Organometallic Chemistry

Spectroscopic and electrochemical properties of mixed-valence Rh^{I}—Rh^{III} complexes with a cyanide bridge

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Electronic spectra and redox potentials of new mixed-valence Rh^{I}—Rh^{III} complexes linked by a cyanide bridge were measured and studied. For these compounds, interaction between rhodium atoms in the molecule is low (a case of "fixed valences"), and no intervalence transition from Rh^{I} to Rh^{III} was observed in the 7000 to 50000 cm^{-1} range. Some of the complexes in the solid state have additional absorption bands in the diffuse reflectance spectra related to the interaction of orbitals (with appropriate symmetry) of Rh(I) fragments of adjacent complex molecules.

Key words: electronic spectroscopy, diffuse reflectance spectra, electrochemistry, mixed-valence complexes, rhodium.

Numerous data on new bi- and polynuclear ruthenium and rhodium complexes containing various bridge ligands have appeared recently. Interest in this type of compounds is caused by the fact that they, on the one hand, have valuable photochemical properties that open wide possibilities for their practical use[1—5] and, on the other hand, study of their electronic structures is of great theoretical interest.

Previously we synthesized homo- and heteronuclear rhodium and ruthenium complexes containing the cyanide bridge and studied their electrochemical and spectral properties.[6—8] In continuation of these studies, we synthesized several dimeric Rh^{I} complexes and new mixed-valence rhodium complexes containing Rh^{I} and Rh^{III} atoms linked by the cyanide bridge.

The purpose of this work is to study the electronic structure of the aforementioned mixed-valence rhodium complexes (**1**—**13**) and to estimate the interaction between the Rh^{I} and Rh^{III} atoms through the cyanide bridge. Electrochemical redox processes of these compunds were studied, and electronic spectra of the complexes in solutions and diffuse reflectance spectra of solid samples were studied.

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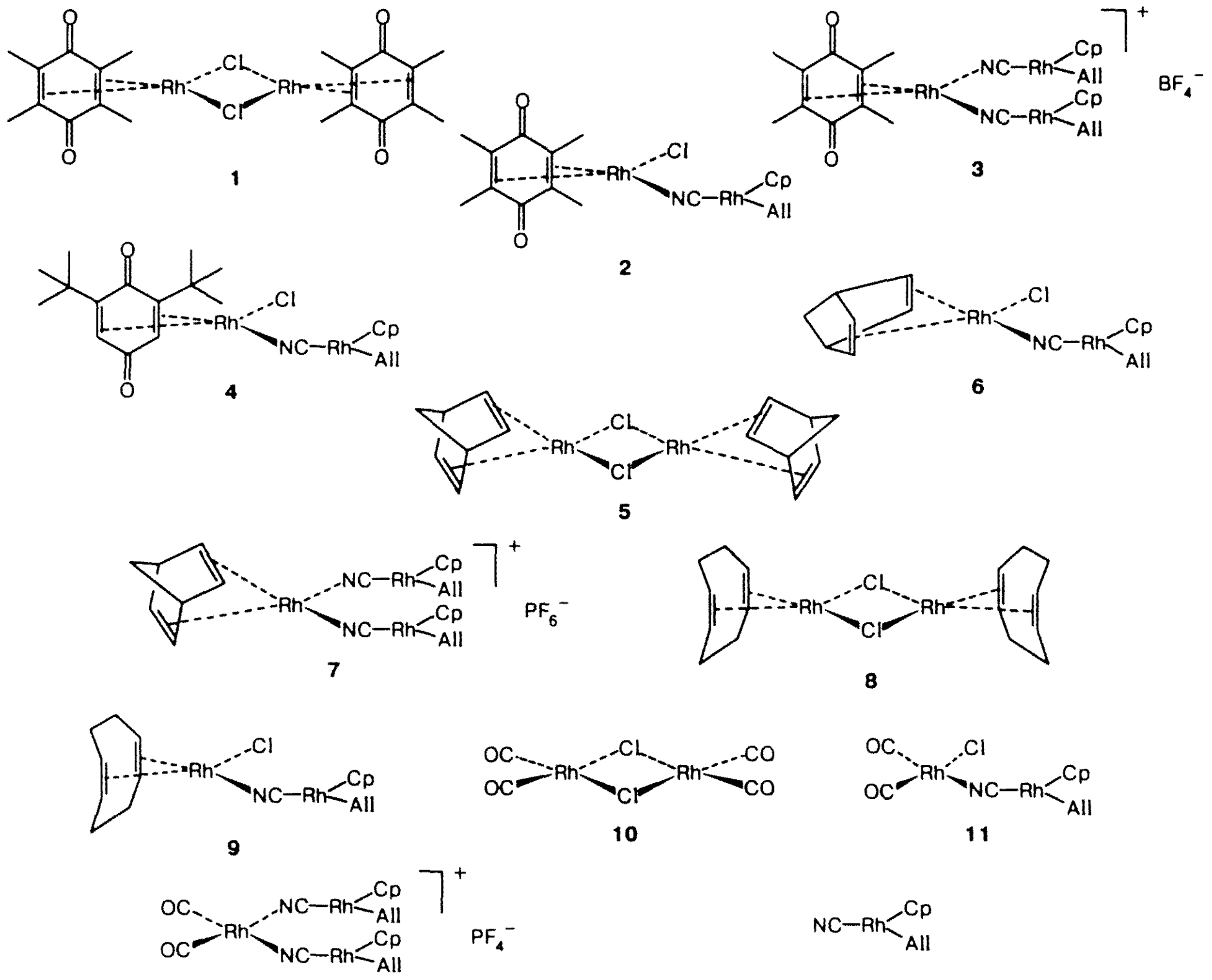

