Terphenyl Ligand Systems in Lanthanide Chemistry: Synthesis and Structural Characterization of Two 2,6-Dimesitylphenyl Derivatives of Trivalent Ytterbium

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While numerous reports have appeared on how sterically demanding terphenyl ligand systems can be used to stabilize Lewis base free and low coordinate main group element complexes as well as unprecedented bonding situations of these,[1,2] there still is a dearth of structural information on terphenyl derivatives of the strongly electropositive lanthanide elements or early transition metals. We were interested in investigating the potential use of sterically demanding terphenyl groups as σ-bonded ligand systems for the relatively large lanthanide cations as well as the usability of such species as an alternative to metallocene-based catalyst systems.

A limited number of lanthanide complexes with σ-bonded aryl ligands[3] as the only organic ligand are known, e.g., the synthesis of $PhLnCl_2{\cdot}n$THF ($n = 4$, Ln = Sm, Gd; $n = 3$, Ln = Pr) and the molecular structure determination of the gadolinium derivative have been reported.[4] Earlier attempts using methyl groups attached to the ortho carbon atoms of the phenyl ring thereby attempting to introduce crowding, reduce bridging tendencies, and isolate neutral monomeric molecular units resulted in formation of $[Li(THF)_4]^+[Ln(2,6\text{-}Me_2C_6H_3)_4]^-$ (Ln = Yb, Lu), the first σ-bonded f-block organometallic compound to be structurally characterized.[5]

We here report the synthesis and crystal structure determination of two novel terphenyl derivatives of trivalent ytterbium. $YbCl_3$ reacts slowly with 1 equiv of the terphenyl lithium salt DmpLi[6] (Dmp = 2,6-dimesitylphenyl) in tetrahydrofuran at room temperature to form a purple complex of unknown composition.[7] No bis substitution at the metal center is observed using 2 equiv or more of DmpLi. Addition of pyridine (py) and *N*-methylimidazole (*N*-MeIm) gave a characterizable complex, **1**·toluene, and single-crystalline material was obtained from toluene at −30 °C.[8]

The molecular structure of **1**·toluene was determined crystallographically[9] as hexacoordinated $DmpYbCl_2$(*N*-MeIm)$_2$(py) (Figure 1), with a toluene solvent molecule present in the crystal lattice. Coordination numbers found in trivalent lanthanide chemistry are typically 8 or 9. Due to the steric bulk of the terphenyl ligand system and the resulting saturation of the coordination sphere of the lanthanide metal, a monomeric species is formed in the case of **1**·toluene with coordination number 6 at the metal center. The deviation from ideal octahedral geometry can best be seen by inspecting the L−Yb−(cis L) interligand angles in **1**·toluene ranging from 71.8(2)° [N(31)−Yb(1)−N(51)] to 110.3(3)° [C(6)−Yb−N(31)] and is mostly pronounced in those (cis L) interligand angles involving the ipso carbon atom C(6). The C(6)−C(1)−C(16) and the C(6)−C(5)−C(26) angles are 121.8(7)° and 123.0(7)°, respectively.

