4708 *Organometallics* **2007,** *26,* 4708−4710

A Unique Organolanthanide Cluster Containing Bulky Cyclooctatetraenyl Ligands

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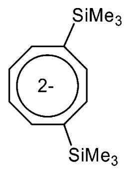
Received June 15, 2007

*Summary: The reaction of anhydrous $PrCl_3$ with $Li_2(COT'')$ ($COT'' = 1,4$-bis(trimethylsilyl)cyclooctatetraenyl) in THF solution afforded an unprecedented cluster-centered Pr/Li multidecker sandwich complex of composition $[Pr(COT'')]_2[Pr_2(COT'')_2]_2Li_2(THF)_2Cl_8$ (**1**), in which a central cube of eight Cl atoms is capped by two $[Pr(COT'')]^+$ half-sandwich and two $[Pr_2(COT'')_2]^{2+}$ sandwich units as well as two $[Li(THF)]^+$ moieties.*

The organometallic chemistry of the rare earth elements continues to be a highly attractive field of research, in particular due to the numerous applications of organolanthanides in catalysis[1] and organic synthesis.[2] An increasingly important area focuses on the development of non-cyclopentadienyl organolanthanide complexes.[3] Here, cyclooctatetraenyl ligands (=COT) play an important role because the large, flat COT dianions are ideally suited to form sandwich complexes of the rare earth metals.[4] Well established are the anionic lanthanide(III) sandwich complexes $M[Ln(COT)_2]$ (M = alkaline metal).[4a,5] Structural investigations revealed that $[Li(THF)_4][Ce(COT)_2]$[6a] consists of separated ions, while heterobimetallic sandwich structures have been found for $K(diglyme)[Ln(COT)_2]$ (Ln = Ce, Yb)[6b] and $Na(THF)_3[Ce(COT)_2]$.[6a] The most complex structure reported so far in this area is that of the tetranuclear K_2Er_2 complex $(COT)Er(\mu\text{-}COT)K(\mu\text{-}COT)Er(\mu\text{-}COT)K(THF)_4$, which was obtained serendipitously from a reaction of (benzylcyclopentadienyl)erbium dichloride, $(PhCH_2C_5H_4)ErCl_2(THF)_3$, with K_2COT in THF solution.[7] More recently, bulky organosilyl-substituted COT ligands such as the 1,4-bis(trimethylsilyl)-cyclooctatetraenyl dianion (=COT″) have become increasingly popular (Scheme 1).[8]

Scheme 1. COT″ Ligand



Anionic sandwich complexes of the type $[Li(THF)_4][Ln(COT'')_2]$ (Ln = Ce, Pr, Sm, Y) are formed upon treatment of anhydrous $LnCl_3$ with 2 equiv of $Li_2(COT'')$.[9] Like $[Li(THF)_4][Ce(COT)_2]$,[6a] the solid-state structure of $[Li(THF)_4][Sm(COT'')_2]$ was found to consist of separated ions and thus displayed no unexpected structural features. Notably, it was found that the analogous reaction of anhydrous praseodymium trichloride with $Li_2(COT'')$ did not yield a pure product, whereas pure $[Li(THF)_4][Pr(COT'')_2]$ could be synthesized starting from $Pr(O_3SCF_3)_3$.[9] When carried out in a molar ratio of 2:3, the same reactions of $LnCl_3$ with $Li_2(COT'')$ have been reported to yield the neutral triple-decker complexes $Ln_2(COT'')_3$, for which structural confirmation is unfortunately still lacking.[10] We report here that the system $LnCl_3/Li_2(COT'')$ can be much more diverse than originally anticipated. A closer inspection of the reaction using anhydrous praseodymium trichloride as starting material led to the discovery of a unique cluster-centered multidecker sandwich complex.

