Synthesis and investigation of mono- and binuclear cyano-bridged complexes of rhodium, ruthenium, and palladium

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Binuclear Rh^{III} and Ru^{II} complexes of the $[M^1—CN—M^2]^+BF_4^-$ (M^1 and/or M^2 are $(\eta^5\text{-}Cp)(\eta^3\text{-}C_3H_5)Rh$ and $(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)Ru$) type, heteronuclear organometallic compound $(\eta^5\text{-}Cp)(\eta^3\text{-}C_3H_5)RhCNPd(\eta^3\text{-}C_3H_5)Cl$, and mononuclear Rh^{III} and Ru^{II} complexes $[(\eta^3\text{-}C_3H_5)LM(MeCN)]^+BF_4^-$ (M = Rh, L = η^5-Cp; M = Ru, L = $\eta^6\text{-}C_6H_6$) were synthesized. An electrochemical study of these compounds in solutions demonstrates that the bond between the bridged CN ligand and the metal atoms is rather strong, and there is no dissociation into mononuclear fragments in solutions. The kinetics of the reaction of $[(\eta^5\text{-}Cp)(\eta^3\text{-}C_3H_5)Rh(MeCN)]^+BF_4^-$ with halide ions was studied by electrochemical methods. The ligand exchange proceeds by a bimolecular dissociative-exchange mechanism.

Key words: palladium, rhodium, ruthenium, binuclear complexes, synthesis; cyclopentadienyl, arenes, allyl, cyano-bridged ligands; electrochemistry; ^1H NMR spectra.

Previously,[1,2] the results of studies on electrochemical and some spectral properties of new homo- and heterobinuclear cationic rhodium and ruthenium complexes, containing a cyanide bridge of the $[M^1—CN—M^2]^+BF_4^-$ type (where M^1 and/or M^2 = $(\eta^5\text{-}Cp)(\eta^3\text{-}C_3H_5)Rh$ and $(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)Ru$); of the neutral bridged complex $(\eta^5\text{-}Cp)(\eta^3\text{-}C_3H_5)RhCNPd(\eta^3\text{-}C_3H_5)Cl$, containing rhodium and palladium; and of mononuclear compounds of the $[(\eta^3\text{-}C_3H_5)LM(MeCN)]^+BF_4^-$ and $(\eta^3\text{-}C_3H_5)LMCl$ types (where M = Rh, L = $\eta^5\text{-}C_5H_5$; M = Ru, L = $\eta^6\text{-}C_6H_6$), being the precursors of binuclear complexes, have been reported. It was shown that the cyanide bridge is involved in distribution of the positive charge along the atomic chain $(M^1—CN—M^2)^+$. As a result, both metal atoms in the binuclear compound have a partial positive charge. Its value is determined by orbital properties of each atom, thus the sites of localization of electronic changes in chemical and electrochemical reactions are not so obvious.

This work deals with synthesis of the above complexes and electrochemical studies on their dissociation and ligand exchange reactions.

The binuclear cyano-bridged cationic complexes of transition metals are usually synthesized by the reaction of mononuclear cyanide complexes of the metals with the corresponding chlorides or bromides in the presence of NH_4PF_6, $TlPF_6$, or other salts with the noncoordinating anions. The binuclear Mn complexes (see Ref. 3), as well as homo- and heterobinuclear complexes containing the Ru and Fe (see Ref. 4) or Fe and Mn (see Ref. 5) atoms, were synthesized by this method. The studied homo- and heterobinuclear cyano-bridged Ru and Rh complexes were synthesized[6] from mononuclear chlorides $(\eta^3\text{-}C_3H_5)MLCl$ (**1, 2**) and the corresponding cyanides $(\eta^3\text{-}C_3H_5)MLCN$ (**3, 4**) in the presence of $AgBF_4$ (Scheme 1). The reaction was carried out in such a way that under the action of $AgBF_4$ in acetone the initial chloride was transformed primarily into the cationic complex $[(\eta^3\text{-}C_3H_5)ML(Me_2CO)]^+BF_4^-$, which was mixed *in situ* with the corresponding cyano derivative to form binuclear cyano-bridged compounds (**5—8**).

