Metalloscorpionates

Metallo-Scorpionates: First Generation of Trimetallic, Homoleptic [Ru]–M–[Ru] Complexes (M = Fe, Co, Ni, Cu)


Abstract: The first metallo-scorpionate ligands, closely related to Trofimenko’s scorpionates, are obtained by formal replacement of the hydrido-boron moiety of hydrido-tris(pyrazolyl)borate by an (arene)RuII fragment. Coordination to divalent and trivalent 3d-transition metals (Fe, Co, Ni, Cu) gives access to a series of homoleptic, heterotrimetallic complexes containing linear metal chains bridged by pyrazole ligands. Synthetic aspects, spectroscopic, structural and electrochemical properties are reported and compared to those of standard scorpionate complexes.

Introduction

Tridentate chelating ligands play an important role in coordination and organometallic chemistry because they allow formation of stable metal complexes whose geometry, steric shielding and reactivity may be tuned more or less at will, depending on chemical interest. They find applications in, for example, catalysis, small molecule activation and materials science. Prominent classes of tridentate ligands comprise neutral, planar, meridionally coordinating pincer ligands[1] and monoanionic, tri-podal hydrido-tris(pyrazolyl)borates[2] (so-called “scorpionates”). The latter were introduced as early as 1966 by Trofimenko. Scorpionates are face-capping, monoanionic 6-electron ligands, almost similar in scope and coordination behavior as the ubiquitous cyclopentadienyl ligands in organometallic chemistry.

In this contribution, we would like to address the following questions: Is it possible to modify scorpionates by replacing their central hydrido-boron moiety by an organometallic group, thereby getting access to “metallo-scorpionates”? Are there any chemically interesting and/or beneficial metal-based effects realizable, for example tuning of electronic ligand properties by the organometallic moiety, metal-metal/spin-spin interactions between the organometallic group and the coordinated metal centers, redox switching and other electrochemical properties?

To address this topic in a retrosynthetic manner, three anionic pyrazolido ligands have to be coordinated to a suitable dicationic organometallic fragment, affording thereby an un-negative metalloligand. There is a range of isolable organometallic dicaticionic solvento complexes of transition metals known,[3] e.g. [Cp*M]2+ (M = Cr3+,Co3+,Rh3+,Ir3+); [(arene)M]2+ (M = Fe2+,Ru2+) and [(cyclobutadiene)M]2+ (M = Ni2+,Pd2+,Pt2+) that might be used for our purposes. In this first contribution on metallo-scorpionate chemistry, we choose the (p-cymene)RuII synthon[3b] due to its ease of access[4] and due to the superior stability of its complexes in comparison to the other options. Scheme 1 illustrates the close structural similarity of standard scorpionates (A) with such a metallo-scorpionate ligand (B) derived by formal replacement of the hydrido-boron [H-B]2+ moiety with a [(p-cymene)Ru]2+ group.

Besides purely electronic metal-based properties briefly mentioned above, metallo-scorpionates might have further beneficial ligand properties: due to the more flexible Ru–N coordination bonding of the three pyrazolyl groups in B compared to the covalent, more rigid B–N bonding in A, thus, an optimized fit with cations of varying size and electronic configuration will be possible, similarly as it is the case for “Kläui-ligands”,[5] e.g. [(cyclopentadienyl)-tris(dialkylphosphito)-}

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Scheme 1. Structural comparison of scorpionate (A) with a cymene-ruthenium metallo-scorpionate (B).
cobaltate], that have been shown to act as surprisingly “soft” ligand systems despite their three “hard” oxygen donor atoms.[5]

Here we report on a series of metallo-scorpionate complexes based on the \([\text{p}-\text{cymene}]\text{Ru(pyz)}_3\) motif to gain knowledge and understanding of their coordinative, electrochemical and other properties as a first entry into metallo-scorpionate chemistry. Overall, the influence of the RuII metal center on the ligand properties of this metallo-scorpionate as well its Ru–metal interactions with coordinated other metal centers will be the prime interest in this work. As outlined above, the general scope of this chemistry is in principle much wider, either by using other transition metal fragments or by using sterically more demanding, substituted pyrazolyl groups, thereby enforcing lower coordination numbers with altered chemical reactivity. Moreover, replacing the pyrazole ligands by \(N\)-alkylated imidazoles might lead to analogous tripodal metallo-tri-N-heterocyclic carbene ligands, in turn comparable to hydrido-boron-tri-NHCs developed in 1996 by Fehlhammer[6] and exploited in recent years by Smith and others.[7]

