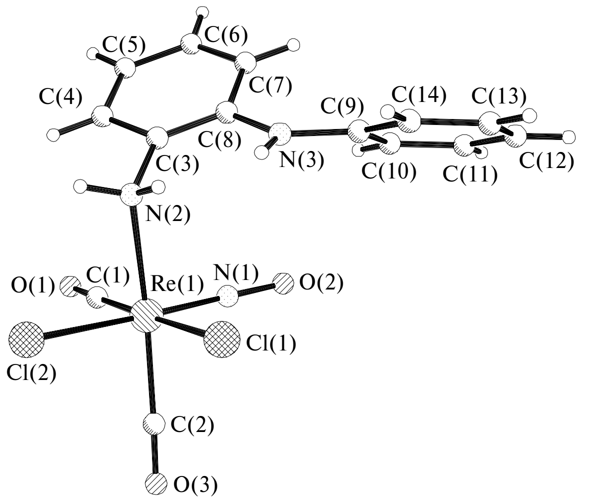


Fig. 2. Structure of complex **5**.

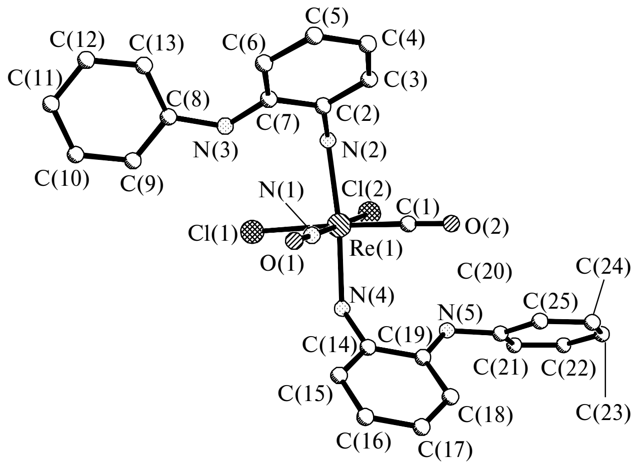


Fig. 3. Structure of complex **6**.

amine (Re—N, 2.204(9) Å). The geometry of the latter is completely identical to that of the free ligand.[2]

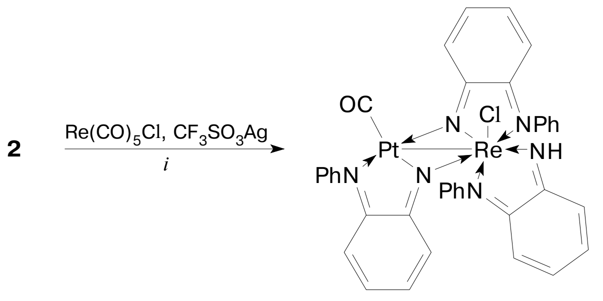
One would expect that heating of complex **5** in toluene in air will lead to elimination of the CO group and to oxidation of the resulting chelate-coordinated ligand by oxygen giving rise to the *o*-semiquinonediimine fragment, analogously to the conversions observed in the syntheses of complexes **1** and **2**.

However, it appeared that refluxing of complex **5** in toluene afforded the disproportionation product of **5**, *viz*., the Re[η^1-$(NH_2)(NHPh)C_6H_4]_2(CO)(NO)Cl_2$ complex (**6**), in low yield.

According to the X-ray diffraction data, the geometry of the Re(NO)(CO)Cl_2 fragment in complex **6** (Fig. 3) is virtually identical to that in complex **5** (Re—Cl, 2.431(2)—2.442(3) Å; Re—N, 1.853(8) Å; and Re—C, 1.850(8) Å). However, the axial positions in the environment about the rhenium atom in complex **6** are occupied by two nitrogen atoms of the amino groups of two *N*-phenyl-*o*-phenylenediamine ligands (Re—N, 2.168(8)—2.188(9) Å).

The heterometallic binuclear (OC)Pt[μ-*N*,*N*-*o*-(N)(NPh)$C_6H_4]_2$ReCl[(NH)(NPh)C_6H_4] complex (**7**) was formed in the reaction of complex **2** with the mononuclear rhenium(I) complex, *viz*., Re(CO)$_5$Cl, which has been preliminarily treated with silver triflate upon UV irradiation in *m*-xylene (80 °C) (Scheme 3).

Scheme 3



7

Conditions: *i*. *hv*, *m*-xylene, 80 °C.