where All is η^3-allyl and Cp is η^5-cyclopentadienyl

Electronic spectra

It seems expedient to begin consideration of the electronic spectra of bi- and trinuclear rhodium complexes from the analysis of the spectra of dimeric Rh^I complexes. The most complete, although somewhat contradictory information on the electronic structure of complex **10** is available. Its electronic,[9] photoelectronic,[10,11] and magnetic circular dichroism[9] spectra were studied. An interesting specific feature of this complex is its dihedral structure with symmetry group C_{2v} in both crystal[12] and solution.[13,14] The "angular" structure is also observed for the $[RhCl(C_2H_4)_2]_2$ complex,[15] while complexes **8** [16] and $[RhCl(PPh_3)_2]_2$ [17] have planar structures with symmetry group D_{2h} (rhodium and chlorine atoms lie in the same plane). It is likely that complex **5** also has a planar structure.

Norman and Gmur showed[18] that the interaction between the rhodium atoms in a molecule **10** is low, and the nonplanar geometry of the complex is due to the interaction of the orbitals, to which 3p-orbitals of the chlorine atoms make the main contribution. The difference in energies of the complexes with D_{2h} symmetry and the complex with C_{2v} symmetry was estimated as several kcal mol^{-1}. Therefore, complexes with bulky ligands have planar structures: the energy gain due to a decrease in symmetry of complexes from the point group D_{2h} to C_{2v} is lower than the energy of mutual repulsion of ligands.

The spectra of solutions of the dimeric Rh^I complexes in methanol contain several charge-transfer bands from the orbitals, to which 4d-orbitals of Rh^I mainly contribute, to the orbitals, which have the π^*-character and are mainly localized in ligands L. The spin-orbital coupling results in an increase in the intensity of singlet-triplet electronic transitions due to a decrease in the intensity of ground singlet-singlet transitions. In the complexes studied, the singlet-singlet transitions are shifted by 2000 to 4000 cm^{-1} to the red range compared to the corresponding singlet-singlet transitions (see

Table 1. Electronic spectroscopy data for rhodium complexes (MeOH, 20 °C)

