Gallium(I)−Lanthanide(II) Donor−Acceptor Bonds

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Summary: Compounds with a gallium−lanthanide metal-to-metal bond, [(η^5-C_5Me_5)$_2$Eu−{Ga(η^5-C_5Me_5)}$_2$] and [(η^5-C_5Me_5)$_2$(THF)Yb−Ga(η^5-C_5Me_5)], were prepared by reacting [(η^5-C_5Me_5)Ga] with the corresponding metallocenes of the lanthanides.

Introduction

Metal-to-metal bonds in clusters are of fundamental interest in many areas in natural science.[1] In coordination chemistry metal-to-metal bonds in rare earth complexes are almost unknown because the 4f valence shell is embedded into the interior of the ion, well-shielded by the filled 5s and 5p orbitals.[2] To the best of our knowledge, only one example of a nonsupported metal-to-metal bond exists between a d-metal and a lanthanide ([(THF)(η^5-C_5H_5)$_2$Lu−Ru(CO)$_2$(η^5-C_5H_5)]).[3]

The discovery of unusual low-valent group 13 compounds such as [(η^5-C_5Me_5)Al]$_4$[4] and [(η^5-C_5Me_5)Ga],[5,6] and many more,[7−10] in the 1990s has inspired a number of research groups to use group 13 diyls as reagents in main group[11−16] and in transition metal chemistry.[6,17−22] In late transition metal chemistry the group 13 diyls are considered as isolobal with CO and PR_3.[18] Theoretical studies have shown that the HOMO of univalent RM molecules exhibits distinctly lone pair character, allowing the group 13 diyls to act also as a Lewis base.[11,23] The first example featuring a group 13 diyl as a pure donor ligand with no back-bonding was the aluminum−boron donor−acceptor adduct [(η^5-C_5Me_5)Al−B(C_6F_5)$_3$].[11] By using this strategy we attached very recently in a solid-state reaction [(η^5-C_5H_5)Al] onto the metallocenes of the divalent lanthanides forming main group−4f-metal bonds of composition [(η^5-C_5Me_5)$_2$Ln−Al(η^5-C_5Me_5)] (Ln = Eu, Yb), which were shown by theoretical investigations to be dominantly electrostatic with insignificant charge-transfer and covalent contributions.[24] Now, we are interested in coordinating the heavier congener, a [(η^5-C_5Me_5)Ga] fragment, onto the lanthanides because to the best of our knowledge there are no known lanthanide−gallium bonds in coordination chemistry.[25] Only LnGa alloys were reported forming a CrB-type solid-state structure.[26]

Reaction of [(η^5-C_5Me_5)Ga] with the divalent metallocenes of europium and ytterbium [(η^5-C_5Me_5)$_2$Eu] and [(η^5-C_5Me_5)$_2$Yb(THF)$_{1-n}$][27] in toluene at room temperature resulted in donor−acceptor complexes of composition [(η^5-C_5Me_5)$_2$Eu−{Ga(η^5-C_5Me_5)}$_2$] (**1**) and [(η^5-C_5Me_5)$_2$(THF)Yb−Ga(η^5-C_5Me_5)] (**2**) (Scheme 1). Surprisingly by using pure [(η^5-C_5Me_5)$_2$Yb(THF)] as starting material fast decomposition of the resulting product was observed. More stable solutions and higher yields are obtained when the coordinated THF was partly removed beforehand. Attempts to prepare a solvent-free Yb complex failed. Nevertheless, compound **2** decomposes, maybe as a result of the coordinated THF molecule, much faster than compound **1**. A similar situation was found in the earlier reported strontium compound [(η^5-C_5Me_5)$_2$(THF)Sr−Ga(η^5-C_5-

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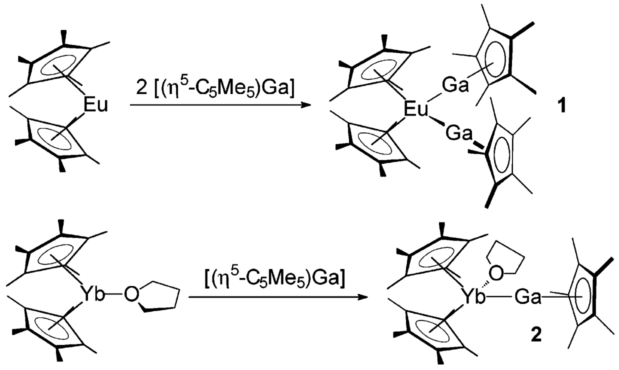
Scheme 1



