Bimetallic Complexes

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Bismetallocenes: Lanthanoid–Transition-Metal Bonds through Alkane Elimination**

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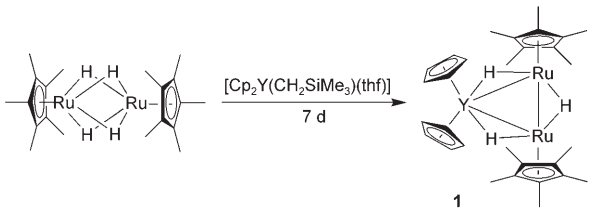
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th anniversary

The synthesis of multinuclear complexes, in particular systems with different metals, is an intensely studied branch of modern coordination chemistry.[1] Metal–metal bonds are of special interest in this regard, because their significance goes far beyond the borders of chemistry.[2] The variety of bonding phenomena among transition metals, which can range from strongly polar direct metal–metal bonds in heterodinuclear complexes[3] to quintuple bonds in homodinuclear complexes,[4] is in contrast to the one example[5] in which a direct bond between a lanthanoid metal and a transition metal is observed: $[(thf)Cp_2Lu\text{-}RuCp(CO)_2]$ (Cp = cyclopentadienyl).[6,7] The donor–acceptor bonds described by Roesky[8] and co-workers are also interesting in this regard, since they represent examples of direct bonds between main-group metals and lanthanoids.[9] In our previous work, we were interested in metal–metal communication in heterodinuclear complexes in which lanthanoids and late transition metals were "held together" by virtue of coordinated bridging aminopyridinato ligands.[10] Herein we report that unsupported metal–metal bonds between transition metals and rare earth elements are accessible by alkane elimination.

Heterobimetallic complexes in which lanthanoids and transition metals are bridged by hydride ligands have been prepared by H_2 elimination,[11] salt elimination,[12] and alkane elimination.[13] The alkane elimination route should be the most promising and efficient method for the stabilization of heterobimetallic complexes with direct metal–metal bonds, since the eliminated alkane is relatively inert, and a difficult workup procedure can be avoided. The treatment of $[\{Cp^*RuH_2\}_2]$ (Cp^* = pentamethylcyclopentadienyl)[14] with $[Cp_2Y(CH_2SiMe_3)(thf)]$[15] afforded the trihydride complex $[H(Cp^*Ru)_2H_2YCp_2]$ (**1**) in 44% yield (Scheme 1).



Scheme 1. Synthesis of **1**.

NMR spectroscopy supports the structural arrangement presented in Scheme 1 as well as the presence of three bridging hydride ligands. At ambient temperature a doublet with a coupling constant of $J_{YH} = 10.5$ Hz is observed for these three hydride ligands. Cooling the sample results in line broadening, and at temperatures below 233 K two signals in the ratio 2:1 are registered. At $\delta = -13.9$ ppm a doublet (Y–Ru bridging hydride ligands) with a coupling constant $J_{YH} = 15.4$ Hz is observed, which is accompanied by a singlet at $\delta = -15.4$ ppm (Ru–Ru bridging hydride ligand).

The molecular structure of **1** was determined by X-ray single crystal analysis and is presented in Figure 1.[16] The Ru–Y separations amount to 3.0396(5) (to Ru1) and 3.0514(5) Å

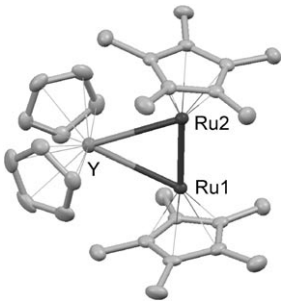


Figure 1. Molecular structure of **1** (ORTEP plot without H atoms, 50% probability level). Selected bond lengths [Å] and angles [°]: Ru1–Y1 3.0396(5), Ru2–Y1 3.0514(5), Ru1–Ru2 2.4881(5), $Cp_{centroid}$–Y1 2.387 (average value); Ru1-Y1-Ru2 48.219(11), $Cp_{centroid}$-Y1-$Cp_{centroid}$ 124.46.