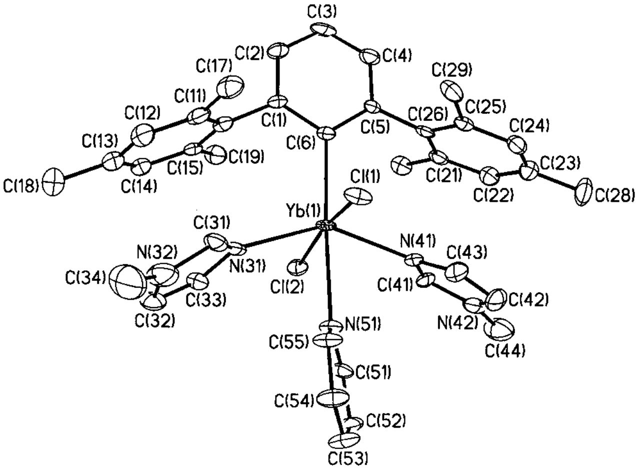

Figure 1. Molecular structure of $DmpYbCl_2$(*N*-MeIm)$_2$(py)·toluene (**1**·toluene) showing the monomeric and distorted octahedral arrangement in the solid state. Hydrogen atoms as well as the cocrystallized toluene molecule in the crystal lattice are omitted for clarity. Selected interatomic separations (Å) and angles (deg): Yb(1)−Cl(1) = 2.591(3), Yb(1)−Cl(2) = 2.592(3), Yb(1)−N(41) = 2.412(8), Yb(1)−N(31) = 2.434(8), Yb(1)−N(51) = 2.624(7), Yb(1)−C(6) = 2.447(9), Yb(1)···C(16) = 3.643(9), Yb(1)···C(26) = 3.702(9); C(6)−Yb(1)−N(31) = 110.3(3), C(6)−Yb(1)−N(41) = 105.4(3), C(6)−Yb(1)−N(51) = 176.6(3), C(6)−Yb(1)−Cl(1) = 94.5(2), C(6)−Yb(1)−Cl(2) = 95.8(2), Cl(1)−Yb(1)−Cl(2) = 169.70(8), N(31)−Yb(1)−N(41) = 144.3(3), N(31)−Yb(1)−N(51) = 71.8(2), N(41)−Yb(1)−N(51) = 72.7(2), Cl(1)−Yb(1)−N(31) = 87.4(2), Cl(1)−Yb(1)−N(41) = 91.5(2), Cl(1)−Yb(1)−N(51) = 82.8(2), Cl(2)−Yb(1)−N(31) = 88.8(2), Cl(2)−Yb(1)−N(41) = 86.0(2), Cl(2)−Yb(1)−N(51) = 86.9(2).

The Yb−C(6) interatomic separation of 2.447(9) Å in **1**·toluene can be compared with the corresponding distance in $(C_5H_4Me)_2YbDmp$ [2.410(3) Å][10] as well as the average terminal Yb(III)−C distance in the mixed valent complex $Ph_2(THF)Yb(\mu\text{-}Ph)_3Yb(THF)_3$ [2.42 Å].[11] Other Yb···C distances in **1**·toluene involve the ipso carbon atoms of the mesityl groups [Yb(1)···C(16) = 3.643(10) Å and Yb(1)···C(26) = 3.702(10) Å]. These interatomic separations are clearly longer than the Yb···C distance of 3.187(3) Å (ipso carbon atom of one of the mesityl rings) in $(C_5H_4Me)_2YbDmp$.[10] Different Yb−N distances are observed for the pyridine ligand on one hand [N(51), 2.624(7) Å] and the two *N*-MeIm ligands on the other [N(41), 2.412(8); N(31), 2.434(8) Å].

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(7) On the basis of our findings reported in this work, the assumption of a composition $DmpYbCl_2{\cdot}LiCl(THF)_2$ for the purple material appears to be reasonable. This assumption is further corroborated by correct elemental analysis data (C, H, Cl, Li) as well as a ^7Li NMR spectrum. An analytically pure sample of the purple complex is slightly soluble in hexanes and well soluble in aromatic solvents. ^7Li NMR (C_6D_6, 155.5 MHz, 25 °C): δ −97.8 (s, $\nu_{1/2}$ = 130 Hz).

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We were interested in investigating whether further functionalization of our $DmpYbCl_2$ system is possible and what other functional groups can be accommodated by the Dmp−Yb moiety. Starting from 1 equiv of DmpLi and 1 equiv of $YbCl_3$ in tetrahydrofuran solution at room temperature followed by addition of 1 equiv of $KN(SiMe_3)_2$, we were able to generate the hexane-soluble bimetallic amide derivative $DmpYb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ (**2**)[8] in a one-pot synthesis in 50% yield. Crystalline material of orange-red **2** suitable for an X-ray diffraction study was obtained from toluene at −30 °C.[9]

