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Metal–Metal Bonding

Molecular Lanthanoid–Transition-Metal Cluster through C–H Bond Activation by Polar Metal–Metal Bonds**

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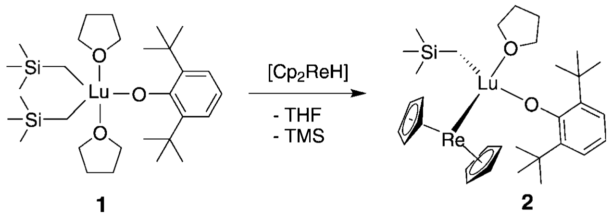
Metal–metal bonds have been fascinating scientists for long time[1] and nowadays a lot of enthusiasm is devoted to unsupported[2] metal–metal bonds.[3–5] Until now unsupported Ln–TM bonds (Ln = lanthanoid, TM = transition metal) could only be found in a few compounds.[6–10] These bonds are rather polar[7,11] and are important for the fundamental understanding of bonding phenomena between these metals. An improved understanding of a Ln–TM bond is important because intermetallic compounds of these metals play an important role in everyday life.[12–14] The high bond polarity should allow a systematic approach towards highly aggregated systems.[9,10,15] To date there has been little exploration of the reactivity of such Ln–TM bonds.[6–10] Herein we show how metal clusters can be prepared by multiple C–H bond activations at Ln–TM bonds, which leads to the formation of doubly deprotonated Cp ligands. (Cp = cyclopentadienyl). The starting point of this reaction sequence is the four-coordinate rare-earth-metal compound **2** which has a chiral lanthanoid atom.

We recently explored the reaction of tris(alkyl) Ln compounds with $[Cp_2ReH]$ and ascertained that in addition to triply Re-bonded Ln complexes, polymeric insoluble by-products are formed in bulk (66–99 %).[9] Since the reaction of $[Cp_2Y(thf)(CH_2SiMe_3)]$ (Me = methyl) with the above-mentioned rhenium hydride proceeds in very good yields,[7] it was suspected, that the presence of one Ln–carbon bond brings about side reactions of the Ln–TM bond leading to those polymeric materials. Now, if one wants to understand and to use such (side) reactions purposefully, a bis(alkyl) Ln compound which allows the substitution of one of the two alkyl ligands by Cp_2Re-ligands should be exploited. The reaction of $[Lu(thf)_2(CH_2SiMe_3)_3]$[16] with one equivalent of 2,6-di-*tert*-butylphenol affords bis(alkyl) **1** in high yields (Scheme 1). The new complex reacts selectively with one equivalent of $[Cp_2ReH]$ to yield compound **2** (Scheme 1).



Scheme 1. Synthesis of **2**.

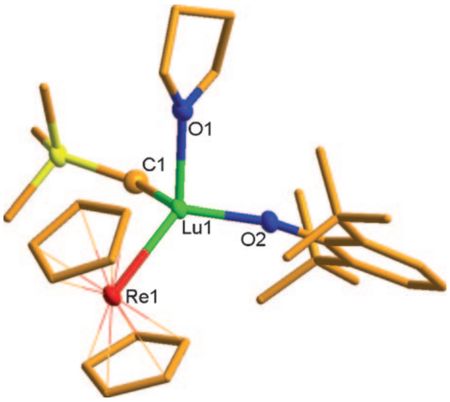


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: O1–Lu1 2.271(7), O2–Lu1 2.054(7), Lu1–Re1 2.8498(6), C1–Lu1 2.359(10); O2-Lu1-O1 98.1(3), O2-Lu1-C1 108.3(3), O1-Lu1-C1 90.3(3), O2-Lu1-Re1 119.1(2), O1-Lu1-Re1 122.76(18), C1-Lu1-Re1 113.9(3).

The molecular structure of **2** as determined by X-ray structural analysis is shown in Figure 1. The lutetium ion in **2** is four-coordinated, in a tetrahedral environment, and is chiral owing to the different substituents. The selective introduction of four different substituents appears to be complicated for rare earth ions, which have a tendency for very high coordination numbers. The Lu–Re distance is 2.8498(6) Å and is significantly shorter than the Lu–Ru distance of 2.955(2) Å in $[Cp_2(thf)Lu\text{-}Ru(CO)_2Cp]$[6] and almost identical with the average value of the Lu–Re bonding distances in $[Lu(ReCp_2)_3]$[9] [2.886(1)]. The Lu–C bond in **2** is 2.359(10) Å and complies with the expected value for such a bond (2.3781 Å).[17]