(to Ru2) and the Ru–Ru separation is 2.4881(5) Å. The positions of the three hydride ligands could not be determined despite the high quality of the crystal structure analysis.[17]

The reaction of monohydride complexes, for example $[Cp_2ReH]$,[18] with lanthanoid monoalkyl complexes should lead to hydride-free bimetallic complexes. Especially promising are alkyl complexes of the type $[Cp_2LnR(thf)]$ (Ln = lanthanoid, R = alkyl). Both metal-complex components will be stabilized by the same ligands, and ligand transfer reactions that could lead to decomposition of lanthanoid–transition-

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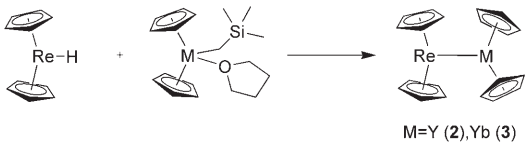
metal complexes[19] are rendered irrelevant. The reaction of $[Cp_2ReH]$[18] with $[Cp_2Y(CH_2SiMe_3)(thf)]$[15] in toluene at −80 °C with subsequent warming to ambient temperature within three hours, removal of volatiles, and washing with hexane afforded orange complex **2** in 91 % yield (Scheme 2).



Scheme 2. Synthesis of **2** and **3**.

The ^{1}H NMR spectrum of **2** shows only two signals assigned to Cp ligands and no signals indicating the presence of hydride ligands in the temperature range from −95 °C to 90 °C. The signal of **2** in the ^{89}Y NMR spectrum shows no coupling, in contrast to the quartet ($J_{HY} = 10.4$ Hz) of **1**, thus additionally excluding the presence of hydride ligands. The molecular structure of **2** was determined by X-ray single crystal structure analysis and is presented in Figure 2 (top).[20]

The value of 2.9617(19) Å determined for the metal–metal separation in **2** in the solid state lies in the range expected for a lanthanoid–transition-metal bond[5] and is consistent with the value found for a Ru–Lu bond (2.995(2) Å).[6] The former is more than 0.12 Å shorter than distances observed for hydride-bridged Re–Y bonds.[13a,b] The arrangement of Cp ligands at the metal centers is different. The observed $Cp_{centroid}$-M-$Cp_{centroid}$ tilt angles differ by about 37°.

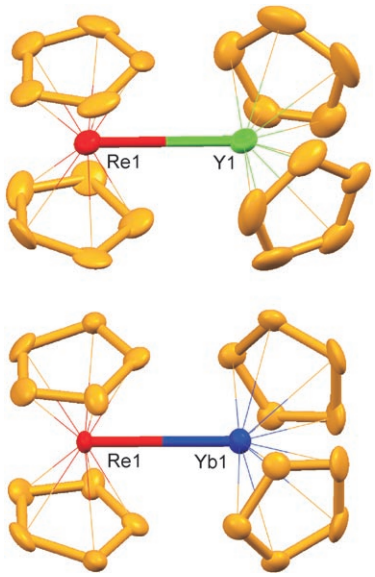


Figure 2. Molecular structure of **2** (top) and of **3** (bottom; ORTEP plot without H atoms, 50% probability level). Selected bond lengths [Å] and angles [°] for **2**: Re1–Y1 2.9617(19), $Cp_{centroid}$–Re1 1.8465, $Cp_{centroid}$–Y1 2.3465 (average value); $Cp_{centroid}$-Re1-$Cp_{centroid}$ 165.63, $Cp_{centroid}$-Y1-$Cp_{centroid}$ 128.56. For **3**: Re1–Yb1 2.8971(17), $Cp_{centroid}$–Re1 1.833, $Cp_{centroid}$–Yb1 2.294 (average value); $Cp_{centroid}$-Re1-$Cp_{centroid}$ 167.41, $Cp_{centroid}$-Yb1-$Cp_{centroid}$ 130.02.

The nature of the metal–metal bond was analyzed at DFT level[21] by means of topological analysis of the electron localizability indicator (ELI-D)[22] and the electron density in position space. The applied molecular structure model was obtained from optimization of the H-atom positions of the experimental structure data. On this basis single-point calculations for the whole molecule $[Cp_2Re\text{-}YCp_2]$ as well as for the separated fragments $[Cp_2Y]^+$ and $[ReCp_2]^-$ were performed. The topological analysis of ELI-D shows three local maxima (attractors) in the hemisphere of the valence region of the Re atom directed towards the Y atom. The attractor that is most pronouncedly directed towards the Y atom is noticeably displaced from the Re–Y bond axis, but nevertheless it displays a (Re,Y)-disynaptic basin (Figure 3 a) indicating a covalent Re–Y interaction.

