

NEW POLYFUNCTIONAL CYCLIC UNSATURATED LIGANDS
IN THE CASCADE-TYPE METAL COMPLEXES

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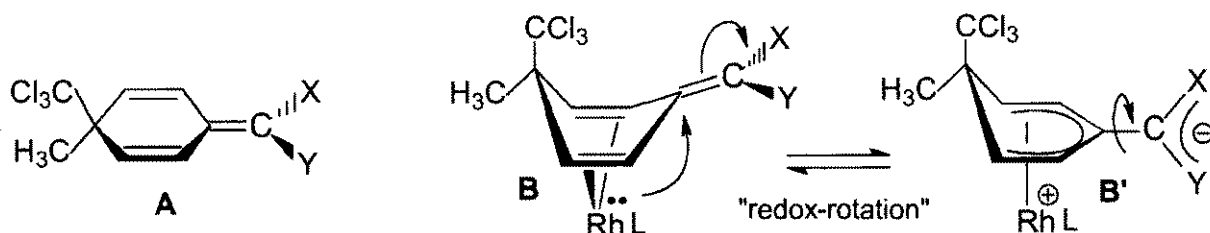
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On the basis of Rh(I) complexes with potentially dipolar ligands A (X, Y - electron-accepting groups) a new stereodynamic "redox-rotation" phenomenon was discovered earlier. The latter has its origin in the reversible Rh(I) \rightleftharpoons Rh(III) oxidative-reductive activation of the internal rotation around the exocyclic double (single) bond of the η^4/η^5 -coordinated ligand (in forms B or B'). In the present work we develop a concept of the "metal-ligand cascades" – a new type of dynamic structures in which redox-conformational transformations imply cooperative electronic and steric interactions between several metal atoms through a polyconjugated ligand system.

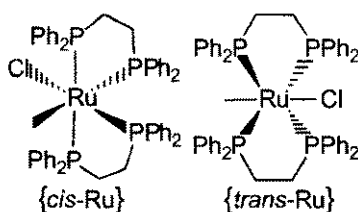


X = CN, Y = CN (**1**), NO₂ (**2**), C(NH)OCH₃ (**3**), CO₂CH₃ (**4**), CONH₂ (**5**), NHCO₂CH₃ (**6**), COOH (**7**), X = Y = CONH₂ (**8**); X = CN \rightarrow {*cis*-Ru}⁺PF₆⁻, Y = CN (**9a,b**), NO₂ (**10a,b**); X = CN \rightarrow {*trans*-Ru}⁺PF₆⁻, Y = CN (**11**); [XY] = =C={*trans*-Ru}⁺PF₆⁻ (**12**).

L = acac, Cp, X = CN, Y = CN (**13, 14**), NO₂ (**15, 16**), CONH₂ (**17, 18**), CO₂CH₃ (**19, 20**), CN \rightarrow {*cis*-Ru}⁺PF₆⁻ (**21a,b, 22a,b**); L = Cp, X = CN \rightarrow {*cis*-Ru}⁺PF₆⁻, Y = CONH₂ (**23a,b**), CO₂CH₃ (**24a,b**); L = Cp, X = CN \rightarrow {*trans*-Ru}⁺PF₆⁻, Y = CN (**25**), CO₂CH₃ (**26**); L = acac, [XY] = =C={*trans*-Ru}⁺PF₆⁻ (**27**); L = 2Cl, [XY] = =C={*trans*-Ru} (**28**).

Dicyanotriene **1** (92 %) and nitrocyanotriene **2** (24 %) were obtained by the Knoevenagel condensation. Then **1** was used to synthesize imino ether **3** (MeOH, NaOH cat.), methyl ester **4** (acid hydrolysis of imino ester **3** hydrochloride), monoamide **5** and diamide **7** (hydration of **1** in conc. H₂SO₄), urethane **6** (the Hoffmann rearrangement of **5**), acid **8** (the Bouveault hydrolysis of **5**).