The reactions were controlled by TLC (on Silufol). Usually, the first stage, *i.e.*, the formation of the mononuclear cationic complex, was completed after 3—4 h, and the second was completed in 4—10 h. The reaction products, *i.e.*, binuclear cyano-bridged compounds **5—8**, are crystalline yellow substances, quite stable in air.

In the reaction of η^5-cyclopentadienyl-η^3-allylrhodium cyanide, possessing a nucleophilic character, with bis(η^3-allylpalladium chloride) chloride-bridged bonds are easily cleaved, and neutral cyano-bridged complex **9** containing Rh and Pd is formed (Scheme 2).

Mononuclear cationic complexes Ru and Rh with acetonitrile (**10** and **11**, respectively) were prepared by the reaction of nucleophilic substitution of the Cl ligand by MeCN in the presence of $AgBF_4$ (Scheme 3).

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Scheme 1

$$(\eta^3\text{-}C_3H_5)L^1M^1Cl + AgBF_4 \xrightarrow[25\ ^\circ C,\ Ar]{Me_2CO} [(\eta^3\text{-}C_3H_5)L^1M^1(Me_2CO)]^+BF_4^- + AgCl$$

1, 2

1: $M^1 = Ru$, $L^1 = \eta^6\text{-}C_6H_6$

2: $M^1 = Rh$, $L^1 = \eta^5\text{-}Cp$

$$(\eta^3\text{-}C_3H_5)L^2M^2CN + [(\eta^3\text{-}C_3H_5)L^1M^1(Me_2CO)]^+BF_4^- \longrightarrow$$

3, 4

$$\longrightarrow [(\eta^3\text{-}C_3H_5)L^1M^1\text{—}NC\text{—}M^2L^2(\eta^3\text{-}C_3H_5)]^+BF_4^-$$

5—8

3: $M^2 = Ru$, $L^2 = \eta^6\text{-}C_6H_6$

4: $M^2 = Rh$, $L^2 = \eta^5\text{-}Cp$

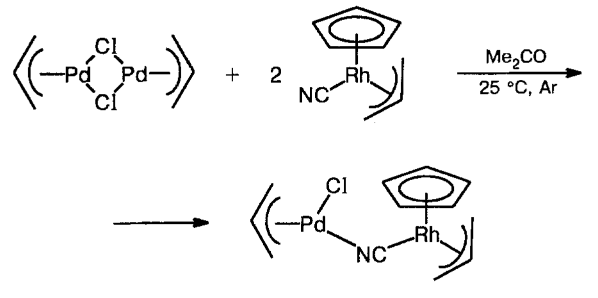
5: $M^1 = M^2 = Ru$, $L^1 = L^2 = \eta^6\text{-}C_6H_6$

6: $M^1 = M^2 = Rh$, $L^1 = L^2 = \eta^5\text{-}Cp$

7: $M^1 = Ru$, $L^1 = \eta^6\text{-}C_6H_6$; $M^2 = Rh$, $L^2 = \eta^5\text{-}Cp$

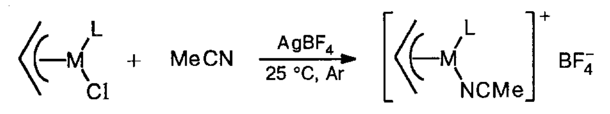
8: $M^1 = Rh$, $L^1 = \eta^5\text{-}Cp$; $M^2 = Ru$, $L^2 = \eta^6\text{-}C_6H_6$