Results and Discussion

Synthesis. One-pot reactions of the dimer of dichlorido-\((\text{p}-\text{cymene})\text{RuBr}_2\) (1) in dry methanol with four equivalents of thallium triflate or silver hexafluoridophosphate in the presence of six equivalents of pyrazole afforded \([\text{p}-\text{cymene}]\text{Ru(Hpz)}_3\)(TfO)\(_2\) (2a) and \([\text{p}-\text{cymene}]\text{Ru(Hpz)}_3\)(PF\(_6\))\(_2\) (2b) in >70 % isolated yields as air-stable, yellow materials (Scheme 2). An alternative stepwise procedure by forming first the dicationic \((\text{p}-\text{cymene})\text{trime}nol)\text{Ru solvento complexe} followed by addition of the pyrazole ligands proved less convenient and gave inferior yields. 2a and 2b are the dicationic ligand precursors for the desired monoanionic metallo-scorpionate ligand. To effect threefold deprotonation, various bases (e.g. metal acetates, \(n\text{BuLi}, t\text{BuLi, KO}t\text{Bu, TlO}t\text{Bu, TIO}t\text{E, Ag}_2O\) and others) under a variety of conditions were tested out. In the end, deprotonation by three equivalents of potassium tert-butoxide in tetrahydrofuran at room temperature over a period of 24 hours worked best according to NMR analysis, giving dark green, air-sensitive THF solutions of the potassium salt of the desired complex 3. Attempts to isolate this material or analogous TlI or AgI complexes met with mixed results, therefore we used 3 in the following in situ without further purification.

Because \(d^6\)-CoIII is well known to form stable diamagnetic octahedral metal complexes with nitrogen ligands, our first goal was to prepare such a homoleptic complex of our metallo-scorpionate ligand. Transmetalation of 3 with half an equivalent of anhydrous CoBr\(_2\) followed by oxidation by O\(_2\) afforded moderately air-stable, red, monocationic CoII\(_3\) complexes 4a and 4b, differing only in their counterions, in isolated yields of 88 % (4a) and 66 % (4b). The oxidation of CoII to CoIII depended critically on the oxidizing agent: molecular oxygen proved to be superior to air and other common one-electron reagents, e.g. NOBF\(_4\), Br\(_2\), I\(_2\) or CsBr\(_3\), gave inferior results. By a similar transmetalation of 3 with anhydrous FeBr\(_2\) the neutral, diamagnetic \(d^6\)-FeII complex 5 was obtained as a brown, quite air-sensitive material in 71 % yield. Interestingly, attempts to deliberately oxidize 5 by various reagents to its paramagnetic, monocationic \(d^5\) complex met with failure, in part due to difficulties in the workup proce-

dure or mostly due to the unexpected high air-sensitivity of the product. In a similar manner, Ni complexes 6 and 7 were generated from two equivalents of 3 and dibromo(dimethoxyethane)nickel(II). Under strictly inert conditions, including purification and workup methods, the air-sensitive, yellow, diamagnetic, neutral, complex 6 with a square-planar coordination environment at nickel was obtained in a moderate yield of 20%. However, in the presence of even only traces of water during workup, the air-stable, yellow, diamagnetic, dicaticonic product 7 was formed in 60% yield, structurally differing from 6 by two pyrazolido ligands being protonated and containing two bromide counterions. Similarly, metathesis of 3 with copper(II) trifluoromethansulfonate under strict protection from air and moisture afforded a slightly longer than the B–Co distance of 3.195 Å of \([\text{(scorpionato)}_2\text{Co}]^+\). As a consequence of the smaller N–Ru–N bond angles in comparison to those of regular tetrahedral scorpionates (vide supra), the through-space Ru–Co distance is 3.746 Å, much longer than the B–Co distance of 3.195 Å of \([\text{(scorpionato)}_2\text{Co}]^+\) complexes.[2]