The starting material $Li_2(COT'')$ was made *in situ* according to a published procedure by Cloke et al. via double deprotonation of 1,4-bis(trimethylsilyl)-1,3,5-cyclooctatriene with 2 equiv of *n*-butyllithium in THF.[8a,b] A subsequent reaction with anhydrous praseodymium trichloride was carried out according to Scheme 2 in THF solution, followed by recrystallization from toluene.[11] Some details of the synthetic procedure deserve special mention. Due to the low solubility of anhydrous

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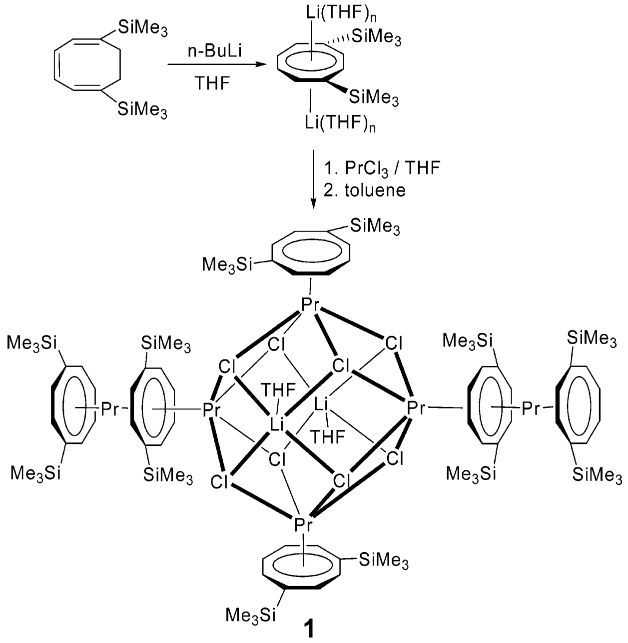
Scheme 2. Synthesis of the Praseodymium Cluster 1



praseodymium chloride in THF, the reaction carried out at room temperature took ca. 2 weeks to proceed to near completion. Subsequent short heating to reflux temperature (1 h) led to dissolution of almost all remaining $PrCl_3$ without altering the reaction pathway. Any insoluble material ($PrCl_3$, LiCl) was completely removed by careful filtration. Although not optimized, this procedure reproducibly gave high yields of **1**. An elemental analysis of the bright orange-yellow product **1** after thorough drying under vacuum indicated the incorporation of LiCl and $PrCl_3$. Especially the retention of alkali metal halides is a common phenomenon in organolanthanide chemistry, which often leads to the formation of so-called "*ate*" complexes.[12]

Orange-yellow, needle-like, X-ray quality crystals were grown by slow cooling of a toluene solution. These crystals were found to contain two toluene molecules per formula unit. An X-ray diffraction analysis of **1** revealed the presence of an unprecedented cluster-centered Pr/Li multidecker sandwich complex of the composition $[Pr(COT'')]_2[Pr_2(COT'')_2]_2Li_2(THF)_2Cl_8$.[13] The structure of **1** (Figure 1) results from capping of a central cube of eight Cl atoms by two $[Pr(COT'')]^+$ half-sandwich and two $[Pr_2(COT'')_2]^{2+}$ sandwich units. The remaining two faces of the Cl_8 cube are capped by $[Li(THF)]^+$ moieties. With respect to the metal atoms the cluster core of **1** consists of a Pr_4Li_2 octahedron with the four Pr atoms being in a plane as imposed by symmetry. All eight faces of this octahedron are capped by chlorine atoms. Figure 2 illustrates the highly symmetrical cluster architecture of **1**.