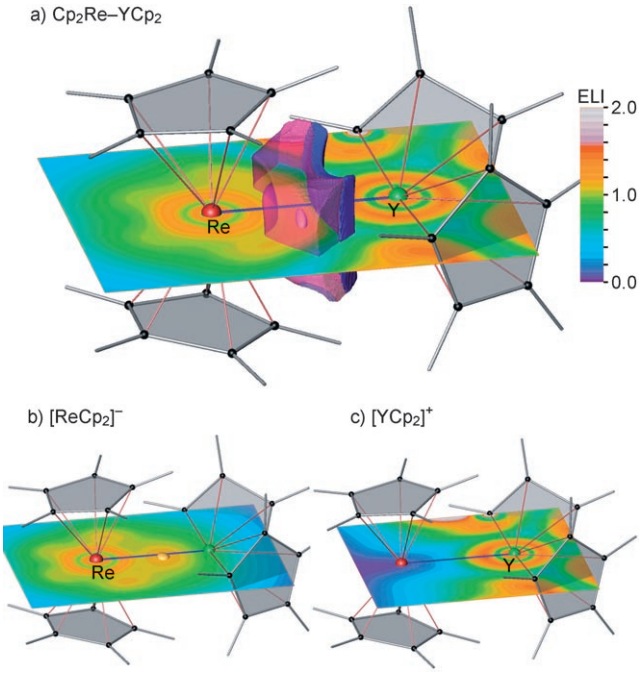


Figure 3. a) ELI-D (values according to color scale) for **2**: the part of the ELI-D bonding basin belonging to the Y atom (blue, opaque) and the part of the ELI–D bonding basin belonging to the Re atom (red, transparent) are shown. The part of the ELI–D bonding basin belonging to the Re atom contains the ELI-D attractor, which is depicted as a 1.14 localization domain of ELI-D. b) ELI-D for the fragment $[ReCp_2]^-$. The ELI-D attractor in the proximity of the (virtual) internuclear line is depicted as a 1.14 localization domain of ELI-D. c) ELI-D for the fragment $[YCp_2]^+$.

To characterize the polarity of the Re–Y bond in position space, a procedure was applied that was originally proposed by Jansen et al.[23] to describe qualitatively the polarity of metal–metal bonds in heterobimetallic complexes and that was only later put on a quantitative basis.[24] For this purpose, the electronic population (charge) of the ELI-D bonding basin is partitioned between the atomic density basins, which define the so-called Bader's atoms (QTAIM method[25]), by means of a spatial intersection procedure. The observed (Re,Y)-disynaptic ELI-D bonding basin displays a basin

population of 0.83 electrons. The density basin of the Re atom contains about 84% of this population, and that of the Y atom only 14%. This result provides a clear indication of the strong polarity of the bond. It is interesting to compare the bimetallic complex with the separated unrelaxed monometallic fragments $[YCp_2]^+$ and $[ReCp_2]^-$ in a computer experiment. In the case of the fragment $[ReCp_2]^-$, ELI-D shows three attractors in the valence region, one of which is directed towards the Y atom in the bimetallic complex (Figure 3b). Even in the absence of the Y bonding partner, the specific bending of the ligands at the Re center effects the formation of a region of high electron localizability in the direction of the subsequent bonding partner. It should be noted that the relaxed $[ReCp_2]^-$ unit (isoelectronic with ferrocene) exhibits a linear arrangement of both ligands as expected, and therefore, the bending is already related to metal–metal bond formation. For the fragment $[YCp_2]^+$, ELI-D shows a local minimum in the valence region in the direction of the subsequent bonding partner (Figure 3c). Thus, the two unrelaxed monometallic fragments exhibit opposed and, hence, compatible regions of electron localizability and electron pairing. On the basis of this finding, the Re–Y bond is classified as a donor–acceptor interaction.

The reaction of $[Cp_2ReH]$[18] with in situ generated $[Cp_2Yb(CH_2SiMe_3)(thf)]$[26] afforded the dark green Yb–Re bimetallic complex **3**, thus underlining the general validity of the chosen synthetic protocol. The molecular structure of **3** was determined by X-ray single crystal analysis and is presented in Figure 2 (bottom).[27] The shorter metal–metal bond in **3** in comparison with **2** is in good accordance with the smaller ionic radius of Yb than Y.[28] The complexes **2** und **3** are not isomorphous and represent different Cp rotation isomers.

In further investigations we are interested in the reactivity of the types of metal–metal bonds discussed herein, in physical properties (for example optical or magnetic) of the bimetallic complexes, and in the general validity of the alkane elimination route for the preparation of complex compounds with direct bonds between a lanthanoid and a transition metal.

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