Complex	Electronic transitions/1000 cm^{-1}					
	of Rh(I) fragment					of Rh(III) fragment
	d_{z^2}(Rh)—π*(L)[a]		d_{yz},d_{xz}(Rh)—π*(L)[a]		π—π*(L)[b]	
	C—T[c]	C—C[d]	C—T[c]	C—C[d]		
1	19.0(sh)	21.7	—	30.4	37.9, 38.9	—
2	19.0(sh)	21.7	—	30.0[e]	37.0	30.0[e], 44.4
3	19.0(sh)	22.0	—	31.0[e]	37.5	31.0[e], 44.8
4	20.0(sh)	24.0(sh)	—	33.8[e]	36.8	33.8[e], 45.3
5	23.8(sh)	26.1, 27.1	33.2(sh)	37.0	44.3	—
6	—	25.8	—	37.0	45.0[e]	32.0, 45.0[e]
7	—	26.0(sh)	—	37.0	45.0[e]	32.0, 45.0[e]
8	25.6(sh)	28.7	32.5(sh)	37.5(sh)	43.5	—
9	—	26.0(sh)	—	37.0	44.6[e]	31.5, 44.6[e]
10	27.8(sh)	30.7	—	38.0	>50.0	—
11	—	31.0[d]	—	38.0	>50.0	31.0[e], 44.9
12	—	32.0[d]	—	38.2	>50.0	32.0[e], 44.9
13	—	—	—	—	—	32.0, 44.4

[a] The direction of the z axis was chosen as perpendicular to the plane of Rh(I)L_4; the x and y axes are arranged between the ligands in Rh(I)L_4. [b] Intraligand π—π*(L)-transition. [c] Spin singlet-triplet transition. [d] Spin singlet-singlet transition. [e] These bands overlap in the electronic spectrum.

Table 1). The bands in Table 1 were assigned using the data[9—11] applied to the experimental results obtained.

Intense absorption band caused by the intraligand π—π*(L) transition are observed for quinone and diene complexes. For free tetramethylquinone, 2,6-di-*tert*-butylquinone, and norbornadiene in methanol, the transition is observed at 37700 and 38600, 39400 and 43000 cm^{-1}. For carbonyl complexes **10**, **11**, and **12**, this transition should be observed in the far-UV region, and, therefore, it is not observed in the absorption spectra at frequencies lower than 50000 cm^{-1}.

The absorption spectra of the solutions of the bi- and trinuclear complexes studied contain broadened absorption bands, which are observed for the corresponding dimers and RhCpAlICN (**13**) (see Table 1).

Appearance of the band of the intervalence transition from rhodium(I) to rhodium(III) might be observed in the electronic spectra of bi- and trinuclear bridged complexes, as in many similar systems.[19] However, we failed to observe such an electronic transition in the range from 7000 to 50000 cm^{-1}. According to the Robin—Day[19] classification, the intervalence transition may be absent in electronic spectra of mixed-valence complexes, if the charge delocalization between intervalence atoms is very low, which likely takes place in the case of the complexes under study despite the nonsaturated CN bond between two different oxidation states.

It is of interest to compare electronic spectra of the complexes studied in solution and in the solid phase (diffuse reflectance spectra (DRS) and absorption spectra of solid films). It is known[20—22] for some Rh^{I} complexes that rhodium atoms of adjacent molecules with the d^8 electronic configuration and planar-square coordination of ligands can interact to form dimers, trimers (in solution), or chains (in the solid state) linking rhodium atoms. This interaction results in additional absorption in the range from 6000 to 25000 cm^{-1} and a difference in color of solutions and solid samples. For the rhodium complexes studied, no additional low-frequency absorption bands in DRS are observed in the 13000 to 21000 cm^{-1} range for the diene complexes compared to the spectra of solutions (Fig. 1). In the series of quinone-containing complexes, the introduction of one Rh^{III} fragment into the molecule (complex **4**) results in the appearance of a low-frequency band at 16500 cm^{-1} in DRS, and DRS of trinuclear complex **3** and dimeric complex **1** are almost identical and contain no new bands in the visible spectral range (Fig. 2). The