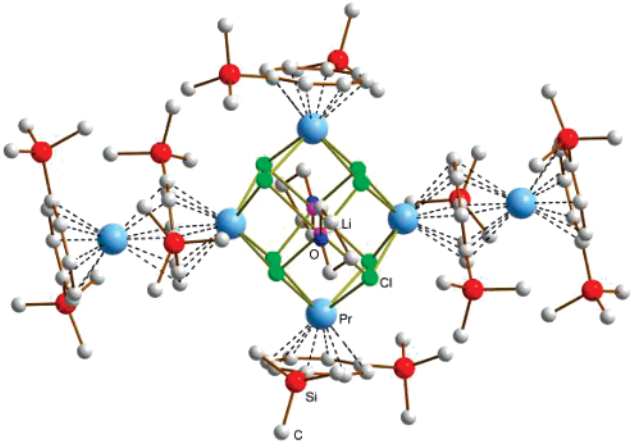


Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [deg]: Pr−C 2.634(8)−2.886(8), $Pr-X_{COT''}$ 1.906(3)−2.206(3), Pr−Cl 2.804(2)−2.998(2), C−C (COT″) 1.39(1)−1.45(1), Li−O 1.88(2), Li−Cl 2.41(2)−2.85(2), $X_{COT''}-Pr-X_{COT''}$ 171.4(3), Cl−Pr−Cl 70.1(1)−121.1(1), Pr−Cl−Pr 104.5(1)−108.2(1), Cl−Li−Cl 79.7(5)−136.1(6), Li−Cl−Pr 93.2(3)−105.4(4) ($X_{COT''}$ = COT″ ring centroid).

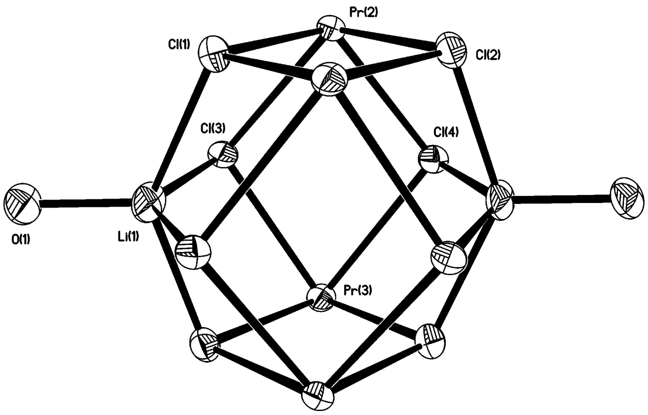


Figure 2. ORTEP view of the cluster core in **1** (including the oxygen atoms of the coordinated THF ligands at Li).

Incorporation of the $[Li(THF)]^+$ units indicates that the presence of THF is an essential prerequisite for the formation of the cluster assembly of **1**. At 171.4(3)°, the angle between Pr and the COT″ ring centroids in the $[Pr_2(COT'')_2]^{2+}$ sandwich units shows little deviation from linearity. The ^1H NMR spectrum of **1** showed two broad resonances in the silyl region in an approximate intensity of 4:1. Although these signals were not well resolved due to the paramagnetic Pr^{3+} center, they may be taken as an indication that the cluster structure is retained in solution. ^1H NMR spectra of the anionic sandwich complexes $[Li(THF)_4][Ln(COT'')_2]$ (Ln = Ce, Pr, Sm, Y)[9] are characterized by a single $SiMe_3$ resonance, while the spectra of the triple-decker sandwiches showed two resonances in an approximate ratio of 2:1.[10] A mass spectrum of the cluster species **1** exhibited

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(11) Preparation and characterization of **1**: Anhydrous $PrCl_3$ (1.6 g, 6.5 mmol) was added to a stirred THF solution (100 ml) of *in situ* prepared $Li_2(COT'')$ (12 mL (19.2 mmol) of a 1.6 M *n*-butyllithium solution in *n*-hexane and 2.35 g (9.4 mmol) of $C_8H_6(SiMe_3)_2$-1,4) at room temperature. The reaction mixture was stirred for 2 weeks and refluxed for another 1 h. Solvents were evaporated under vacuum, and the residue was extracted with boiling toluene (ca. 40 mL). Concentration and cooling to 3 °C afforded **1** as orange-yellow needles (2.5 g, 83%), which were suitable for X-ray crystallography. Anal. Calc for $C_{92}H_{160}Cl_8Li_2O_2Pr_6Si_{12}$ (2778.25): C 39.77, H 5.80. Found: C 39.91, H 5.88. (The crystals lose toluene of crystallization upon thorough drying under vacuum.) ^1H NMR (C_6D_6, 400.1 MHz, 20 °C): 6.42−5.58 (br m, $C_8H_6(SiMe_3)_2$), 3.32 (br s, THF), 1.27 (br s, THF), 0.20 to −0.20 (br m, $C_8H_6(SiMe_3)_2$), −1.80 to −2.20 (br m, $C_8H_6(SiMe_3)_2$). ^{13}C NMR (C_6D_6, 100.6 MHz, 20 °C): 148.8, 148.5, 140.3, 139.1, 134.5, 133.1, 132.4, 129.3 ($\mathit{C}_8H_6(SiMe_3)_2$), 7.1, −1.4, −1.6, −3.05 ($C_8H_6(Si\mathit{Me}_3)_2$). ^{29}Si NMR (C_6D_6, 79.5 MHz, 20 °C): −5.13, −38.42, −41.25. MS (EI): *m/z* 1026 (100%) $[(COT'')_3Pr_2]$, 954 (10%), 779 (8%), 389 (40%), 315 (8%), 73 (8%). IR (KBr disc): ν 2954vs, 1590m, 1494m, 1450m, 1404s, 1317m, 1247vs, 1123w, 1064m, 1044s, 981m, 936m, 844vs, 749vs, 719s, 689s, 651m, 635s cm^{-1}.