The molecular structures of square-planar complexes 6 (Figure 3), 7 (Figure 4) and 8 (Figure 5) are overall quite similar. Slightly distorted square-planar coordination is observed with N–Ni/Cu–N bond angles close to 90°. The averaged bond lengths Ni–N (1.888 Å) and Cu–N (1.984 Å) are in line with expectations. The main difference in these three structures is the observation that both complexes 6 and 8, synthesized under strictly inert conditions, contain two Ru-coordinated, but not Ni/Cu-coordinated monoanionic pyrazolido ligands, whereas complex 7 represents the diprotonated form of 6, formally its conjugate Brønsted acid. These non-Ni/Cu-bonded pyrazolido (6, 8) or pyrazole (7) ligands are pointed away from the central metal, thereby opening up the formal axial octahedral donor

**Figure 2.** Molecular structure of the monocation of Co complex 4b. Counterions hexafluoridophosphate, hydrogen atoms of \(p\)-cyrene ligand and methanol solvent molecules omitted for clarity. Selected bond lengths [Å]: Ru1–N1 = 2.099(3), Ru1–N3 = 2.1007(18), Ru1–N5 = 2.099(3), Co1–N2 = 1.907(3), Co1–N4 = 1.935(3), Co1–N6 = 1.920(3), N1–N2 = 1.363(4), N3–N4 = 1.367(4), N5–N6 = 1.357(4); N1–Ru1–N3 = 85.26(12), N1–Ru1–N5 = 87.14(12), N3–Ru1–N5 = 82.61(12), N2–Co1–N4 = 91.01(13), N2–Co1N6 = 90.77(13), N4–Co1–N6 = 90.83(13).

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In comparison, standard scorpionates containing small hydrido-substituted HB(pz)3 ligands are undistorted tetrahedral molecules that have N–B–N bond angles very close to 109.5°.[2] The average Ru–N bond length in 2a is 2.106 Å, as expected much longer than the shorter covalent B–N bonds in scorpionates (appr. 1.54 Å).[2] The structure of monocaticonic Co complex 4b (Figure 2) shows a homoleptic octahedral complex containing two crystallographically related tridentate \([\text{N,N,N}]-\text{ligands. Structural metrics of the Co-coordinated, monoanionic (}\text{p-cymene})-\text{Ru(pyrazolido)}_2\text{ligand are very similar (averaged Ru–N bond lengths: 2.099 Å, averaged N–Ru–N bond angle: 85.0°) to those in the uncoordinated dicaticonic ligand precursor 2a (vide supra). The central Co atom is situated in an almost perfect octahedron with N–Co–N bond angles very close to 90°, showing that this metallo-scorpionate ligand is fully compatible with a d6-Co3+ metal center. The Co–N bond lengths are in the range of 1.907 Å–1.920 Å, slightly shorter than those of standard \([\text{(scorpionato)}_2\text{Co}]^+\) complexes (Co–N averaged = 1.921 Å).[2] As a consequence of the smaller N–Ru–N bond angles in comparison to those of regular tetrahedral scorpionates (vide supra), the through-space Ru–Co distance of 4b is 3.746 Å, much longer than the B–Co distance of 3.195 Å of \([\text{(scorpionato)}_2\text{Co}]^+\) complexes.[2]

**Figure 1.** Molecular structure of the dication of ligand precursor 2a. Counterions trifluoromethansulfonates omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 = 2.1136(18), Ru1–N3 = 2.1007(18), Ru1–N5 = 2.1049(18), N1–N2 = 1.351(3), N3–N4 = 1.354(3), N5–N6 = 1.338(3); N1–Ru1–N3 = 82.95(7), N1–Ru1–N5 = 83.33(7), N3–Ru1–N5 = 88.79(7).