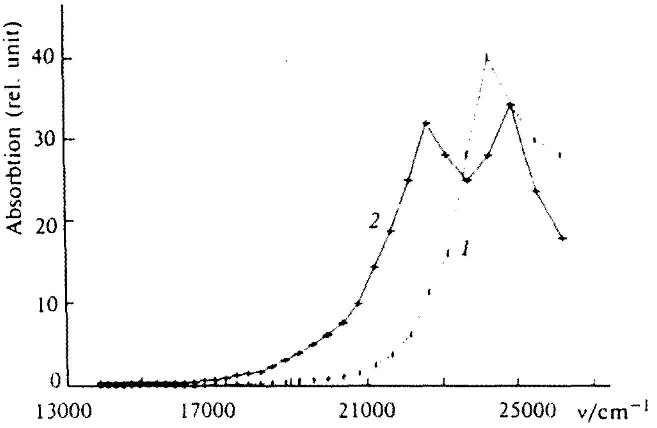

Fig. 1. Diffuse reflectance spectra of complexes **5** (*1*) and **8** (*2*).

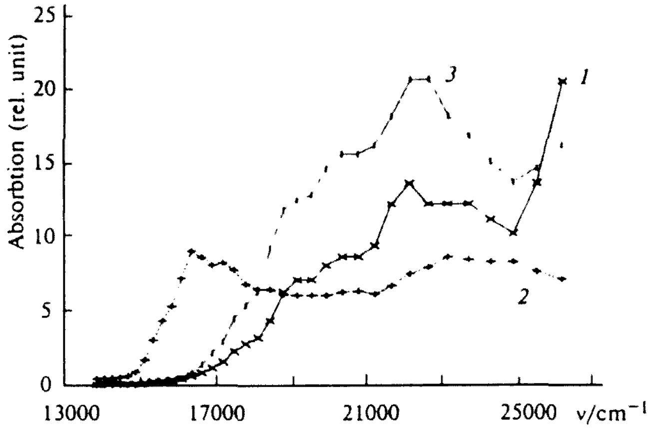

Fig. 2. Diffuse reflectance spectra of quinone-containing complexes **1** (*1*), **4** (*2*), and **3** (*3*).

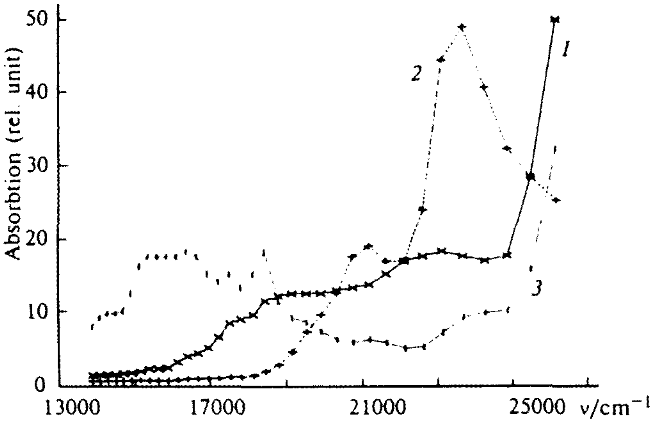

Fig. 3. Diffuse reflectance spectra of carbonyl complexes **10** (*1*), **11** (*2*), and **12** (*3*).