Me_5)].[16] The new complexes have been characterized by standard spectroscopic techniques, and the structures were confirmed by single-crystal X-ray diffraction in the solid state (Figure 1 and 2). Whereas the lanthanide−aluminum complexes [(η^5-C_5Me_5)$_2$Ln−Al(η^5-C_5Me_5)], which are formed via a solid-state reaction, rapidly decompose in solution, compounds **1** and **2** are stable in hydrocarbon solvents. They are formed in toluene, and NMR spectra could be obtained. This is a bit surprising because [(η^5-C_5Me_5)Al] is considered to be a slightly stronger base than [(η^5-C_5Me_5)Ga], which is consistent with the general trend that basicity decreases upon descending a group in the periodic table.[11] In the ^{1}H NMR spectrum compound **1** shows, as a result of the paramagnetic center metal, only an uncharacteristic broad peak for the (η^5-C_5Me_5) ligands. In contrast for the diamagnetic compound **2** two sharp singlets are observed for each set of the (η^5-C_5Me_5) ligands. The observed chemical shifts are very close to those reported for the starting materials. Thus, the signal of the [(η^5-C_5Me_5)Ga] fragment is observed at δ 1.92 ppm, which is the same as the reported resonance of pure [(η^5-C_5Me_5)Ga] (δ 1.92 ppm).[6] A similar effect is seen for the [(η^5-C_5Me_5)$_2$Yb] fragment, which shows a resonance at δ 2.04 ppm (2.12 ppm in [(η^5-C_5Me_5)$_2$Yb(THF)]).[27] The NMR indicates that the oxidation state of the diamagnetic compound **2** correlates with the corresponding starting materials. No signal of any hydrido species could be observed.

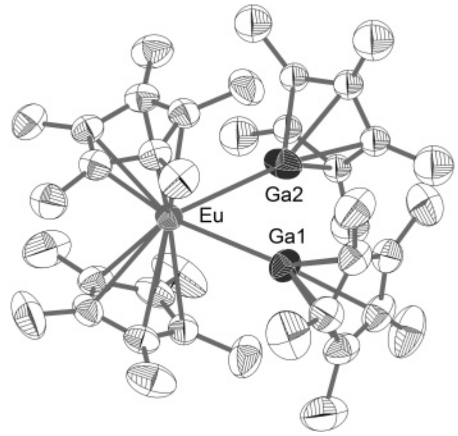


Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Eu−Ga1 3.2499(6), Eu−Ga2 3.3907(6), Cg_{Ga1}−Ga1 1.997(1), Cg_{Ga2}−Ga2 2.000(1), Cg_1−Eu 2.516(1), Cg_2−Eu 2.529(3); Ga1−Eu−Ga2 79.42(2), Cg_{Ga1}−Ga1−Eu 176.89(10), Cg_{Ga2}−Ga2−Eu 167.77(10), Cg_1−Eu−Cg_2 142.29(10), Cg_1−Eu−Ga1 101.5(10), Cg_2−Eu−Ga1 103.24(10), Cg_1−Eu−Ga2 10.87 (10), Cg_2−Eu−Ga2 104.34(10), (Cg = ring centroid).

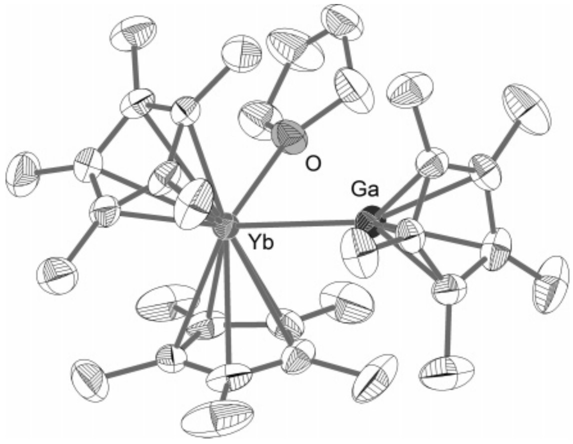


Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Yb−Ga 3.2872(4), Yb−O 2.418(2), Cg_{Ga}−Ga 2.012(10), Cg_1−Yb 2.434(10), Cg_2−Yb 2.440(10); Ga−Yb−O 89.69(6), Cg_{Ga}−Ga−Yb 176.10(10), Cg_1−Yb−Cg_2 140.37(10), Cg_1−Yb−Ga 99.02(10), Cg_2−Yb−Ga 103.09(10).