In comparison, standard scorpionates containing small hydrido-substituted HB(pz)3 ligands are undistorted tetrahedral molecules that have N–B–N bond angles very close to 109.5°.[2] The average Ru–N bond length in 2a is 2.106 Å, as expected much longer than the shorter covalent B–N bonds in scorpionates (appr. 1.54 Å).[2] The structure of monocaticonic Co complex 4b (Figure 2) shows a homoleptic octahedral complex containing two crystallographically related tridentate \([\text{N,N,N}]-\text{ligands. Structural metrics of the Co-coordinated, monoanionic (}\text{p-cymene})-\text{Ru(pyrazolido)}_2\text{ligand are very similar (averaged Ru–N bond lengths: 2.099 Å, averaged N–Ru–N bond angle: 85.0°) to those in the uncoordinated dicaticonic ligand precursor 2a (vide supra). The central Co atom is situated in an almost perfect octahedron with N–Co–N bond angles very close to 90°, showing that this metallo-scorpionate ligand is fully compatible with a d6-Co3+ metal center. The Co–N bond lengths are in the range of 1.907 Å–1.920 Å, slightly shorter than those of standard \([\text{(scorpionato)}_2\text{Co}]^+\) complexes (Co–N averaged = 1.921 Å).[2] As a consequence of the smaller N–Ru–N bond angles in comparison to those of regular tetrahedral scorpionates (vide supra), the through-space Ru–Co distance of 4b is 3.746 Å, much longer than the B–Co distance of 3.195 Å of \([\text{(scorpionato)}_2\text{Co}]^+\) complexes.[2]
sites of the square-planar coordination of d8-Ni (6, 7) or d9-Cu (8). Clearly the larger ligand-field stabilization of a d8 or d9 ion in a square-planar rather than an octahedral environment dictates, that even in the presence of geometrically ideally positioned, anionic pyrazolido ligands no octahedral complexes are formed. However, normal scorpionates have been shown to form Jahn–Teller-distorted octahedral CuII complexes,[8] again indicating that metallo-scorpionates are significantly weaker ligands in comparison to regular scorpionates.[2] A structural feature common to complexes 6, 7 and 8 is the transoid arrangement of the half-sandwich cymene ruthenium moieties at the central, four-coordinate MII+ ion.

Spectroscopic properties. 1H and 13C NMR spectroscopy of diamagnetic 2a,b, 4a,b, 5, 6 and 7 gave the expected signal patterns of n-coordinated p-cymene ligands in addition with corresponding pyrazole signals (1H: δ = 5.35–8.19 ppm, δ × δ × t; 13C: δ = 101.83–144.81 ppm); for detailed assignments compare experimental section and spectra in the supporting information. Square-planar complexes 6 and 7 displayed two sets of pyrazole signals integrating in a 2:1 ratio, ruling out intramolecular exchange of deprotonated pyrazolido ligands (6) or tautomeric equilibria between protonated and deprotonated pyrazoles (7) in solution, respectively, in accordance with their solid-state structures (vide supra). The chemical identity of 2a, 4a, 5, 6 and 7 was further confirmed by high-resolution mass spectrometry. Experimental data were in excellent agreement with calculated values of corresponding mono-isotopic species (see experimental part). ATR-IR spectroscopy was used to detect the presence of hexafluoridophosphate or trifluoromethanesulfonate anions (2a,b, 4a,b) by their diagnostic absorptions (see experimental part). Moreover, during synthesis and purification of air-sensitive complexes 4a,b, 5, 6 and 8, IR spectroscopy was a convenient tool to prove their identity; undesired hydrolysis may easily be detected by observation of N-H absorptions >3000 cm−1.

Electrochemistry. The electrochemical properties of the heterotrimetallic complexes and of precursor 2a were explored in CH2Cl2/0.1 M NBu4PF6 as the supporting electrolyte. Contrary to the myriad of neutral or monocationic pseudooctahedral (p-cymene)RuL3 half-sandwich complexes with either two anionic and one neutral imine or one anionic and two neutral imine ligands L, 2a shows no anodic redox-wave assignable to the Ru(II/III) couple in its cyclic voltammogram. The expected wave is probably shifted out of the accessible potential range due to the dispositive complex charge. Rather, two consecutive reduction waves were observed in the cathodic potential range. The first one (peak A in Figure 6a) corresponds to a chemically irreversible process with a peak potential of ~0.905 V, while the second one (peaks B/C) is constituted by a quasi reversible redox couple with an E1/2 of ~1.41 V. The current associated with the first cathodic peak strongly decreases on repetitive scanning while the second, quasi reversible wave is retained (see
supporting information, Figure S6). This suggests that the species corresponding to the B/C couple is formed in a chemical process following the initial reduction of 2a.

Figure 6. Cyclic voltammetry of complex 2a (a), 5 (b), 6 (c), and 8 (d), in CH₂Cl₂/0.1 M NBu₄PF₆ as the supporting electrolyte.