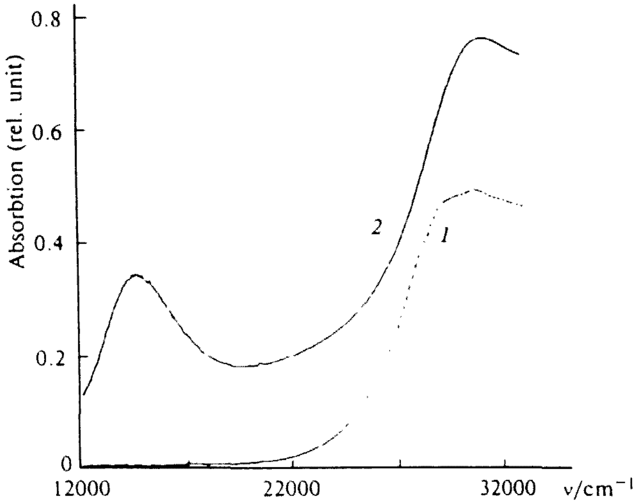

Fig. 4. Absorption spectra of a solution of complex **12** in methanol (*1*) and a solid film of complex **12** (*2*).

change in color on going from the solid substance to solution is most noticeable for carbonyl complexes. The red (**10**), yellow-orange (**11**), and blue (**12**) complexes dissolve to form yellow solutions with null absorption in the visible range (Figs. 3 and 4). It is likely that additional bands appear in DRS due to the interaction of electronic orbitals of adjacent molecules (first of all between d_{z^2}- and p_z-orbitals of Rh^I atoms of adjacent molecules[20,21]). The Rh^{III} complexes, in which the metal atom has the d^6 electronic configuration, do not allow the interaction of Rh^{III} with rhodium atoms of other molecules due to their coordination saturation. Thus, the appearance of new low-frequency bands in DRS of mixed-valence complexes can be related only to the interaction of orbitals of Rh^I atoms with appropriate symmetry; however, the extent of interaction depends on the structure of the complexes. Bulky ligands of the cyclooctadiene or norbornadiene type linked to Rh^I prevent $Rh^I—Rh^I$ contacts, and, therefore, no new low-frequency absorption bands are observed. On the other hand, the Rh^I—ligand interaction should also exert some effect on the $Rh^I—Rh^I$ interaction.

Electrochemical oxidation and reduction of bi- and trinuclear rhodium complexes

Electrochemical properties of mixed-valence and dimeric Rh^I complexes were studied using rotating and stationary platinum electrodes in acetonitrile with 0.05 *M* Bu_4NBF_4 as a supporting electrolyte. It turned out that all of them are rather readily oxidized and reduced, the electrochemical processes occur stepwise, and several waves can be observed in voltammograms. The potentials of the oxidation and reduction waves registered are presented in Table 2. In several cases, strong passivation of the electrode by the products of the electrode reaction was observed, and attempts to record current-voltage curves in the classic regime on a rotating Pt electrode with potential scanning of 20 mV s^{-1} were unsuccessful. Therefore, the potentials of the peaks (E_p) of the cyclic voltammograms with fast potential scanning are presented in Table 2 instead of potentials of half-waves ($E_{1/2}$). As follows from the data of cyclic voltammetry, all compounds studied are oxidized and reduced irreversibly, and hence, the electron transfer is followed by cleavage of any bond.

Oxidation. As can be seen from Table 2, free quinones are not oxidized in the potential range studied. Comparison of the oxidation potentials of compounds **1** and **2**, **5** and **6**, and **8** and **9** testifies that the $NCRh^{III}CpAll$ fragment linked by the cyanide bridge is accepting relative to the Rh^I fragment. Since the observed oxidation processes of these compounds are two-electron, it can be assumed that the oxidation degree of rhodium changes upon oxidation: $Rh^I \rightarrow Rh^{III}$. Compari-

Table 2. Electrochemical oxidation (E^{Ox}) and reduction (E^{Red}) potentials of rhodium complexes (CH_3CN, Pt, 0.05 *M* Bu_4NBF_4, Ag/AgCl, 20 °C, 200 mV s^{-1})

