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Experimental and Theoretical Evidence for the First Example of an Organolanthanide(II) Compound Having an Indenyl Ligand Bonded to the Metal through the Benzo Ring in η^4 Hapticity

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Summary: The reaction of 2 equiv of C_9H_6-1-$SiMe_3$-3-CH_2CH_2-NC_5H_{10} (**2**) *with the ytterbium(III) amide* $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ *produced a novel ytterbium(II) complex with an indenyl ligand bonded to the metal via the benzo ring with* η^4 *hapticity,* $[\eta^4{:}\eta^2{:}\eta^1\text{-}(C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)Li(\mu\text{-}Cl)]Yb(\eta^5{:}\eta^1\text{-}C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)$ (**1**)*, as verified by a solid-state structure determination and theoretical calculations.*

The chemistry of lanthanide complexes has long been of interest to chemists because of their unique structures and potential applications as catalysts in organic transformations.[1,2] The indenyl ligand is known to bond to transition metals through the C_5 ring with η^1, η^2, η^3, and η^5 hapticity[3] and to group 4 and group 6 metals through the benzo ring as an η^6 ligand.[4,5] Most recently, the η^9 bonding mode of indenyl with a transition metal has been reported.[6] In the reaction of (isopropylindenyl)$_2$Yb(THF)$_2$ with excess $AlMe_3$ an ytterbium(II) complex having the indenyl ligands bonded to the metals through the benzo ring in η^6 hapticity has been proposed.[7] However, the structure of this ytterbium(II) complex remains to be elucidated. In this paper, we report the synthesis and the first structurally authenticated example of an ytterbium(II) complex exhibiting an indenyl

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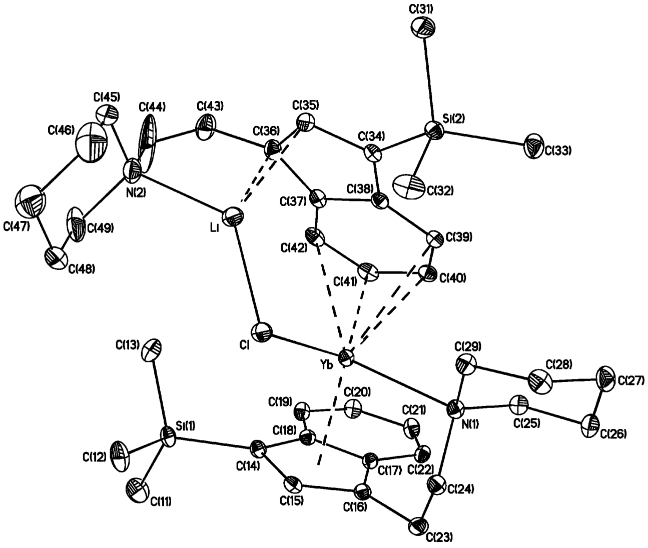
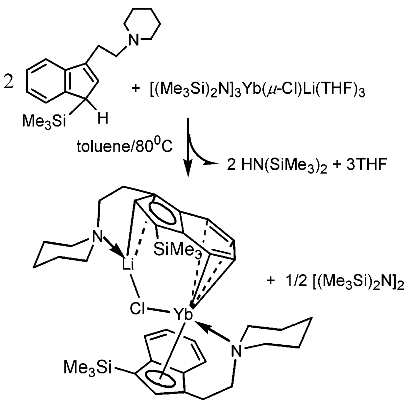


Figure 1. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

Scheme 1



ligand η^4-bonded through the benzo ring to the metal. This mode of bonding has been confirmed by theoretical calculations.

The ytterbium(II) complex $[\eta^4{:}\eta^2{:}\eta^1\text{-}(C_5H_{10}NCH_2CH_2C_9H_5\text{-}SiMe_3)Li(\mu\text{-}Cl)]Yb(\eta^5{:}\eta^1\text{-}C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)$ (**1**) was prepared as red crystals in 54% yield by treatment of 2 equiv of C_9H_6-1-$SiMe_3$-3-$CH_2CH_2NC_5H_{10}$ (**2**) with the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ in toluene at 80 °C (Scheme 1). The compound was fully characterized by spectroscopic methods and elemental analyses,[8] and its solid-state structure was determined by single-crystal X-ray diffraction (Figure 1). The complex is extremely sensitive to air and moisture and is soluble in THF, DME, pyridine, and toluene.