The solid-state structures of **1** and **2** both consist of individual Lewis acid−base adducts without any unusually short intermolecular contacts.[28] Compound **1** is a trimetallic species in which two [(η^5-C_5Me_5)Ga] units are coordinated to the Eu center (Figure 1). The Ga−Eu distances are 3.2499(6) and 3.3907(6) Å, and the Ga1−Eu−Ga2 angle is 79.42(2)°. All four C_5Me_5 groups are η^5-coordinated. The ring centroid−Ga−Eu angles differ by about 9° with values of 176.89(10) (Cg_{Ga1}−Ga1−Eu) and 167.77(10)° (Cg_{Ga2}−Ga2−Eu). The Ga−C distances of **1** range from 2.250(11) to 2.330(5) Å and thus are in the range of those observed in the carbonyl complexes [$(CO)_5$Cr−Ga(η^5-C_5Me_5)][6] (2.236(3) to 2.282(4) Å) and [$(CO)_4$Fe−Ga(η^5-C_5Me_5)][6] (2.193(2) to 2.2576(15) Å).

As a result of the smaller ion radius of Yb(II) compared to Eu(II), only one [(η^5-C_5Me_5)Ga] unit is coordinated to the lanthanide atom of **2** (Figure 2). All three C_5Me_5 groups in one molecule are attached in a η^5-fashion. The ring centroid−Ga−Yb angle is slightly bent (176.10(10)°), which may be the result of packing effects. This is in agreement with related d-metal complexes such as [$(CO)_5$Cr−Ga(η^5-C_5Me_5)][6] and [$(CO)_4$Fe−Ga(η^5-C_5Me_5)],[6] as well as the Sr−Ga complex [(η^5-C_5Me_5)$_2$(THF)Sr−Ga(η^5-C_5Me_5)] (175.15(10)°).[16] The Yb−ring centroid bond distances (Cg_1−Yb 2.434(10) Å and Cg_2−Yb 2.440(10) Å) are in the range of [(η^5-C_5Me_4Et)$_2$Yb(THF)] (2.408(7) Å[29]) and [(η^5-C_5Me_5)$_2$Yb(THF)] (av 2.37 Å).[27] The gallium−ytterbium bond distance is 3.2872(4) Å. Since we present the first gallium−lanthanide(II) bonds, the observed Ga−Eu and Ga−Yb distances cannot be compared with other data from molecular compounds.

Quite interesting is a comparison between **1** and **2** and the related alkaline earth metal complexes. It is well-established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals are somewhat similar.[30] This similarity in coordination chemistry

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[28] Crystal data for **1** and **2**: **1**: space group *C2/c* (No. 15), $a = 20.0374(14)$ Å, $b = 12.304(2)$ Å, $c = 32.450(2)$ Å, $\beta = 93.294(6)°$, $V = 7987.1(13)$ Å^3, $T = 200$ K, $Z = 8$, 28 190 reflections collected, 7035 unique reflections ($R_{int} = 0.0750$), $R_1 = 0.0385$ and $wR_2 = 0.1014$. **2**: space group *Pbca* (No. 61), $a = 15.9742(7)$ Å, $b = 22.7462(11)$ Å, $c = 18.2842(13)$ Å, $V = 6643.6(6)$ Å^3, $T = 200$ K, $Z = 8$, 16 462 reflections collected, 5848 unique reflections ($R_{int} = 0.0380$), $R_1 = 0.0259$ and $wR_2 = 0.0496$.