Complex	E^{Ox}/V	$-E^{Red}/V$
1	1.12, 2.18	0.85, 1.30
2	1.16, 1.71, 2.03	0.70, 0.97, 1.35
3	1.60	0.63, 1.18
4	1.28	0.59, 0.95, 1.35
5	0.70, 1.11, 1.87	1.88, 2.10
6	0.81, 1.27, 1.42	1.71, 1.94
7	1.94, 2.42	1.75, 1.94
8	0.68	1.75, 2.18
9	0.87, 1.71	1.58, 1.93
10[a]	1.79, 2.40	1.65, 2.60
11	1.83	2.08
12	1.80, 2.35	0.95, 2.14
13	1.64	—
TMQ[b]	—	0.83
DBQ[c]	—	0.81

[a] In CH_3CN, complex **10** transforms into $(CO)_2RhCl(NCCH_3)$.[9] [b] Tetramethylquinone ($C_{10}H_8O_2$). [c] 2,6-Di-*tert*-butylquinone ($C_{14}H_{20}O_2$).

son of E^{Ox} of compounds **2** and **4** testifies that 2,6-di-*tert*-butylquinone is a somewhat stronger acceptor than duroquinone; however, the oxidation involves the Rh^{I} fragment in this case as well. In the case of trinuclear cationic complexes, the situation is less unambiguous. The oxidation can occur to both the cationic Rh^{I} fragment and the Rh^{III} fragment linked with it. Under the assumption that the oxidation occurs to Rh^{I}, the introduction of one more acceptor group NCRhCpAll should result in the shift of E^{Ox} of trinuclear complexes towards more positive potentials compared to dimeric and binuclear mixed-valence complexes, which is observed in fact. Complex **13** is oxidized at +1.64 V. The conclusion that the complexes are oxidized at Rh^{I} agrees with the data of electronic spectroscopy: the first absorption band corresponds to the electron transfer from the d_{z^2}-orbital of Rh^{I} (see Table 1).

Reduction. As seen from Table 2, quinone-containing complexes are reduced easier than the other complexes. Comparison of the potentials of the first reduction waves of complexes **1**, **2**, **3**, and **4** as well as free duroquinone and di-*tert*-butylquinone allows one to draw the conclusion that the reduction of these compounds involves the orbitals, which are mainly localized on quinone; this agrees with the fact that the $d_{z^2}(Rh)-\pi^*(L)$-transition is the first electronic transition in the absorption spectrum (see Table 1). Binuclear complexes containing octadiene, norbornadiene, and carbonyl ligands are reduced by approximately 1 V more difficultly than quinone-containing complexes. In this case, the reduction likely occurs to the Rh^{I} atom (presumably, to the unoccupied orbital of the $d_{x^2-y^2}$ character), but not to the ligand or Rh^{III} atom. Complex **13** is reduced very difficultly (−1.7 V on mercury), and its reduction on platinum was not observed. Coordination with the Rh^{I} fragment should not result in facilitation of the reduction of Rh^{III}. If the direction of scanning is changed to the anodic one after passing the reduction peak of binuclear complexes, the oxidation peak of chloride ions can be observed, whose formation testifies that the electron transfer to Rh^{I} is followed by the cleavage of the Rh—Cl bond. It is likely that the bridge Rh—N bond does not cleave.

Experimental

Electronic spectra of solutions of complexes in methanol were recorded on Specord UV-VIS, Specord NIR, and Hewlett Packard 8452A spectrophotometers in quartz cells with optical lengths of 1 and 10 mm. To obtain spectra of solid films, solutions of complexes in methanol were applied on a quartz plate, and the solvent was left to evaporate. Diffuse reflectance spectra of solid samples were obtained on a Spektroton instrument. The reflection coefficient (*R*) was recalculated to the *F* value proportional to the absorption coefficient by the formula $F = 0.5(1-R)^2/R$.[23] Electrochemical measurements were performed with an SVA-1B-M voltammetric system on stationary and rotating platinum electrodes against a supporting electrolyte of 0.05 *M* Bu_4NBF_4 in anhydrous MeCN at 20 °C. Platinum served as an auxiliary electrode, and a saturated Ag/AgCl electrode was used as a reference electrode. Dioxygen was removed from the cell with a flow of dry argon. Voltammetric curves were recorded by cyclic voltammetry at rates of voltage scanning of 50, 100, 200, and 500 mV s^{-1}. The rotation velocity of the electrode was varied from 480 to 3450 rpm. Ohmic losses were taken into account. Acetonitrile ("pure" grade) was purified by stirring over CaH_2 for 24 h, then the latter was filtered off, KNO_3 (5 g) and concentrated H_2SO_4 (10 mL) were added, and the mixture obtained was refluxed for 3 h and distilled. Then MeCN was refluxed over P_2O_5 for 2 h and distilled, collecting the fraction with b.p. 81—82 °C.