According to the data of X-ray diffraction study of complex **7** (Fig. 4), the platinum and rhenium atoms in the molecule are linked through a direct bond (3.055(1) Å), which is supplemented with two chelate-bridging *N*-phenyl-*o*-quinoneiminoimide ligands (L). The imide nitrogen atoms in these ligands are coordinated to both metal atoms (Pt—N, 2.006(6) and 2.004(6) Å; Re—N, 2.019(5) and 1.894(5) Å; and N=C, 1.339(10) and 1.363(11) Å). The chelate coordination of the ligands to the rhenium and platinum atoms is achieved through

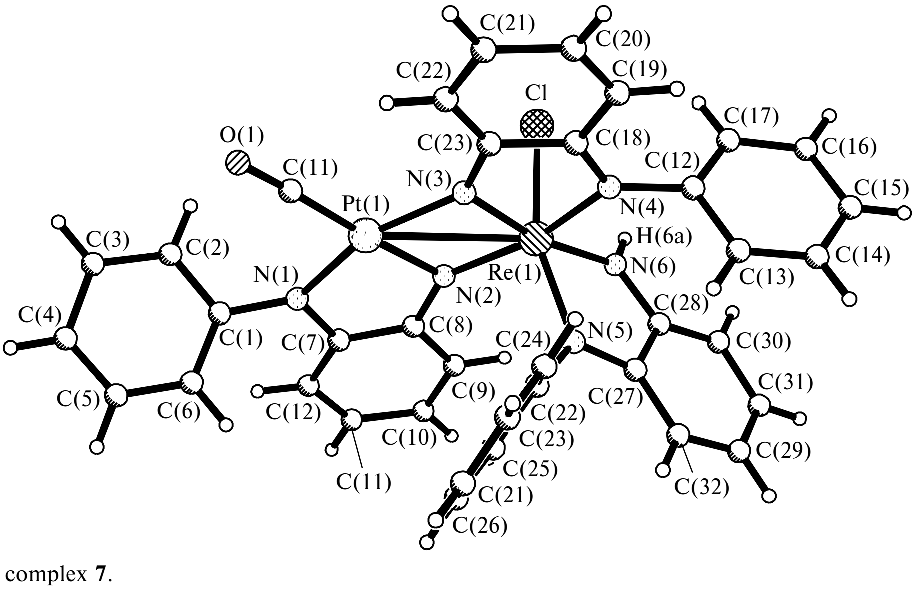


Fig. 4. Structure of complex **7**.

the N atoms of the NPh group (Pt—N, 2.026(8) Å; and Re—N, 2.076(5) Å). In spite of this mode of coordination, both bridging L ligands, like the third *N*-phenyl-*o*-quinonediimine ligand, which is coordinated only to the Re atom (Re—N, 1.997(9) and 2.023(9) Å; N=C, 1.346(11) and 1.359(11) Å; N—H, 0.91(2) Å; the position of the hydrogen atom was located from the Fourier synthesis and refined), have the quinoid structure (N=C 1.336(11) and 1.396(12) Å). As a result, the platinum atom is formally reduced to platinum(I) by adding the CO group (Pt—C, 1.884(9) Å; C—O, 1.148(15) Å; and the Pt—C—O angle is 175.3(11)°), the planar-square ligand environment being retained, whereas the rhenium atom bearing the halide ligand (Re—Cl, 2.344(2) Å) is oxidized to rhenium(II) and has a distorted octahedral environment.

Therefore, isolation of heterometallic complex **7** suggests that heteronuclear derivatives can be formed as intermediates in the reactions of *o*-semiquinonediimine complexes of nickel and platinum with various metal-containing fragments.

Experimental

The complexes were synthesized under an inert atmosphere (Ar) with the use of anhydrous solvents.[3] The starting complexes M[*o*-(NH)(NPh)C_6H_4]$_2$ (M = Ni (**1**) or Pt (**2**)), [Re(CO)$_2$(NO)Cl_2]$_2$, and Re(CO)$_2$(NO)Cl_2(thf) were prepared according to known procedures.[4,5,6] The reagents Fe(CO)$_5$, Re(CO)$_5$Cl, and AgO_3SCF_3 were purchased from Fluka. Column chromatography was carried out with the use of Kiesilgel 60 (Fluka). The IR spectra were recorded on a Specord M80 instrument in KBr pellets.