The ^1H NMR spectrum of **2** shows strong temperature dependence (at 188–295 K; see the Supporting Information). By virtue of the chirality, the signal belonging to the protons of the CH_2-group of the alkyl ligand appears as AB spin system. By analogy the protons of the coordinated THF ligand should display more than two groups of signals. At room temperature, however, only two broad signals are observed for the H atoms of THF ligand and for the CH_2 group merely one broad signal. Upon cooling to 253 K signal separation occurs and for the CH_2 group (typical) geminal

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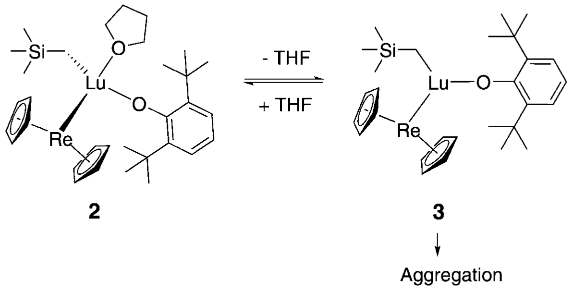
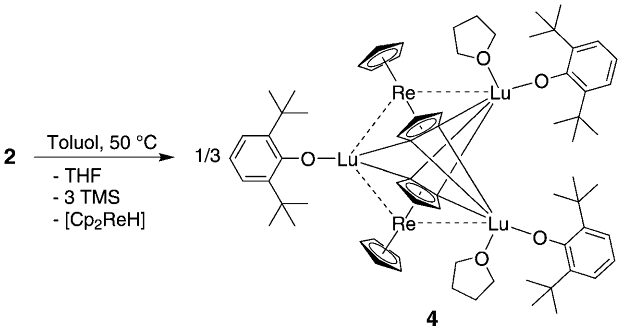
coupling of 12 Hz is observed. Such dynamic behavior can be interpreted by racemization which is “frozen” at low temperatures. Feasibly the dissociation of the THF ligand occurs which leads to three-coordinated intermediate **3** (Scheme 2).



Scheme 2. Dynamic behavior of **2**.

Further cooling leads to the broadening of all signals. This process starts at 243 K and a coalescence for the signals of the Cp rings and of the *tert*-butyl groups is observed at 225 K. Simple freezing of the rotation around the metal-metal bond can be excluded from consideration since the signals do not become sharp upon further cooling. The Cp signals become even broader at lower temperature ($\nu_{1/2} = 23$ and 45 Hz [188 K]). Taking into account the formation of the cluster from **2** (Scheme 3), we assume that aggregation of the low-coordinate compound **3** occurs at lower temperatures. At the same time it can lead to intermolecular interaction of the Cp rings with the Lu atom of the second aggregation partner, which induces C–H activation and, therefore, explains the broadening of the signals.



Scheme 3. Synthesis of **4**.

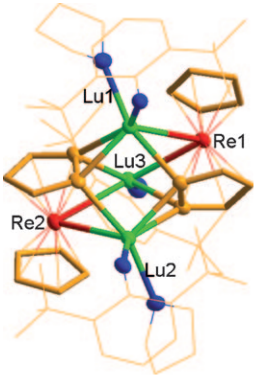


Figure 2. Molecular structure of **4**. The whole molecule (ORTEP-Plot thermal ellipsoids are set at 50% probability for selected atoms, H-atoms are omitted). Selected bond lengths [Å] and angles [°]; C1 and C5 as well as C6 and C10 are neighboring deprotonated carbon atoms of the Cp ligands]: C1–C5 1.511(10), C6–C10 1.505(9), C1–Re2 2.233(6), C1–Lu1 2.378(7), C1–Lu2 2.415(8), C5–Re2 2.220(7), C5–Lu3 2.441(7), C5–Lu1 2.463(7), C6–Re1 2.234(7), C6–Lu2 2.373(7), C6–Lu1 2.408(7), C10–Re1 2.224(7), C10–Lu3 2.413(7), C10–Lu2 2.446(7), Lu1–Re1 2.9981(4), Lu2–Re2 2.9842(4), Lu3–Re1 2.9120(4), Lu3–Re2 2.9197(4); Lu3-Re2-Lu2 72.929(11), Lu3-Re1-Lu1 73.442(10).