One or two reduction waves are also observed in the voltammograms of complexes 4a, 5 and 8. For cobalt complex 4a this process is chemically irreversible and appears at a peak potential of –1.595 V. That wave could either arise from the reduction of the metallo-scorpionate ligands or correspond to the Co(III/II) couple. Thus, CoT₃ (Tp = κ²-hydrido[tris(pyrazolyl)bora]) and mixed CpCoTp (Cp = η⁵-cyclopentadienide) were reported to oxidize at –0.500 V and –0.590 V, respectively.[9] An additional wave of likewise unclear origin was observed at a peak potential of +0.915 V. The proximity of this wave to the anodic discharge limit of our electrolyte however precludes a meaningful comparison of their associated peak currents (see supporting information, Figure S14). The closely related FeII complex displays two chemically almost reversible, consecutive reductions at –1.025 V (peaks A/B) and –1.225 V (peaks C/D) with nearly equal peak currents (see Figure 6b) but no defined oxidation processes. Nickel complex 6 in contrast only undergoes a chemically irreversible oxidation at a peak potential of 0.610 V (Figure 6c). Scanning this process caused almost immediate electrode passivation. Copper complex 8 finally displays one chemically reversible and electrochemically quasi reversible reduction at a half-wave potential of –1.223 V (peaks A/B) as well as chemically irreversible oxidations at 0.615 V (peak C) and 1.270 V (peak D, Figure 6d). The latter two processes also lead to rapid electrode passivation on repetitive scanning. Again, the reduction could either be due to the Cu(II/I) redox couple or the reduction of the metallo-scorpionate entities. The redox properties of several CuTp complexes have been investigated by voltammetry due to their relevance to the active sites of copper redox proteins,[10] and their redox potentials were found to vary over a rather broad range, from ~0.07 V for the cationic Cu⁺ acetonitrile complex[10b] with the tris[3-isopropyl][5-tert-butyl]pyrazoly]borate ligand (note here the necessary adjustment of the potential reference scale[11]) to ~1.03 V for a neutral alkoxide complex of the tris[3-methyl][5-tert-butyl]pyrazoly]borate ligand.[10c] Reversible behavior of the Cu(II/I) couples was, however, only observed when rigid coordination environments and/or bulky ligands prevented the structural rearrangement from a square planar (Cu²⁺) to a tetrahedral (Cu³⁺) coordination geometry.[10b] We also note here that the electrochemistry of complexes of the hydridotris(pyrazolyl)-borate ligand and its many ring-substituted variations are often complicated by structural rearrangement accompanying electron transfer. For example, a change of hapticity of the Tp-ligands from κ³ to κ² and vice versa or the coexistence of species showing both hapticity modes have been reported on occasions.[10e,12] The unusually large half-wave potential splittings observed in all instances may thus have a similar origin (Table 1).

Table 1. Electrochemical properties of the complexes.[a]

<table>
<thead>
<tr>
<th>Complex</th>
<th>E¹/₂ red [V] (ΔEₚ [mV])</th>
<th>Eₚ ox [V]</th>
</tr>
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<tbody>
<tr>
<td>2b</td>
<td>–0.905,[b] –1.413 (277)</td>
<td>–</td>
</tr>
<tr>
<td>4b</td>
<td>–1.595[b]</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>–1.025 (146), –1.225 (125)</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>–</td>
<td>0.610[b]</td>
</tr>
<tr>
<td>8</td>
<td>–1.223 (133)</td>
<td>0.615[b], 1.270[b]</td>
</tr>
</tbody>
</table>

[a] Data in CH₂Cl₂/nBu₄PF₆ (0.1 M) at r. t. and at a scan rate v = 0.100 V/s. [b] Peak potential of an irreversible peak.