Scheme 2



9

Scheme 3



10, 11

10: M = Ru, L = $\eta^6\text{-}C_6H_6$

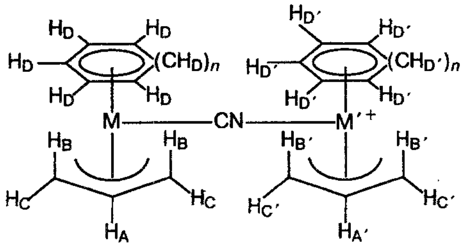
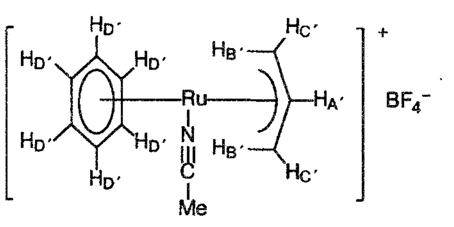
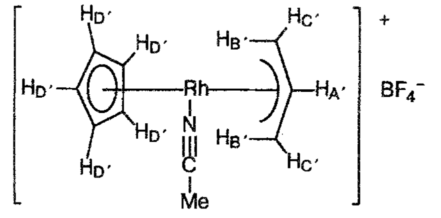
11: M = Rh, L = $\eta^5\text{-}Cp$

All synthesized compounds were characterized by elemental analysis data and IR, UV,[2] and ^1H NMR spectra. The ^1H NMR spectral data for six cationic bi- and mononuclear complexes are presented in Table 1. It is interesting to compare the chemical shifts of protons of the allyl ligand (H_A at position 2; H_B are terminal protons at the *anti*-position in relation to H_A; H_C are terminal protons in *syn*-position), in the first place, for metals of different natures and, then, for metals possessing different formal charges (0 or ±1). In cationic mononuclear complexes **10** and **11** (see Table 1), during the transition from Ru to Rh, a downfield shift of all signals of the allyl protons is observed (0.69, 0.73, and 0.55 ppm for H_A, H_B, and H_C, respectively). This phenomenon is apparently related to the larger charge transfer from the allyl to the metal in the case of Rh complexes. A similar, but not so large downfield shift (0.03 ppm) is observed also for protons of the MeCN ligand. The assignment of signals of the allyl protons in mixed ruthenium-rhodium complexes **7** and **8** was rather simple due to the additional doublet splitting of ligands connected to Rh; the splitting resulted from spin coupling of the ^{103}Rh and ^1H nuclei. In complex **8** the proton signals of the allyl ligand at Rh^+ also shifted downfield in relation to those of the ligand connected to Ru^0, while the change of chemical shifts ($\Delta\delta = 0.59$, 0.70, and 1.14 ppm for H_A, H_B, and H_C, respectively) for H_A and H_B are smaller, and for H_C is greater, than those observed for mononuclear complexes **10** and **11**.

In complex **7**, the signals of H_A and H_B protons of the allyl ligand at Rh^0 are also located in a lower field than the signals of the corresponding protons of the ligand at Ru^+ ($\Delta\delta = 0.65$ and 0.45 for H_A and H_B, respectively); however, the signal of the H_C proton of the Rh ligand is observed in an upper field ($\Delta\delta = 0.08$). Therefore, the chemical shifts of the allyl protons are both determined by the nature of the metal and its formal charge.

In the case of homobinuclear compounds **5** and **6**, the assignment was carried out by assuming that the proton signals of ligands at the cationic center must be in a lower field than the signals of ligands at the neutral center. For complex **5**, the $\Delta\delta$ values are 0.07, 0.12, and

Table 1. ^{1}H NMR spectral parameters of binuclear cyano-bridged Ru^{II} and Rh^{III} complexes