Upon warming the unstable compound **2**, tetramethylsilane (TMS) and [Cp_2ReH] are eliminated and cluster compound **4** (Scheme 3) is formed. The molecular structure of **4** is shown in Figure 2. The central structural element of this cluster consists of two rhenium ions, three lutetium ions and two doubly deprotonated Cp ligands. The aggregation of **3** can probably induce the formation of **4**. The activation of the C–H bonds of the Cp ligands leads to the formation of η^5-μ^4-Cp ligands. Upon four of these C–H activation reactions three trimethylsilylmethyl ligands and one Cp_2Re “ligand” are eliminated as tetramethylsilane and as [Cp_2ReH], respectively. Such selective multiple deprotonations of Cp ligands are rare and were observed for ferrocene and related Ru or Os compounds in the form of 1,3-deprotonations.[18] The here observed selective 1,2-bis-deprotonation of one Cp ring of a metallocene is unusual.[19] The three Lu ions of the central structural element form an approximately equilateral triangle with two sides being bridged by C_2Re triangles.

To clarify the bonding situation in **4** the electronic structure was calculated at scalar relativistic level of density functional theory (DFT/BLYP).[20] The quantum chemical analysis of chemical bonding with focus on rare earth-transition metal interactions was performed, as in our thematically related investigations on organometallic molecules[7,9,10] and intermetallic solids,[21,22] on the basis of electronic properties in position space. The employed quantities are the electron density and the electron localizability indicator ELI-D.[23] Topological analysis of the electron density and ELI-D yields the QTAIM atoms (QTAIM method[24]) and atomic shells, bond and lone-pair regions, respectively. (Further information about ELI-D as well as its relation to electron localization function ELF[25] is available in the Supporting Information.)

All unsupported rare-earth–transition-metal bonds in molecular systems[6–10] known to date feature polar two-center bonds of the type TM→Ln. The topological analysis of ELI-D reveals one or two bond maxima per TM–Ln contact with basins always touching only the core of one TM and one Ln atom, that is, (1TM,1Ln) disynaptic basins. The topological analysis of ELI-D for **4** yields three local bonding maxima in the valence region between each Re and the two bridged Lu atoms. The three basins belonging to them are connected with each other and arranged in a way that the middle one (ca. 0.8 e) is directed exactly between both bridged Lu atoms, while each of the other two (ca. 0.4 e and 0.6 e) is directed towards one Lu neighbor only (Figure 3). Each of the two

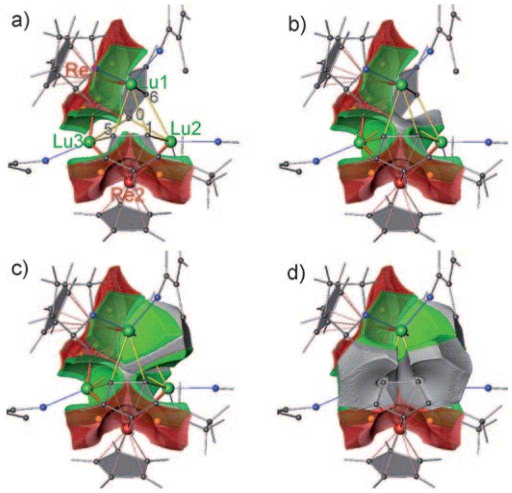


Figure 3. Compound **4**, ELI-D/QTAIM intersection of lone-pair basins: a) the Re lone-pair basins (QTAIM Re contribution red, Lu contribution green) with ELI-D Maxima (yellow–brown), b) additionally the C10 lone pair (QTAIM C contribution gray), c) additionally the C6 lone pair, d) additionally the C1 and C5 lone pairs.

outer basins is touching the ELI-D core region of one respective Lu and the Re atom, which is characterized as (1Re,1Lu)-disynaptic and is considered as a feature of two-center bonding.[26] On the other hand the middle basin touches all three core regions and is therefore characterized as (1Re,2Lu)-trisynaptic indicating a three-center bond. Altogether a three-center bonding situation is revealed, for which also separate two-center parts can be identified.[27] However, such a detailed analysis of separate two- and three-center parts is not intended. Since the maxima of the corresponding basins are connected with each other by very flat gradient paths, they were combined in one (1Re,2Lu)-trisynaptic basin set[28] and analyzed together. The electronic populations of the resulting bonding regions Lu1-Re1-Lu3 und Lu2-Re2-Lu3 are 1.78 e and 1.81 e.