The initial carbonyl, diene, quinone, and allyl complexes were synthesized by the procedures described: **1**,[24] **5**,[25] **8**,[26] **10**,[27] $[(DBQ)RhCl]_2$ (DBQ is 2,6-di-*tert*-butylbenzoquinone),[28] and **13**.[29]

μ-Cyano-η^3-allyl-η^5-cyclopentadienylrhodium-η^4-2,3,4,5-tetramethyl-1,4-benzoquinonechlororhodium (2). Compound **13** (0.30 g, 1.28 mmol) was added to compound **1** (0.39 g, 1.29 mmol) in 60 mL of acetone in an argon atmosphere at ~20 °C. A red-orange precipitate was formed in 3 to 5 min. The mixture was stirred for 4 to 6 h. The precipitate (0.28 g) was filtered off. An additional amount of the complex (0.34 g) was extracted from the mother liquor, which was concentrated *in vacuo* until a small volume was achieved, hexane was added, and the complex was filtered off. The total yield of the complex was 89.8 %. The compound was purified by double crystallization from an acetone—hexane (3 : 1) mixture. Red crystals with m.p. 168—170 °C (decomp.) were obtained. Found (%): C, 42.32; H, 4.08; N, 2.53. $C_{19}H_{20}ClNO_2Rh_2$. Calculated (%): C, 42.60; H, 3.76; N, 2.62.

Bis(μ-cyano-η^3-allyl-η^5-cyclopentadienylrhodium)-η^4-2,3,4,5-tetramethyl-1,4-benzoquinonerhodium tetrafluoroborate (3). A powder of $AgBF_4$ (0.18 g, 0.92 mmol) was added to a solution of compound **2** (0.40 g, 0.75 mmol) in acetone (100 mL) in an argon atmosphere at ~20 °C. A white precipitate of AgCl was formed. The mixture was stirred for

4 h. Then compound **13** (0.18 g, 0.77 mmol) was added to the reaction mixture, which was stirred for 2 h. The mixture was let to stay for 12 h, and the precipitate of AgCl was filtered off. A red solution was concentrated *in vacuo* until a small volume was achieved, and hexane was added. A red precipitate formed was filtered off. The compound was purified by double reprecipitation with hexane from dilute acetone solutions. The yield of red crystals with m.p. 232—234 °C (decomp.) was 0.55 g (89.4 %). Found (%): C, 40.87; H, 3.79; N, 3.27. $C_{28}H_{32}BF_4N_2O_2Rh_3$. Calculated (%): C, 40.81; H, 3.91; N, 3.40.

μ-Cyano-η^3-allyl-η^5-cyclopentadienylrhodium-η^4-2,6-di-*tert*-butyl-1,4-benzoquinonechlororhodium (4). The complex was obtained similarly to complex **2** from [(DBQ)RhCl]$_2$ (0.30 g, 0.84 mmol) and compound **13** (0.2 g, 0.85 mmol). The yield of red crystals with a decomposition temperature of 178—185 °C was 72.4 %. Found (%): C, 46.10; H, 5.11; N, 2.23. $C_{23}H_{30}ClNO_2Rh_2$. Calculated (%): C, 46.52; H, 5.09; N, 2.36.