Reactions of the M[*o*-(NH)(NPh)C_6H_4]$_2$ complexes with Fe(CO)$_5$ (M = Ni or Pt). A mixture of a solution of Pt[*o*-(NH)(NPh)C_6H_4]$_2$ (**2**) (0.92 g, 0.164 mmol) in benzene (30 mL) and Fe(CO)$_5$ (0.2 mL, 1.49 mmol) was irradiated with UV light (a PRK-4 lamp) for 6 h. The resulting bright-red solution was filtered from a black precipitate of metallic platinum and concentrated to dryness at 20 °C (0.1 Torr). Then hexane (5 mL) was added to the solid precipitate, the resulting suspension was applied to a column (5 × 25 cm) with SiO_2, and the red zone was eluted with a 1 : 1 benzene—hexane mixture (50 mL; R_f 0.70). The solution was concentrated to 15 mL at 20 °C (0.1 Torr) and kept at 5 °C for one day. The dark-red crystals that precipitated were separated from the solution by decantation, washed with cold hexane, and dried *in vacuo*. Complex **3** was obtained in a yield of 0.152 g (40%). Found (%): C, 46.2; H, 1.9; N, 5.9. $C_{18}H_{10}Fe_2N_2O_6$. Calculated (%): C, 46.80; H, 2.18; N, 6.06. IR (KBr), ν/cm^{-1}: 3800 w, 3736 w, 3648 w, 3481 w, 3430 w, 2920 m, 2856 m, 2368 w, 2344 w, 2320 w, 2176 w, 1976 w, 1888 w, 1824 w, 1760 w, 1688 w, 1608 s, 1520 s, 1488 s, 1443 w, 1384 m, 1352 w, 1288 s, 1240 s, 1160 m, 1071 w, 1024 m, 952 w, 912 m, 816 m, 760 m, 720 w, 680 m, 632 s, 608 w, 552 m, 512 m, 472 w, 424 w.

The reaction with the use of Ni[*o*-(NH)(NPh)C_6H_4]$_2$ (**1**) as the staring complex performed analogously afforded complex **3** in 20% yield. In the reaction, volatile nickel tetracarbonyl was detected by IR spectroscopy (ν/cm^{-1}: 2045).

Reaction of the Pt[*o*-(NH)(NPh)C_6H_4]$_2$ complex with Re(CO)$_2$(NO)Cl_2(thf). A solution of Re(CO)$_2$(NO)Cl_2(thf) (0.18 g, 0.43 mmol) in anhydrous toluene (10 mL) was added to a solution of Pt[*o*-(NH)(NPh)C_6H_4]$_2$ (0.21 g, 0.37 mmol) in toluene (30 mL) containing 2—3% of water and the reaction mixture was refluxed for 1 h. The resulting green solution was concentrated to 10 mL at 50 °C (0.1 Torr) and kept at 5 °C for one day. The crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried *in vacuo*. (*N*-Phenyl-*o*-phenyleneaminoamide)nitrosylcarbonylphenyl-*cis*-dichlororhenium(III) (**4**) was obtained in a yield of 0.12 g (48%). Found (%): C, 40.2; H, 3.1; N, 6.9. $C_{19}H_{16}Cl_2N_3O_2Re$. Calculated (%): C, 39.66; H, 2.80; N, 7.30.

Reaction of *o*-(NH$_2$)(NHPh)C_6H_4 with [Re(NO)(CO)$_2$$Cl_2$]$_2$. A solution of *o*-(NH$_2$)(NHPh)$C_6H_4$ (0.26 g, 1.40 mmol) in toluene (10 mL) was added to a solution of [Re(NO)(CO)$_2$$Cl_2$]$_2$ (0.43 g, 0.63 mmol) in toluene (60 mL). The reaction mixture was stirred at ~20 °C for 1 h. The resulting dark-brown solution was concentrated to 10 mL at 50 °C (0.1 Torr) and cooled to ~20 °C. The crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried at 20 °C (0.1 Torr). (*N*-Phenyl-*o*-phenylenediamine)nitrosyl-*cis*-dicarbonyl-*cis*-dichlororhenium(I) (**5**) was isolated in a yield of 0.33 g (50%). Found (%): C, 32.2; H, 2.5; N, 7.5. $C_{14}H_{12}Cl_2N_3O_3Re$. Calculated (%): C, 31.89; H, 2.29; N, 7.97. IR (KBr), ν/cm^{-1}: 3722 w, 3364 m, 3191 w, 3142 w, 3031 w, 2108 s, 2044 s, 1778 s, 1721 m, 1716 w, 1684 w, 1662 m, 1596 w, 1556 m, 1540 s, 1520 w, 1504 w, 1164 w, 1084 s, 1050 m, 1015 m, 716 m, 744 s, 692 m, 630 w, 500 w.