Assignment	δ	^3J /Hz*	$J_{^{103}Rh-^1H}$ /Hz
			
5—8**			
[Ru—CN—Ru]$^+$BF$_4^-$ (**5**)			
H_A	4.372 (tt, 1 H)	11.1 (H_AH_B); 6.9 (H_AH_C)	
H_B	1.528 (d, 2 H)	11.1 (H_AH_B)	
H_C	3.384 (d, 2 H)	6.9 (H_AH_C)	
H_D	5.789 (s, 6 H)	—	
$H_{A'}$	4.440 (tt, 1 H)	11.0 ($H_{A'}H_{B'}$); 6.8 ($H_{A'}H_{C'}$)	
$H_{B'}$	1.647 (d, 2 H)	11.3 ($H_{A'}H_{B'}$)	
$H_{C'}$	4.018 (d, 2 H)	6.8 ($H_{A'}H_{C'}$)	
$H_{D'}$	5.967 (s, 6 H)	—	
[Rh—CN—Rh]$^+$BF$_4^-$ (**6**)			
H_A	5.094 (ttd, 1 H)	11.4 (H_AH_B); 6.8 (H_AH_C)	1.2
H_B	2.272 (ddt, 2 H)	11.4 (H_AH_B)	1.4
H_C	4.015 (ddt, 2 H)	6.8 (H_AH_C)	1.3
H_D	5.665 (d, 5 H)	—	0.8
$H_{A'}$	5.084 (tt, 1 H)	11.1 ($H_{A'}H_{B'}$); 6.8 ($H_{A'}H_{C'}$)	
$H_{B'}$	2.407 (d, 2 H)	11.1 ($H_{A'}H_{B'}$)	≤0.7
$H_{C'}$	4.599 (dd, 2 H)	6.8 ($H_{A'}H_{C'}$)	0.8
$H_{D'}$	5.705 (d, 5 H)		0.7
[Rh—CN—Ru]$^+$BF$_4^-$ (**7**)			
H_A	5.058 (ttd, 1 H)	11.4 (H_AH_B); 6.9 (H_AH_C)	1.4
H_B	2.183 (d, 2 H)	11.4 (H_AH_B)	1.1
H_C	3.982 (dt, 2 H)	6.9 (H_AH_C)	1.1
H_D	5.673 (d, 5 H)	—	0.4
$H_{A'}$	4.407 (tt, 1 H)	11.4 ($H_{A'}H_{B'}$); 6.8 ($H_{A'}H_{C'}$)	
$H_{B'}$	1.731 (d, 2 H)	11.4 ($H_{A'}H_{B'}$)	
$H_{C'}$	4.063 (d, 2 H)	6.8 ($H_{A'}H_{C'}$)	
$H_{D'}$	5.838 (s, 6 H)	—	
[Ru—CN—Rh]$^+$BF$_4^-$ (**8**)			
H_A	4.467 (tt, 1 H)	11.0 (H_AH_B); 6.8 (H_AH_C)	
H_B	1.622 (d, 2 H)	11.0 (H_AH_B)	
H_C	3.416 (d, 2 H)	6.8 (H_AH_C)	
H_D	6.003 (s, 6 H)	—	
$H_{A'}$	5.055 (ttd, 1 H)	11.7 ($H_{A'}H_{B'}$); 6.8 ($H_{A'}H_{C'}$)	1.9
$H_{B'}$	2.317 (d, 2 H)	11.7 ($H_{A'}H_{B'}$)	≤0.6
$H_{C'}$	4.551 (d, 2 H)	6.8 ($H_{A'}H_{C'}$)	≤0.6
$H_{D'}$	5.621 (d, 5 H)	—	0.5
			
10			
$H_{A'}$	4.512 (tt, 1 H)	11.3 ($H_{A'}H_{B'}$); 6.9 ($H_{A'}H_{C'}$)	
$H_{B'}$	1.952 (d, 2 H)	11.3 ($H_{A'}H_{B'}$)	
$H_{C'}$	4.177 (d, 2 H)	6.9 ($H_{A'}H_{C'}$)	
$H_{D'}$	6.021 (s, 6 H)	—	
Me	2.428 (s, 3 H)	—	
			
11			
$H_{A'}$	5.197 (ttd, 1 H)	11.7 ($H_{A'}H_{B'}$); 6.8 ($H_{A'}H_{C'}$)	1.7
$H_{B'}$	2.680 (d, 2 H)	11.7 ($H_{A'}H_{B'}$)	≤0.9
$H_{C'}$	4.723 (d, 2 H)	6.8 ($H_{A'}H_{C'}$)	≤0.9
$H_{D'}$	5.811 (d, 5 H)	—	≤0.9
Me	2.460 (s, 3 H)	—	—

* $^2J_{H,H}$ and $^4J_{H,H}$ were *ca.* 0.4—0.5 Hz.