In comparison with the corresponding diatomic contacts known to date, the present triatomic contacts Lu-Re-Lu clearly show the highest electronic populations both in the bonding basin and in the valence region of the Re atoms.

A similar observation was already made during the analysis of lower populated four- and the higher populated six-center Os–La bonds in the solid-state compound $La_7Os_4C_9$.[21] Clearly there seems to be a direct correlation between the number of electrons in two- or multicenter TM–Ln_n bonding basin and the number n of significantly involved rare-earth-metal atoms.

The polarity of the Re–Lu bond was determined, as in related investigations,[7,9,10,21,22] employing the ELI-D/QTAIM-intersection (in analogy to Ref. [29]) procedure. In this procedure the spatial region of the ELI-D bonding basin is partitioned between QTAIM atoms (atomic electron density basins) and the electronic population is divided correspondingly. It turns out that 81 % of the population belong to the Re atom and 8 % belong to each of the Lu atoms. The comparison with already known molecular compounds with Ln–TM two-center bonds shows that the portion belonging to TM is always roughly (82 ± 5) %, also in cases of clearly increased absolute electron populations, and it is relatively independent from the number of significantly involved rare earth atoms. This was already found for the solid state compound $La_7Os_4C_9$ with two chemically different Os species,[21] where a corresponding Os "lone pair" is connected to three or five La atoms in each of the four- or six-center Os–La bonds, respectively. It is a new observation that such rare earth-transition metal bonding situations can be obtained for molecules as well. Thus, in this framework a new scenario at the molecular scene was found, namely a polar $ReLu_2$ three-center bond for compound **4**.

It is interesting to compare Lu–Re und Lu–C bonds with each other in **4**. All three edges of Lu_3 triangles are doubly bridged, one of them by two carbanions of different Cp-(C_5H_3)Re moieties and two of them each by one Re atom and one carbanion from the other Cp(C_5H_3)Re moiety. Each four atoms Lu1, Lu3, Re1, C5 and Lu2, Lu3, Re2, C10 are almost lying within one plane and the corresponding "lone pairs" of one carbanion and one Re cation are directed towards each other (Figure 2 and 3 b,d). Owing to the small bonding angle Lu-Re-Lu of 73° the distance d(Re-C) of 4.04 or 4.05 Å is relatively large. In this way strong "lone-pair–lone-pair" interaction is avoided and the Lu atoms can coordinatively share the free electron pairs. Considering the results of ELI-D/QTAIM intersections of all chemically relevant bonding basins for each Lu species (Table S1 in the Supporting Information) one can ascertain the following: each of the comparatively strongly populated (2.9 e) "lone-pair" basins of the carbanions ($C_5H_3^{3-}$) donates to the Lu QTAIM atoms only (0.19 ± 0.01) e on average, while each Re "lone pair" (basin set) with basin populations of approximately 1.9 e donates already 0.29 e on average. The donor ability of the Re "lone pairs" with regard to the Lu atoms is, therefore, more pronounced than that of the carbon "σ-lone pairs" in $C_5H_3^{3-}$ ligands. As it is shown in the following, this leads to the result that the effective charge of the Lu species Lu3 with two Re ligands is +1.78, which is slightly lower compared to both other species Lu1 and Lu2 (each +1.91). With the aid of the ELI-D partitioning this charge difference of the QTAIM atoms can be divided into a part from the internal atomic shells and a part from the valence shell. The number of electrons in the valence shell of the QTAIM Lu atoms is given by the portions of the donor "lone-pair" ELI-D basins that are intersected by the QTAIM atom. It turns out (Table S1 in the Supporting information) that the valence shell of Lu3 contains 0.66 e, which is 0.10 e more than those of Lu1,2, although the coordination number (CN) of Lu3 (CN = 5) is one less than that of Lu1,2 (CN = 6). Just the comparison (Table S1 in the Supporting information) of the coordination "2Re + 2C" (donates 0.54 e in total) for Lu3 with "1Re + 3C" (donates 0.42 e in total) for Lu1,2 reveals the significant difference. The additional THF ligand (donates 0.04 e) on Lu1,2 is not able to compensate this difference.

Polar Ln–TM bonds undergo spontaneous C−H activation reactions. These can be rationally used to prepare Ln–TM clusters containing metal–metal bonds. This synthetic concept should find application and, for example, should allow the combination of paramagnetic centers to give molecular materials with interesting magnetic phenomena. Such novel clusters are also of interest as multimetal platforms for the activation of small (inert) molecules.

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