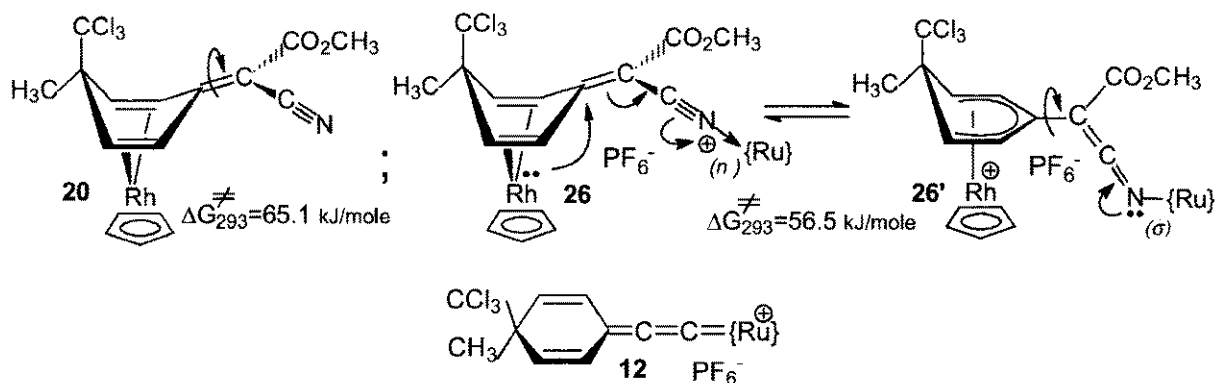
π -Diene mixed-ligand complexes **13-20** with Rh(acac) and Rh(Cp) metal centers have been obtained from triene ligands containing following exocyclic moieties: =C(CN)₂ (**1**), =C(CN)(NO₂) (**2**), =C(CN)(CO₂CH₃) (**4**), and =C(CN)(CONH₂) (**5**). NMR ¹H data for **15-20** revealed the regular acceleration of the redox-rotation with increasing electron-accepting ability of Y (NO₂ > CO₂CH₃ > CONH₂) and electron-donating ability of the metal center (Rh(Cp) > Rh(acac)). Thus, complexes **13, 14, 17-20** (in the ground state) can be referred to the form B, while **15** and **16** - to the form B'.



The metal-ligand cascade molecular design - by using the trienes and their Rh-complexes as nitrile ligands coordinated to Ru(II) as the second metal center - revealed the fact that the stereochemistry of the latter plays a decisive role in controlling the nature of the dynamic processes observed. For *cis*-configuration of the Ru-octahedron, a reversible metal-to-ligand coordination process takes place. In case of bimetallic complexes **21a,b, 23a,b** we observed such a reversible ligand exchange as a sole dynamic process in the reacting system at room temperature while when passing to bimetallic **22a,b** and **24a,b** the ligand exchange was accompanied with the redox-rotation (the rate of the latter is not influenced significantly by the coordination to the {*cis*-Ru}⁺-moiety). Some characteristic stereochemical features of the system investigated allowed us to develop a new methodology for recognizing chirality of octahedral diphosphine Ru(II) complexes which is based on an idea of mono-coordination mode [RCN \rightarrow {*cis*-Ru}⁺]PF₆⁻ of prochiral **1, 13, 14** and chiral **2, 18, 20** resulting in the formation of mixtures of diastereomeric mono-metallic complexes **9** (a:b=1:1), **10** (a:b=1:0.8), as well as bimetallic complexes **21** (a:b=5:1), **22** (a \rightleftharpoons b), **23** (a:b=7:1), and **24** (a \rightleftharpoons b) (the ratios of isomers are given in parentheses). For free trienes **1** and **2**, by this means, the weak diastereoselectivity (**10a,b**) or its full absence (**9a,b**) was observed that is in