** Complexes of the general formula [M—CN—M′]$^+$BF$_4^-$; with M and/or M^1 = Rh, *n* = 0; with M and/or M^1 = Ru, *n* = 1. The protons of ligands bonded with metal (M′) having a formal positive charge are marked with an apostrophe.

0.63 for H_A, H_B, and H_C, and for complex **6** they are 0.01, 0.14, and 0.58, respectively.

Thus, the most sensitive to change of the metal charge are the chemical shifts of *syn*-protons H_C. The sensitivity of proton chemical shifts of allyl ligands to the nature of the metal is high for protons of all types. The observed ^{1}H NMR spectra are affected by a combination of these two factors.

One can estimate the strength of the bridging bonds in the synthesized binuclear complexes by studying their state in solution. An electrochemical study of solutions of the mixtures of complexes (**3** + **11**) and (**3** + **8**) or (**4**

+ **10**) and (**4** + **7**) having different composition did not confirm the significant dissociation of cyano-bridged compounds in MeCN, because the values of the oxidation and reduction potentials (E^{ox} and E^{red}) of complexes **7** and **8** were independent of the composition of the mixtures even in the presence of a large excess of the second component, *i.e.*, compound **3** or **4**.

On the contrary, mixing of solutions of complexes **10** or **11** in MeCN and compounds **4** afforded bridged binuclear complexes **7** and **6**, respectively. This can be observed in electrochemical experiments by disappearance of the reduction wave for the cations $[(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)(\text{MeCN})\text{Rh}]^+$ or $[(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)(\text{MeCN})\text{Ru}]^+$ (−0.60 and −1.40 V on a mercury dropping electrode *vs.* s.c.e.), respectively, and also by the appearance of waves that are typical of binuclear complexes.[2] The bridging bond in binuclear complexes is cleaved quite easily only by the action of rather strong nucleophiles, *e.g.*, chloride anions. For example, an addition of Et_4NCl to a solution of complex **6** results in appearance of a peak on the voltammogram; the peak is related to oxidation of compound **2** (Fig. 1).[2] It must be emphasized that the mechanism of this reaction is not dissociative, because the dissociation of binuclear complexes in solution does not occur.

The process of ligand exchange in mononuclear cationic complexes was investigated for compound **11** as an example. The rates of the reaction of this complex with halide ions were calculated from the current corresponding to the first wave of oxidation of Hal^-. It appears that the reaction has a first order relative to each reagent, *i.e.*, it proceeds by a bimolecular mechanism. The following rate constants were calculated (MeCN, 50 °C):

Nucleophile	Cl^-	Br^-
k/L mol^{-1} s^{-1}	0.32±0.03	0.44±0.02

As can be seen, in the case of Br^-, a slight increase in the reaction rate in comparison with Cl^- was observed (by 1.4 times). At the same time, the ratio of the Swain—Scott parameters for the reaction of Cl^- and Br^- with MeI indicates that under conditions of the pure $\text{S}_\text{N}2$ process the transition from Cl^- to Br^- must increase the rate of ligand exchange by *ca.* 6.3 times.[7] Therefore, the mechanism of this reaction is close to a dissociative one, *i.e.*, the MeCN molecule in the transition state mainly leaves the coordination sphere of the metal as opposed to introduction of the halide ion into it.