Conclusions

A first metallo-scorpionate ligand precursor based on the p-cymene-tri-pyrazolido-Ru²⁺ motif, structurally related to standard hydrido-tris(pyrazolyl)borates, was easily synthesized and fully characterized. Deprotonation and transmetalation reactions afforded homoletic, heterotrimetallic [Ru]–[M]–[Ru] complexes (M = Fe²⁺, Co³⁺, Ni²⁺, Cu²⁺). In contrast to expectations, these first members of metallo-scorpionate complexes were surprisingly air-sensitive. Spectroscopic properties as well as X-ray single structure analyses proved an octahedral coordination for d⁶ metal centers (Fe²⁺, Co³⁺) and a square-planar coordination for d⁸ (Ni²⁺) and d⁹ (Cu²⁺) metal centers, indicating p-cymene-Ru-
based metallo-scorpionate to be a significantly weaker ligand in comparison to Trofimenko’s hydrido-tris(4-pyrazolyl)borate ligands. Cyclic voltammetry showed mostly irreversible redox processes that are difficult to assign in these heterotrimetallic complexes. Future work will be directed towards electronically and/or sterically new versions of metallo-scorpionate ligands that contain either other organometallic central moieties or substituted pyrazolido ligands, aiming at systems of increased stability and more potential for further chemistry and applications.

**Experimental Section**

**General Procedures:** All preparations were carried out under an inert atmosphere of Ar or N₂ by standard Schlenk techniques and/or in a glovebox. Starting material dichlorido(4-cymene) ruthenium(II) dimer (1) was synthesized according to literature. All other chemicals were obtained from commercial suppliers and used as received. Solvents were dried, deoxygenated and purified before usage. NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer and were referenced against 13C/1H residual solvent peaks. Mass spectrometry was performed on a Thermo Finnegan Q Exactive Orbitrap spectrometer, IR analyses were performed on a Bruker ALPHA spectrometer, and melting points were determined on a Leica Galen III Kofler microscope. Single crystal X-ray data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and structures were solved by direct methods as published. Electrochemical measurements were performed as described recently with the exception they were performed inside a nitrogen-filled glovebox.

**Ru-Precursor 2a and 2b:** A Schlenk vessel was charged under an atmosphere of argon with a stirring bar and dichlorido(4-cymene) ruthenium(II) dimer (1) (1.29 g, 2.11 mmol) in methanol (100 mL). Pyrazole (1.08 g, 15.8 mmol, 7.5 equiv.) and thallium tributoxy (2.54 g, 10.5 mmol, 5.0 equiv.) were added and the reaction mixture was stirred at room temperature for 24 h. Workup under ambient conditions: The mixture was filtered through a paper filter to remove thallium chloride, solvents were removed on a rotary evaporator, and the crude product was precipitated by addition of methanol/diethyl ether. After a second filtration, the filter cake was washed with petroleum ether or pentane into a dichloromethane solution of 2a. Yellow crystals of 2a were obtained by slow evaporation of a solution of 2a in methanol covered with n-hexane or anisole. Single crystal structure analysis: Figure 2. Spectra: supporting information.

**Fe Complex 5:** In a similar manner as described above in the synthesis of 4a, ligand precursor 2a (148 mg, 0.201 mmol) was converted to its potassium salt 3. The mixture was cooled to –80 °C, anhydrous iron(II)iodide (22.3 mg, 0.103 mmol) was added and stirring was continued at –80 °C for 4 h. The mixture was warmed to room temperature and stirring was continued for 4 d, affording a brown mixture. Workup under protection from air: Side products were removed by filtration, tetrahydrofuran was stripped off in vacuo, the residue was dissolved in dry dichloromethane, the solution was filtered and the crude product was obtained by removal of dichloromethane in vacuo. The material was dissolved in a mixture of dry dichloromethane/dry diethyl ether (1:30) and placed overnight in a freezer to precipitate the pure product, affording thereby red complex 4a in 88 % yield (102 mg, 0.0942 mmol) which shows a short-term stability in contact with air or polar solvents. M. p. 313 °C.}