μ-Cyano-η^3-allyl-η^5-cyclopentadienylrhodium-η^4-norborna-2,5-dienechlororhodium (6). This complex was obtained similarly to complex **2** from compound **5** (0.40 g, 0.87 mmol) and compound **13** (0.41 g, 1.74 mmol) in 200 mL of acetone. The yield of yellow crystals with a decomposition temperature of 140—150 °C was 0.7 g (86.6 %). Found (%): C, 41.46; H, 4.07; N, 2.85. $C_{16}H_{18}ClNRh_2$. Calculated (%): C, 41.27; H, 3.90; N, 3.01.

Bis(μ-cyano-η^3-allyl-η^5-cyclopentadienylrhodium)-η^4-norborna-2,5-dienerhodium hexafluorophosphate (7). This complex was obtained similarly to complex **3** from compound **6** (0.30 g, 0.64 mmol), $AgBF_4$ (0.14 g, 0.72 mmol), and compound **13** (0.15 g, 0.64 mmol). The complex was isolated by precipitation from an aqueous solution by the action of a concentrated aqueous solution of NH_4PF_6. The yield of white solid with a decomposition temperature of 145—155 °C was 0.37 g (71.2). Found (%): C, 36.32; H, 3.39; N, 3.23. $C_{25}H_{28}F_6N_2PRh_3$. Calculated (%): C, 37.05; H, 3.48; N, 3.46.

μ-Cyano-η^3-allyl-η^5-cyclopentadienylrhodium-η^4-cyclooctadi-1,5-enechlororhodium (9). The complex was obtained similarly to complex **2** from compound **8** (0.30 g, 0.61 mmol) and compound **13** (0.29 g, 1.23 mmol). The yield was 0.55 g (93.9 %). Yellow crystals, m.p. 155—157 °C (decomp.). Found (%): C, 43.03; H, 4.74; N, 2.72; Rh, 42.23. $C_{17}H_{22}ClNRh_2$. Calculated (%): C, 42.39; H, 4.60; N, 2.91; Rh, 42.73.

μ-Cyano-η^3-allyl-η^5-cyclopentadienylrhodiumdicarbonylchlororhodium (11). Compound **13** (0.40 g, 1.7 mmol) was rapidly added to a solution of compound **10** (0.33 g, 0.85 mmol) in 70 mL of acetone in an argon atmosphere at −20 °C. The mixture was stirred for 15 min and filtered. The complex was precipitated by addition of heptane followed by slow evaporation of acetone *in vacuo*. The complex was purified by reprecipitation with heptane from an acetone solution. The yield of orange-yellow crystals with a decomposition temperature of 125—135 °C was 0.59 g (80.7 %). Found (%): C, 30.83; H, 1.83; N, 2.95. $C_{11}H_{10}ClNO_2Rh_2$. Calculated (%): C, 30.76; H, 2.35; N, 3.26.

Bis(μ-cyano-η^3-allyl-η^5-cyclopentadienylrhodium)-dicarbonylrhodium tetrafluoroborate (12). A solution of $AgBF_4$ (0.15 g, 0.77 mmol) in acetone was rapidly added to a solution of compound **11** (0.30 g, 0.70 mmol) in 60 mL of acetone in an argon atmosphere at −20 °C, and a white precipitate of AgCl was immediately formed. Compound **13** (0.17 g, 0.72 mmol) was rapidly added to the reaction mixture, which was stirred for 20 min. The mixture was filtered in an argon atmosphere, and the yellow-green solution obtained was evaporated *in vacuo* to dryness. A blue residue was dissolved in CH_2Cl_2 and filtered off. The complex was precipitated by addition of heptane. The yield of blue solid with m.p. 135—136 °C was 0.44 g (88 %). Found (%): C, 33.37; H, 3.10; B, 1.65. $C_{20}H_{20}BF_4N_2O_2$. Calculated (%): C, 33.55; H, 2.82; B, 1.51.

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