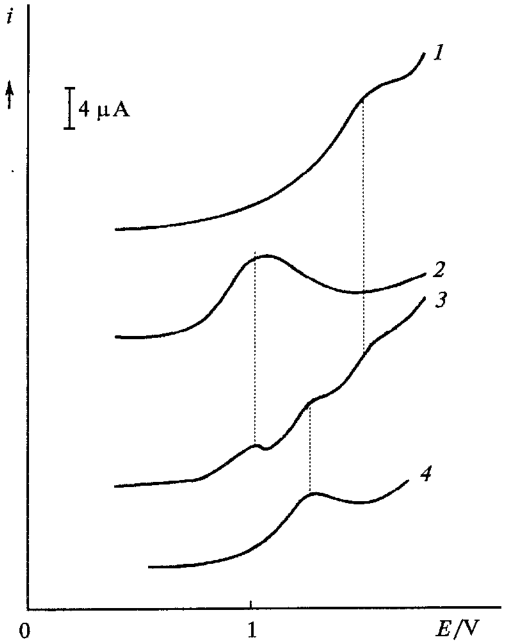


Fig. 1. Oxidation curves with the Pt electrode in MeCN: *1*, complex **6** ($3 \cdot 10^{-4}$ mol L^{-1}); *2*, Et_4NCl ($3 \cdot 10^{-4}$ mol L^{-1}); *3*, an equimolar mixture of **6** and Et_4NCl (30 min after mixing the reagents and keeping them at 50 °C); *4*, complex **2** ($3 \cdot 10^{-4}$ mol L^{-1}).

The pure dissociative mechanism of the reaction of complex **11** with Hal^-, in which initially the equilibrium

$$[(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)(\text{MeCN})\text{Rh}]^+ \rightleftharpoons$$

$$\rightleftharpoons [(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)\text{Rh}]^+ + \text{MeCN} ,$$

occurs, should be rejected, because in this case, the replacement of a solvent (slightly coordinating MeNO_2 instead of MeCN) would increase the rate of the process due to a shift of the equilibrium to the right. The calculated rate constant for the reaction of complex **11** with Br^- at 50 °C in MeNO_2 (k = 0.4 L mol^{-1} s^{-1}) is only slightly lower than in MeCN.

Thus, the ligand exchange apparently proceeds by a dissociative-exchange mechanism, according to the generally accepted Langford—Gray terminology.[8]

Experimental

The starting π-allyl complexes of ruthenium, rhodium and palladium $(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)\text{RuCl}$ (**1**),[9] $(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)\text{RhCl}$ (**2**),[9] $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$,[10] $(\eta^6\text{-C}_6\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)\text{RuCN}$ (**3**),[11] and $(\eta^5\text{-Cp})(\eta^3\text{-C}_3\text{H}_5)\text{RhCN}$ (**4**)[12] were synthesized using procedures previously described. Their constants agreed with the literature data. The UV and IR spectra of the newly prepared complexes were given and discussed in our previous paper.[2]

The ^{1}H NMR spectra were registered with a Bruker WP-200-SY instrument (200.13 MHz) in acetone-d_6 (δ 2.050).

The procedure of electrochemical measurements was thoroughly described previously.[2] The kinetic measurements were carried out in MeCN and MeNO_2 in a thermostatted cell at 50 °C. Tetraalkylammonium salts were the sources of halide-ions. The concentrations of the reagents were varied within the $(1\text{—}6) \cdot 10^{-4}$ mol L^{-1} range.