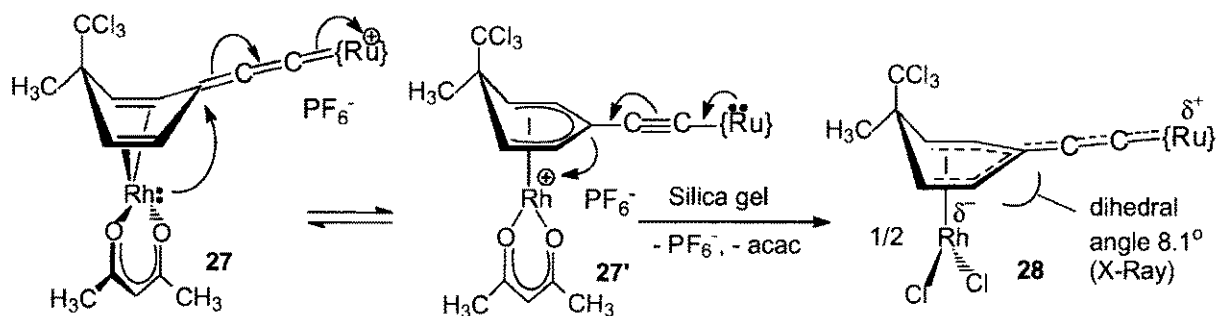
contrast to the case of the strongly pronounced diastereoselectivity for much more bulky Rh-complexes **13** and **18** acting as nitrile-centered "n-ligands" to ruthenium atom (**21a,b**, **23a,b**).

For complexes **9**, **22**, **24** we succeeded to discover a thermally induced *cis-trans* configurational rearrangement of the Ru-chelate surrounding resulting in the formation of $[RCN \rightarrow \{trans-Ru\}^+][PF_6^-]$ species (**10**, **25**, **26**), which are characterized (in contrast to $[RCN \rightarrow \{cis-Ru\}^+][PF_6^-]$ complexes) by more strong nitrile coordination. By virtue of this fact an opportunity is being opened to *concert* the redox-rotation with cooperative redox participation of *two* metal centers in a bimetallic system. A comparison of the free energy barrier for **20** with that of its $\{trans-Ru\}^+$ -derivative **26** shows a sharp acceleration (35 times faster) of the internal rotation. It is possible to consider this fact as the first example of reversible change of "rehybridizational" contributions to the common bonding pattern ($n \rightleftharpoons \sigma$ coordination modes) of the second coordinating metal (Ru(II)) in cascades (namely, "metal-ligand-metal") with heteroorganic multiconjugated main chain of such a kind:



The possibility of the high degree participation of Ru d-orbitals in positive charge delocalization is established by X-Ray, NMR ¹³C, and IR techniques for model compound **12** constructed by introduction of the —C=C—{*trans*-Ru^{IV}} substituent /Ru(II) oxidation state/ into 1-position of a 4,4-disubstituted cyclohexadienylidene cation (counter-ion PF₆⁻) that represents the first example of previously unknown ruthenacumulenated cyclohexadienylidene systems. Thus, in polyheteroconjugated complex **12** the ruthenium atom gains the oxidation state (+IV) when being incorporated into a strictly linear ("rod-like") exocyclic chain =C=C={Ru}^+.

The possibility of the Rh(acac)-moiety coordination to the π-diene system of **12** has been demonstrated. The resultant bimetallic complex **27** can be described (IR, NMR ³¹P, ¹³C) as an intermediate structure with competing participations of two limiting forms: η⁴-Rh(I)-cyclohexadienylidene-allenylidene-Ru(IV) (**27**, the positive charge is localized on ruthenium) and η⁵-Rh(III)-cyclohexadienyl-acetylide-Ru(II) (**27'**, the positive charge is localized on rhodium):



Upon passing through silica gel (eluent benzene-ethanol = 5:1), **27** unexpectedly transforms to highly stable neutral **16e** complex **28**. Apparently, **27** itself acts as a source of chlorine for **28** (yield ~50%). IR, NMR ¹³C, ³¹P and X-Ray data for **28** are consistent with its zwitter-ionic nature as a consequence of active redox interaction between two transition metal atoms through the purely carbon conjugated chain. This fact proves the fundamental opportunity for the creation of metal-ligand cascades by cooperative molecular-architectural coupling cyclohexadienylidene-cyclohexadienyl (redox-rotational) and allenylidene-acetylide dynamic structural motifs integrated in one organobimetallic molecule.

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