^{1}H NMR spectra of compound **1** in pyridine-d_5 and in benzene-d_6 show different chemical shifts for the ligands. In benzene-d_6 the indenyl ligands resonate in the range 9.27−6.18 ppm. Two sharp singlets (0.39 and 0.20 ppm) are observed for the two silyl groups, indicating that there are two distinct Me_3Si groups in **1**. However, in pyridine-d_5 the indenyl ligand resonates in the range 8.15−6.47 ppm, and only one broad singlet is observed for the two Me_3Si groups. These results suggested that the integrity of complex **1** is retained in a nonpolar solvent such as benzene, whereas it differs in pyridine due to coordination of Li^+ and Yb^{2+}. This could lead to dissociation of LiCl from complex **1**. However, attempts to isolate a compound without coordinated LiCl from pyridine failed.

X-ray analysis revealed that **1** is a neutral compound, which means that the central ytterbium metal is in an oxidation state of +2. This result suggests that the formation of the complex takes place through a homolysis of the Yb−N bond process, consistent with our previous works.[9]

The Yb−C(C_6 ring) bond distances range from 2.733(6) to 3.221(6) Å, and the corresponding Yb−C(37) and Yb−C(38) distances of 3.221(6) and 3.139(6) Å are significantly longer than the other Yb−C(C_6 ring) distances. The Yb−C(39) and Yb−C(42) distances of 2.903(6) and 3.010(7) Å (with an average of 2.956(7) Å) found in **1** are comparable to the average Yb−C distance of 2.973(9) Å found in $Yb^{II}(SAr^*)_2$ ($Ar^* = 2,6\text{-}Trip_2C_6H_3$ with Trip = $2,4,6\text{-}{}^iPr_3C_6H_2$) with Yb−arene π-bonding.[10] They are also comparable to the Yb−C distances of 3.070(5)−3.421(6) Å associated with η^4 bonding in $[Dmp(Tph)\text{-}N_3YbC_6F_5]$ (Dmp = $2,6\text{-}Mes_2C_6H_3$ with Mes = $2,4,6\text{-}Me_3C_6H_2$; Tph = $2\text{-}TripC_6H_4$ with Trip = $2,4,6\text{-}{}^iPr_3C_6H_2$).[11] The value of 3.104(5) Å found in $Yb(Dpp)I(thf)_3$ (Dpp = $2,6\text{-}Ph_2C_6H_3$) is assigned to an Yb−arene π-interaction[12] when the change in Yb^{2+} ionic radius with different coordination numbers is taken into account. The Yb−C(40) and Yb−C(41) distances of 2.733(6) and 2.772(6) Å found in **1** are comparable to the Yb−C(μ-C_2H_4) distances of 2.770(3) and 2.793(3) Å found in $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)$[13] and the Yb−C($\eta^2$-MeC≡CMe) distance of 2.659 ± 0.009 Å in $(Me_5C_5)_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$.[14] Therefore, the ligand bonding in **1** is best described as an η^4 bonding. This structure represents the first example of an organolanthanide(II) compound having the indenyl ligand bonded to the metal through the benzo ring in an η^4 fashion. It is found that the C_5 ring (C(34)−C(38)) and the C_6 ring (C(37)−C(42)) in **1** are bent away from the lithium and ytterbium atoms along the C(37)−C(38) line with a folding angle of 5.9°, to render possible the formation of the Li−Cl, Yb−Cl, Li−C(35), and Li−C(36) bonds.

To get a better insight into the nature of the peculiar bonding mode of Yb in compound **1**, density functional theory (DFT) calculations have been carried out.[15] Full geometry optimization leads to a structure which is in very good agreement with the experimental structure, as exemplified by the major optimized metrical data given in Table 1. The agreement is particularly satisfying for the Yb−C interatomic distances. This result confirms that the X-ray structure is also a minimum in the gas phase: i.e., the peculiar X-ray structure of **1** is not the result of crystal packing effects. Very small, but positive, Yb−C(37) and −C(38) Mulliken overlap populations (Table 1) suggest a very weak attractive interaction. No Yb···H agostic interaction is supported by the optimized structure, as the shortest contact is 3.32 Å. The optimized Li−C distances show a more dissym-

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(8) Experimental details for the preparation of **1** and **2** can be found in the Supporting Information.

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(15) DFT calculations were carried out with the Amsterdam Density Functional package, version 2002.01, with the BP86 functional (SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands http://www.scm.com). The standard ADF STO TZP basis set was used: i.e., a triple-ζ Slater-type orbital (STO) basis for all the atoms. The frozen-core approximation was considered as follows: Yb, 5p; Cl, 2p; Si, 2p; N, 1s; C, 1s. Relativistic corrections were added using the ZORA (zeroth order regular approximation) scalar Hamiltonian.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the DFT-Optimized Structure of 1 and Its Various Models in Comparison with the X-ray-Determined Values[a]