[μ-Cyano-η^6-benzene-η^3-allylruthenium-η^5-cyclopentadienyl-η^3-allylrhodium] tetrafluoroborate (8). AgBF_4 (0.16 g, 0.82 mmol) was added to a solution of compound **2** (0.17 g, 0.7 mmol) in acetone (30 mL) under argon at *ca.* 20 °C, and a precipitate of AgCl formed immediately. The reaction mixture was stirred for 3—4 h, and the completion of the reaction was determined by TLC (Silufol, acetone—CH_2Cl_2, 1 : 4) as the disappearance of a spot of starting complex **2**. Then compound **3** (0.17 g, 0.7 mmol) was added to the reaction mixture, and it was stirred for 2 h. The mixture was kept for 12 h; then it was filtered through a thin layer of Al_2O_3. The obtained yellow solution was concentrated *in vacuo* to a small volume, and hexane was added. The yellow precipitate was filtered off. The complex may be purified by column chromatography under inert atmosphere on Al_2O_3 in hexane (eluted with acetone—CH_2Cl_2, 1 : 15) or by multiple precipitation with hexane from an acetonic solution. Yield 0.280 g (74.7 %), decomposed at 180—194 °C. Found (%): C, 39.16; H, 3.71; N, 2.87; Rh, 18.95; Ru, 18.45. $C_{18}H_{21}BF_4NRhRu$. Calculated (%): C, 39.87; H, 3.90; N, 2.58; Rh, 18.98; Ru, 18.65.

[μ-Cyano-bis(η^5-cyclopentadienyl-η^3-allylrhodium)] tetrafluoroborate (6) was synthesized analogously to complex **8** from compound **2** (0.2 g, 0.82 mmol), $AgBF_4$ (0.20 g, 1.0 mmol), and cyanide **4** (0.192 g, 0.82 mmol). Yield 0.330 g (75.5 %), yellow crystals, decomposed at 182—184 °C. Found (%): C, 38.75; H, 3.78; N, 2.78; Rh, 39.70. $C_{17}H_{20}BF_4NRh_2$. Calculated (%): C, 38.45; H, 3.80; N, 2.64; Rh, 38.76.

[μ-Cyano-η^5-cyclopentadienyl-η^3-allylrhodium-η^6-benzene-η^3-allylruthenium] tetrafluoroborate (7) was synthesized analogously to complex **8** from compound **1** (0.11 g, 0.43 mmol), $AgBF_4$ (0.10 g, 0.51 mmol), and cyanide **4** (0.10 g, 0.43 mmol). The obtained complex was purified by column chromatography under Ar on Al_2O_3 in hexane (CH_2Cl_2 as the eluent). Yield 0.210 g (90.1 %), yellow crystals, decomposed at 185—195 °C. Found (%): C, 38.61; H, 3.79; N, 2.81. $C_{18}H_{21}BF_4NRhRu$. Calculated (%): C, 39.87; H, 3.90; N, 2.58.

[μ-Cyano-bis(η^6-benzene-η^3-allylruthenium)] tetrafluoroborate (5) was synthesized analogously to complex **8** from compound **1** (0.208 g, 0.81 mmol), $AgBF_4$ (0.20 g, 1.0 mmol), and cyanide **3** (0.2 g, 0.81 mmol). The obtained complex was purified by column chromatography under Ar on Al_2O_3 in hexane (CH_2Cl_2—acetone, 4 : 1, as the eluent). Yield 0.309 g (68.7 %), yellow crystals, decomposed at 195—205 °C. Found (%): C, 41.33; H, 3.95. $C_{19}H_{22}BF_4NRu_2$. Calculated (%): C, 41.23; H, 4.01.

[η^5-Cyclopentadienyl-η^3-allyl(acetonitrile)rhodium] tetrafluoroborate (11). $AgBF_4$ (0.77 g, 3.95 mmol) was added to a solution of compound **2** (0.8 g, 3.27 mmol) in dry MeCN (40 mL) at *ca.* 20 °C under Ar; and the mixture was stirred for 6 h. A precipitate of AgCl was formed. The red solution turned yellow-orange. The mixture was kept for 12 h; then the precipitate of AgCl was filtered off. The yellow solution was evaporated *in vacuo* to dryness, the residue was dissolved in CH_2Cl_2, and the solution was filtered. The complex was precipitated with benzene using subsequent slow evaporation of CH_2Cl_2 *in vacuo*. Yield 0.99 g (89.9 %), yellow-orange crystals, m.p. 109—110 °C. Found (%): C, 36.39; H, 4.08; N, 3.74; Rh, 30.08. $C_{10}H_{13}BF_4NRh$. Calculated (%): C, 35.65; H, 3.89; N, 3.79; Rh, 30.54.