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originates from the similar ion radii (for CN 6 (pm): Ca^{2+} 100, Yb^{2+} 102, Sr^{2+} 118, Eu^{2+} 117, Ba^{2+} 135).[31] In contrast to these observations the Yb compound **2** is not, as expected, similar to the recently reported Ca−Ga compound $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ca}{-}\text{Ga}(\eta^5\text{-C}_5\text{Me}_5)]$. Instead the coordination polyhedron of **2** resembles the Sr complex $[(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})\text{Sr}{-}\text{Ga}(\eta^5\text{-C}_5\text{Me}_5)]$. Moreover, the Eu compound **2** is thus not, as expected, an analogue of the Sr complex but similar to the trimetallic Ba−Ga cluster $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ba}{-}\{\text{Ga}(\eta^5\text{-C}_5\text{Me}_5)\}_2]$.[16] Nevertheless, the Ln−C bond distances of **1** and **2** to the $(\eta^5\text{-C}_5\text{Me}_5)$ rings are in the expected range.[29] There is also a striking difference between the Ln−Ga and the Ln−Al complexes. Whereas for Al only complexes of composition $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ln}{-}\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]$ (Ln = Eu, Yb) are obtained, additional ligands are coordinated on the Ga complexes. The additional coordination sites of the Ln−Ga complexes may be a result of the larger Ln−Ga bond distance.

In summary, we present for the first time the coordination of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ga}]$ onto the lanthanide metals. Thus, we have prepared the first gallium−lanthanide(II) bonds.[25] Depending on the size of the lanthanide metal, either one or two $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ga}]$ fragments can be coordinated.

Experimental Section

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high vacuum (10^{-3} Torr) line, or in an argon-filled MBraun glovebox. THF was predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH_4. All solvents for vacuum line manipulations were stored *in vacuo* over LiAlH_4 in resealable flasks. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom % D). NMR spectra were recorded on a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Raman spectra were performed on a Bruker RFS 100. Elemental analyses were carried out with an Elementar vario EL. $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Eu}]$ was made in an analogues way to $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}]$ (M = Ca, Ba),[32] and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ga}]$[33] was prepared according to a literature procedure. $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_{1-n}]$ was obtained by supending crushed single crystals of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})]$[34] in pentane. Solvent removal at 30 °C and pentane condensation were repeated 10 times.

$[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Eu}{-}\{\text{Ga}(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ (1). $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ga}]$ (133 mg, 0.65 mmol) was added to a stirred solution of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Eu}]$ (127 mg, 0.30 mmol) in toluene (15 mL). After stirring for 16 h at room temperature the dark red solution was concentrated *in vacuo*. Dark red-purple crystals formed after several hours. Yield: 178 mg (71%). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.97 (s_{br}, 60 H, C_5Me_5). Raman (solid [cm^{-1}]): 552 (m), 590 (s), 1161 (w), 1365 (m), 1385 (m), 1421 (s), 1448 (m), 2850 (m), 2901 (s). Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{EuGa}_2$ (M = 832.31 g mol^{-1}): C, 57.72; H, 7.27. Found: C, 57.39; H, 7.66.

$[(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})\text{Yb}{-}\text{Ga}(\eta^5\text{-C}_5\text{Me}_5)]$ (2). $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ga}]$ (102 mg, 0.5 mmol) was added to a stirred solution of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_{1-n}]$ (112 mg, 0.22 mmol) in toluene (15 mL). Immediate darkening of the red solution was observed. After stirring for 16 h at room temperature the solution was concentrated *in vacuo*. Dark red crystals formed after several hours. Yield: 63 mg (40%). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.23 (m, 4 H, THF), 1.92 (s, 15 H, C_5Me_5Ga), 2.04 (s, 30 H, C_5Me_5Yb), 3.16 (m, 4 H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6, 100.4 MHz, 25 °C): δ 9.9 ($\text{C}_5\textit{Me}_5$Ga), 10.8 ($\text{C}_5\textit{Me}_5$Yb), 112.3 ($\textit{C}_5\text{Me}_5$Ga), 113.8 ($\textit{C}_5\text{Me}_5$Yb).

X-ray Crystallographic Studies of 1 and 2. Crystals of **1** and **2** were obtained from toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out on a Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97[35]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_\text{o} - F_\text{c})^2$, where the weight is defined as $4F_\text{o}^2/2(F_\text{o}^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97, respectively.[36] In the final cycles of each refinement, all non-hydrogen atoms except the disordered $(\eta^5\text{-C}_5\text{Me}_5)$ ring (C31−C40) in **1** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated. The hydrogen atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication nos. CCDC-650403 and -650404. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2** are available free of charge via the Internet at http://pubs.acs.org.

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