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(13) Complex **1**: $C_{92}H_{160}Cl_8Li_2O_2Pr_6Si_{12}\cdot 2toluene$; M_r = 2962.49, triclinic, space group $P\bar{1}$, a = 12.426(3) Å , b = 16.114(3) Å, c = 17.969 Å, α = 101.02(3)°, β = 108.50(3)°, γ = 91.41(3)°, Z = 1, T = 150(2) K, μ = 2.457 mm^{-1}, orange-yellow needle. Of 26 123 reflections measured, 14 353 were independent (R_{int} = 0.0855). Final R1 = 0.0577, wR2 = 0.1426 (all data). CCDC-641044.

the molecular ion of the neutral $Pr_2(COT'')_3$ triple-decker sandwich[10] with high intensity. The reaction sequence depicted in Scheme 2 reproducibly affords the cluster **1** in $>80\%$ yield, clearly establishing this novel species as the major product of the reaction.

Recent years have witnessed the successful preparation and characterization of exciting new organolanthanide clusters, most of which contain cyclopentadienyl or substituted cyclopentadienyl ligands.[14] The metal arrangements in these clusters range from triangular,[15] butterfly,[15,16] and tetrahedral[17] geometries to octahedral,[18] trigonal prismatic (in a lanthanide alkoxide cluster),[19] icosahedral,[18] and irregular shapes.[20] In the chemistry of cyclooctatetraenyl lanthanide complexes, compound **1** to our knowledge represents the first fully characterized cluster molecule. Initial experiments already indicated that the cluster formation is not restricted to praseodymium. Similar reactions of other anhydrous lanthanide trichlorides ($LnCl_3$, Ln = Ce, Er, Tb) with $Li_2(COT'')$ according to Scheme 2 in THF in a molar ratio of 3:2, followed by recrystallization from toluene, afforded brightly colored products (Ce, green; Tb, Er, yellow-orange). In all three cases elemental analyses and IR spectra are in good agreement with the formation of cluster molecules analogous to **1**. Thus far all attempts to grow X-ray quality crystals of the Ce, Tb, and Er derivatives failed, as these compounds crystallize from THF or toluene in the form of extremely thin needles with a cotton-like appearance. They are virtually insoluble in pentane and *n*-hexane, whereas in DME solution the cluster is irreversibly disrupted, presumably under formation of DME solvates of the anionic sandwich complexes $Li[Ln(COT'')_2]$.[9] Similar to **1**, the mass spectra of these species show the molecular ions of the neutral $Ln_2(COT'')_3$ triple-decker sandwich complexes[10] with high intensity. However, this should not be seen as a positive proof of the clusters being intermediates in the synthesis of the triple-decker sandwiches in solution. These initial results show that the system $LnCl_3/Li_2(COT'')$ is still far from being fully understood and that it clearly deserves further elucidation in the future.

In summary, the results reported here demonstrate that the use of sterically demanding COT ligands such as COT″ can dramatically alter reaction patterns as compared to the parent COT complexes and can lead to the formation of unique cluster aggregates having no precedent in organo-*f*-element chemistry. The work reported here can be expected to further stimulate the use of such bulky COT ligands not only in *f*-element chemistry.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft (SPP 1166 "Lanthanoid-spezifische Funktionalitäten in Molekül und Material").

Supporting Information Available: Text and CIF file giving synthetic details and X-ray structural data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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