	1		important overlap pop. in **1** ($\times 10^4$)	**1**-Li	**1**-LiCl	$(H_2NCH_2CH_2C_9H_5SiH_3)_2Yb$
	X-ray	DFT		DFT	DFT	DFT
Yb−C(14)	2.777(6)	2.758		2.757	2.761	2.712
Yb−C(15)	2.683(6)	2.692		2.697	2.714	2.696
Yb−C(16)	2.680(6)	2.720		2.718	2.705	2.701
Yb−C(17)	2.755(6)	2.820		2.807	2.739	2.723
Yb−C(18)	2.826(6)	2.847		2.834	2.774	2.740
Yb−C(37)	3.220(6)	3.225	277	3.210	3.068	2.807
Yb−C(38)	3.139(6)	3.313	113	3.113	2.989	2.793
Yb−C(39)	2.903(6)	2.878	511	2.889	2.795	2.750
Yb−C(40)	2.733(6)	2.729	762	2.741	2.659	2.697
Yb−C(41)	2.772(6)	2.778	606	2.781	2.689	2.691
Yb−C(42)	3.010(7)	3.004	857	2.996	2.884	2.752
Yb−Cl	2.671	2.729		2.675		
Yb−N(1)	2.626	2.692		2.710	2.716	2.603
Yb−N(2)	5.573	5.528		5.617	5.725	5.485
Li−Cl	2.225	2.286				
Li−C(34)	2.882	2.896				
Li−C(35)	2.302	2.362				
Li−C(36)	2.259	2.233				
Li−C(37)	2.797	2.699				
Li−C(38)	3.151	3.082				
Cl−Yb−N(1)	96.45(12)	92		91		
N(2)−Li−Cl	129.7(6)	127				

[a] Legend: **1**-Li = $[(C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)_2ClYb]^-$; **1**-LiCl = $(C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)_2Yb$.

metrical η^2-bonding mode to the C_5 ring than the X-ray structure, with the Li−C(36) bond being shorter than the Li−C(35) one.

The seven highest occupied MO's are the nonbonding 4f orbitals. They are situated 1.72 eV above the next occupied orbitals, which have a ligand dominant character. The HOMO/LUMO gap (0.73 eV) separates the 4f block from two indenyl π^*-type orbitals. The metal Mulliken atomic populations, $(4f)^{13.95}(5d)^{0.88}(6s)^{0.32}(6p)^{0.13}$, are indicative of a significant ligand donation into the formally vacant valence 5d, 6s, and 6p AO's. These results are fully consistent with the existence of a d^0 Yb(II) 14-electron center.

The removal of Li^+ from the structure of **1** followed by the geometry reoptimization of the remaining anion $[(C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)_2ClYb]^-$, i.e. with the C_6 ring bonded to Yb, resulted in a shortening of 5−6% of the Yb−C(37) and −C(38) distances (Table 1). Further removal of Cl^- from the structure, i.e. optimizing $(C_5H_{10}NCH_2CH_2C_9H_5SiMe_3)_2Yb$ in a local minimum in which coordination to the C_6 ring is forced and N(2) is not allowed to coordinate, resulted in an additional shortening of the Yb−C(37) and −C(38) distances (Table 1) in such a way that the coordination mode is now intermediate between η^4 and η^6. A simplification of this latter model by changing $SiMe_3$ into SiH_3 and the $C_5H_{10}N$ rings into NH_2 units, i.e. optimizing $(H_2NCH_2CH_2C_9H_5SiH_3)_2Yb$ in the same local minimum, yielded a clear η^6 coordination mode in which the Yb−C(37) and −C(38) distances are, as expected, still somewhat longer than the distances of Yb to C(39−42). Clearly, there is a soft potential linking the η^4 and η^6 coordination modes of the C_6 ring in **1**. The stabilization of the η^4 mode in **1** is the result of a subtle balance among strain, steric, and electronic effects.

In conclusion, the homolysis of the Yb−N bond provides the first example of an ytterbium(II) complex having an indenyl η^4 ligand. For the first time theoretical calculations on an ytterbium(II) complex with the ligand have been carried out. This work suggests a new class of organometallic compounds possessing an indenyl ligand bound in an η^4 fashion via the benzo ring.[16] There are strong hints that different substituents or coordination of a salt may lead to a new bonding mode of the ligand. Further studies exploring the chemistry of this unique molecule are currently under way.

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Supporting Information Available: Text giving a full description of the experimental details, tables giving Cartesian coordinates for the optimized structures in XYZ format, a figure giving the MO energy diagram of **1**, and a CIF file giving X-ray crystallographic data for the structure determination of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Bridging μ-η^5:η^4 coordination of an indenyl ligand of mixed-valent ytterbium complexes was reported as our paper was in revision. See: Trifonov, A. A.; Fedorova, E. A.; Fukin, G. K.; Baranov, E. V.; Druzhkov, N. O.; Bochkarev, M. N. *Eur. J. Chem.* **2006**, *12*, 2752.