**Ru Complexes 4a and 4b:** A Schlenk tube was charged under protection from air with 2a (158 mg, 0.214 mmol) and dry tetrahydrofuran (50 mL). Potassium tert-butoxide (81.3 mg, 0.725 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. A dark green solution with a yellow glint was obtained, containing the potassium salt 3 of deprotonated 2a. The mixture was cooled to –80 °C, anhydrous cobalt(II)iodide (24.4 mg, 0.112 mmol) was added and stirring was continued at –80 °C for 5 h. The mixture was warmed to room temperature and stirring was continued for 4 d, affording a brownish mixture containing the corresponding paramagnetic neutral Co complex. To effect oxidation to the corresponding diamagnetic cationic Co complex 4a the argon atmosphere was replaced by dioxygen and stirring was continued for a maximum of 2 h, affording a burgundy red solution of 4a. Workup under protection from air: Side products were removed by filtration, tetrahydrofuran was stripped off in vacuo, the residue was dissolved in dry dichloromethane, the solution was filtered and the crude product was obtained by removal of dichloromethane in vacuo. The material was dissolved in a mixture of dry dichloromethane/dry diethyl ether (1:30) and placed overnight in a freezer to precipitate the pure product, affording thereby red complex 4a in 88 % yield (102 mg, 0.0942 mmol) which shows a short-term stability in contact with air or polar solvents. M. p. 313 °C. **NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 7.99 (d, J = 2.62 Hz, 3 H, pzh), 7.97 (d, J = 2.30 Hz, 3 H, pzh), 6.70 (t, J = 2.54 Hz, 3 H, pzh), 6.27 (d, J = 6.23 Hz, 2 H, ArH), 5.96 (d, J = 6.24 Hz, 2 H, ArH), 2.25 (sept, J = 6.85 Hz, 1 H, πH), 1.74 (s, 3 H, MeH), 1.08 (d, J = 6.96 Hz, 6 H, πH) ppm. **13C NMR (75.5 MHz, CD₂Cl₂, 25 °C): δ = 147.27 (pzC), 134.95 (pzC), 119.44 (pzC), 109.62 (pzC), 108.65 (pzC), 106.48 (AcC), 88.37 (AcC), 85.39 (AcC), 83.61 (πC), 55.70 (πC), 31.98 (πC), 22.24 (πC), 18.07 (MeC) ppm. IR (ATR): ν = 3193, 3159 (NH), 3069, 3009, 2985, 2932, 2882 (CH), 1539, 1474, 1445, 1411, 1359 (C=C, C–N, N–N), 1293, 1233, 1026 (SO₃), 1158, 1134 (Csp²), 769, 632 (SO₃) cm⁻¹. HRMS (FAB pos): C₂₀H₂₆F₃SO₃N₆Ru, calcd. most abundant isotope peak 589.0777 (M – TFO), found m/z = 589.0792. Compound 2b was prepared similarly from silver hexafluorophosphate in 70 % isolated yield with 1H NMR spectroscopic data almost identical to those of 2a. Yellow single crystals of 2a were grown by slow diffusion of diethyl ether or pentane into a dichloromethane solution of 2a. Single crystal structure analysis: Figure 1. Spectra: supporting information.
cm⁻¹. HRMS (ESI pos): C₃₀H₄₀FeN₁₂Ru₂, calcld. most abundant isotope peak 932.1410 [M – e⁻], found m/z = 932.1371. Spectra: supporting information.

**Ni Complex 6**: In a similar manner as described above in the synthesis of 4a, ligand precursor 2a (148 mg, 0.201 mmol) was deprotonated to its potassium salt 3. The mixture was cooled to −80 °C, dibromo(dimethoxyethane)nickel(II) (32.6 mg, 0.106 mmol) was added and stirring was continued at −80 °C for 5 h. The mixture warmed to room temperature and stirring was continued for 4 d, affording a brown mixture. Workup under protection from air: Side products were removed by filtration, tetrahydrofuran was stripped off in vacuo, the residue was dissolved in dry dichloromethane, the solution was filtered and the crude product was obtained by removal of dichloromethane in vacuo. Contaminations were precipitated in a mixture of dry dichloromethane/n-hexane (1:20) at low temperature (−15 °C) overnight and removed by filtration. After evaporation of the solvent mixture the red, paramagentic complex 8 was obtained in 61 % yield (0.0613 mmol, 59.1 mg). IR (ATR): ν = 2962, 2926, 2907, 2855 (CH), 1483, 1446, 1413, 1365, 1341 (C=H, C=O, N=N), 1258, 1082, 1011 (CH), 790 (CH), 627 (CC) cm⁻¹. HRMS (ESI pos): C₃₀H₄₀Ni₂Ru₂, calcld. most abundant isotope peak 940.1435 [M + H⁺], found m/z = 940.1386. Single crystals were obtained from a dichloromethane/n-hexane solvent mixture. Single crystal structure analysis: Figure 5. Spectra: supporting information.

CCDC 1850062 (for 2a), 1850063 (for 4b), 1850064 (for 6), 1850065 (for 7), and 1850066 (for 8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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