Synthesis of bis(*N*-phenyl-*o*-phenylenediamine)nitrosylcarbonyl-*cis*-dichlororhenium(I), Re[η^1-(NH$_2$)(NHPh)C_6H_4]$_2$(CO)(NO)Cl_2 (6). A solution of complex **5** (0.22 g, 0.42 mmol) in toluene (60 mL) was refluxed for 5 h. The reaction mixture was concentrated to 20 mL under a stream of argon and then slowly cooled on an oil bath to ~20 °C. The yellow crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried at 20 °C (0.1 Torr). Complex **6** was obtained in a yield of 0.13 g (45%). Found (%): C, 42.2; H, 3.8; N, 9.5. $C_{25}H_{24}Cl_2N_5O_2Re$. Calculated (%): C, 43.92; H, 3.54; N, 10.24. IR (KBr), ν/cm^{-1}: 3744 w, 3360 m, 3200 w, 3136 w, 2928 w, 2864 w, 2840 w, 2352 m, 2320 w, 2176 w, 2112 m, 2040 m, 1992 s, 1784 m, 1744 s, 1600 s, 1512 m, 1496 s, 1464 m, 1424 w, 1336 m, 1296 m, 1256 w, 1168 s, 1088 w, 1032 w, 888 w, 744 s, 696 s, 488 m.

Synthesis of bis[μ-*N*′,*N*′-η^2-(*N*-phenyl-*o*-benzoquinoneiminoimide)]carbonylplatinum(I)-η^2-(*N*-phenyl-*o*-benzoquinonediimine)chlororhenium(II), (OC)Pt[μ-*N*,*N*-*o*-(N)(NPh)C_6H_4]$_2$ReCl[(NH)(NPh)C_6H_4] (7). A solution of CF_3SO_3Ag (0.25 g, 1 mmol) in *m*-xylene (10 mL) was added to a solution of Re(CO)$_5$Cl (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 **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 solution was 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 SiO_2. 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 one day. The dark-brown crystals that precipitated were separated from the solution by decantation, washed with hexane, and dried in air. Complex **7** was obtained in a yield of 0.28 g (28%). Found (%): C, 45.2; H, 3.3; N, 8.3. $C_{37}H_{28}ClN_6OPtRe$. Calculated (%): C, 44.91; H, 2.85; N, 8.49. IR (KBr), ν/cm^{-1}: 3728 w, 3480 m, 3408 m, 2920 s, 2858 m, 2032 w, 1952 w, 1912 w, 1704 w, 1656 w, 1624 w, 1568 w, 1464 m, 1384 w, 1256 s, 1096 s, 1032 s, 872 w, 808 s, 616 w, 464 w.

Table 1. Crystallographic parameters and details of refinement of complexes **4**—**7**

Parameter	**4**	**5**	**6**	**7**
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.628(5)	9.582(6)	10.287(2)	11.290(3)
b/Å	30.036(15)	10.262(5)	11.378(2)	12.191(3)
c/Å	9.579(5)	11.648(6)	11.717(2)	14.627(4)
α/deg		65.99(4)	111.23(3)	83.98(2)
β/deg	101.69(2)	77.26(4)	91.64(3)	73.69(2)
γ/deg		82.71(4)	107.59(3)	82.67(2)
V/Å^3	2431(2)	1019.5(9)	1203.8(4)	1911.3(10)
Z	4	2	2	2
d_{calc}/g cm^{-3}	1.786	1.839	1.886	1.855
μ/cm^{-1}	5.246	6.242	5.304	6.932
θ-2θ scanning range/deg	2—50	3.9—56.1	3.8—60.1	3—52
Number of independent reflections	4314	4962	6757	7550
Number of reflections with $I > 2\sigma$	2608	3944	3644	2438
R_1	0.053	0.086	0.055	0.031
wR_2	0.068	0.207	0.098	0.052

X-ray diffraction study. The X-ray diffraction data sets were collected according to a standard procedure on a four-circle automated Siemens R3v/m diffractometer (λMo-Kα radiation, λ = 0.71074 Å, T = 22 °C) for complexes **4**, **5**, and **7** and on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, T = 110 °C, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) for complex **6**. The crystallographic parameters and details of the refinement of all structures are given in Table 1.

The structures of all complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. For the structures of **4** and **5**, absorption corrections were applied.[7] The positions of the hydrogen atoms of the phenyl rings were calculated geometrically and refined using the riding model. The hydrogen atoms of the NH and NH_2 fragments were located from difference Fourier syntheses and refined isotropically. All calculations were carried out with the use of the SHELX97 program package.[8] The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

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