[η^5-Cyclopentadienyl-η^3-allyl(acetonitrile)rhodium] tetraphenylborate was synthesized analogously to complex **11** from compound **2** (0.6 g, 2.45 mmol) and $NaBPh_4$ (0.84 g, 2.46 mmol) in dry MeCN (30 mL). The obtained complex was purified by washing with ether and benzene followed by crystallization from a CH_2Cl_2—benzene (2 : 1) mixture. Yield 1.29 g (92.1 %), orange crystals. Found (%): C, 72.32; H, 5.82; B, 1.86; N, 3.18. $C_{34}H_{33}BNRh$. Calculated (%): C, 71.72; H, 5.84; B, 1.90; N, 2.46.

[η^6-Benzene-η^3-allyl(acetonitrile)ruthenium] tetrafluoroborate (10) was synthesized and purified analogously to complex **11** from compound **1** (0.4 g, 1.56 mmol) and $AgBF_4$ (0.37 g, 1.90 mmol) in dry MeCN (30 mL). Yield 0.52 g (94.5 %), yellow crystals, m.p. 122—124 °C (decomp.). Found (%): C, 37.44; H, 4.01; Ru, 28.55. $C_{11}H_{14}BF_4NRu$. Calculated (%): C, 37.95; H, 4.05; Ru, 29.04.

[η^6-Benzene-η^3-allyl(acetonitrile)ruthenium] tetraphenylborate was synthesized analogously to complex **11** from compound **1** (1.9 g, 7.47 mmol) and $NaBPh_4$ (2.86 g, 8.36 mmol) in dry MeCN (60 mL). The obtained complex was purified by column chromatography on Al_2O_3 in an inert atmosphere (benzene—CH_2Cl_2, 1 : 1, as the eluent). Yield 3.47 g (80.3 %), yellow crystals, decomposed at 170—180 °C. Found (%): C, 72.05; H, 5.93; B, 1.92; N, 3.00. $C_{35}H_{34}BNRu$. Calculated (%): C, 72.41; H, 5.90; B, 1.86; N, 2.41.

μ-Cyano-η^5-cyclopentadienyl-η^3-allylrhodium-η^3-allylchloropalladium (9). Compound **4** (0.3 g, 1.28 mmol) was added to a solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.23 g, 0.63 mmol) in acetone (120 mL) with stirring. The precipitate was filtered off after 1 h and recrystallized from acetone. Yield 0.44 g (82.5 %), yellow crystals, m.p. 185—187 °C (decomp.). Found (%): C, 35.20; H, 3.78; N, 2.80; Pd, 24.30; Rh, 24.80. $C_{12}H_{15}ClNPdRh$. Calculated (%): C, 34.46; H, 3.35; N, 3.35; Pd, 25.46; Rh, 24.62. ^{1}H NMR ($(CD_3)_2CO$), δ: 2.594 (d, 2 H_{anti}, C_3H_5, J = 11.7 Hz, $J_{^{103}Rh-^{1}H} \le 0.9$ Hz); 3.885 (dd, 2 H_{syn}, C_3H_5, J = 6.0 Hz, $J_{^{103}Rh-^{1}H}$ = 1.4 Hz); 5.065 (tt, 1 H, $CH_2\underline{C}\underline{H}CH_2$, J = 11.7 Hz, J = 6.0 Hz, $J_{^{103}Rh-^{1}H} \le$ 0.9 Hz); 5.729 (s, 5 H, C_5H_5); 2.786 (d, 2 H_{anti}, C_3H_5, J = 12.2 Hz); 3.931 (d, 2 H_{syn}, C_3H_5, J = 6.6 Hz); 5.352 (t.t, 1 H, $CH_2C\underline{H}CH_2$, J = 12.2 Hz, J = 6.6 Hz).

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