The molecular structure of complex **2** features an ytterbium atom in a heavily distorted tetrahedral coordination environment with interligand angles around the lanthanide metal center ranging from 88.12(4)° [Cl(1)−Yb(1)−Cl(2)] to 127.27(12)° [C(6)−Yb(1)−Cl(2)] (Figure 2). The Yb(1)−C(6) separation [2.403(4) Å] can be compared with the corresponding distance in **1**·toluene, and the C(6)−C(1)−C(16) and C(6)−C(5)−C(26) angles [121.8(7)° and 123.0(7)°, respectively] match the corresponding distances in **1**·toluene. In addition to the four ligands attached to the lanthanide metal center, one of the methyl groups of one $SiMe_3$ group [atom C(30)] points toward the lanthanide metal−center exhibiting a relatively short metal carbon distance at 2.954(5) Å. This interatomic separation is clearly longer than the corresponding number reported for the Yb−C(methyl) distance in $Cp_2YbMe(THF)$ [2.36(1) Å].[12] It can further be compared with the Yb···C(methyl) distance of 2.852(13) Å in divalent $Yb[C(SiMe_3)_3]_2$.[13] Also, given the fact that Y^{3+} and Yb^{3+} cations have a similar radial size, comparisons can be made with the Y···C(methyl) distances found in $Cp^*_2YN(SiMe_3)_2$ [2.970(6) Å] and $Cp^*_2YCH(SiMe_3)_2$ [2.878(7) Å].[14] As one would expect, the Yb(1)−N(1) distance of 2.158(3) Å in formally four-coordinate **2** is significantly shorter than the three Yb−N distances in hexacoordinate **1**·toluene. On the other hand, the Yb−N distance in **2** matches the average Yb−N distance of 2.17 Å in pentacoordinate tris(2,6-diisopropylphenylamido)bis(tetrahydrofuran)ytterbium.[15] The coordination environment around the nitrogen atom in **2** is planar within the error limits of the determination.

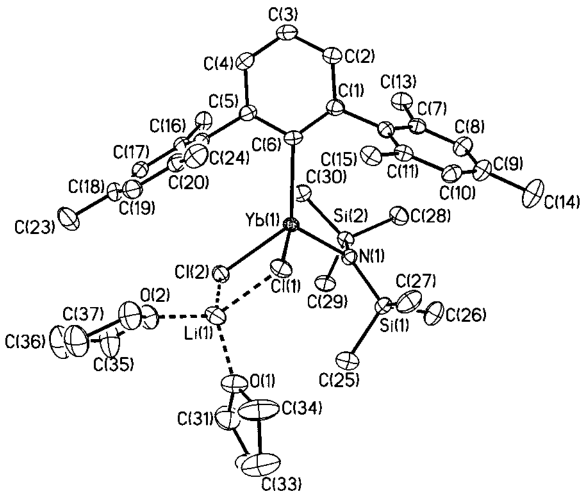

Figure 2. The molecular structure of $DmpYb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ (**2**). Hydrogen atoms are omitted for clarity. Selected interatomic separations (Å) and angles (deg): Yb(1)−N(1) = 2.158(3), Yb(1)−C(6) = 2.403(4), Yb(1)···C(30) = 2.954(5), Yb(1)−Cl(1) = 2.5467(11), Yb(1)−Cl(2) = 2.5596(12), Li(1)−Cl(1) = 2.379(10), Li(1)−Cl(2) = 2.396(10), Li(1)−O(1) = 1.895(10), Li(1)−O(2) = 1.913(10), N(1)−Si(1) = 1.728(4), N(1)−Si(2) = 1.707(4); N(1)−Yb(1)−C(6) = 118.91(15), N(1)−Yb(1)−Cl(1) = 108.30(10), N(1)−Yb(1)−Cl(2) = 101.77(10), C(6)−Yb(1)−Cl(1) = 107.39(11), C(6)−Yb(1)−Cl(2) = 127.27(11), Cl(1)−Yb(1)−Cl(2) = 88.12(4), Li(1)−Cl(1)−Yb(1) = 88.2(2), Li(1)−Cl(2)−Yb(1) = 87.5(2), Yb(1)−N(1)−Si(1) = 126.98(19), Yb(1)−N(1)−Si(2) = 108.83(18), Si(1)−N(1)−Si(2) = 121.7(2), O(1)−Li(1)−O(2) = 103.9(5)°.

Our work introduces the 2,6-dimesitylphenyl ligand as the only supporting organic ligand for the strongly electropositive lanthanide elements, thereby offering new opportunites in organolanthanide chemistry with respect to reaction chemistry and catalysis. Further investigations in this area of chemistry are underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of complexes **1**·toluene and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Characterization data for $DmpYbCl_2(N\text{-}MeIm)_2(py)$ (**1**): In the glovebox, addition of a solution of 2,6-dimesitylphenyllithium (0.30 g, 0.9 mmol) in 10 mL of tetrahydrofuran to a colorless suspension of $YbCl_3$ (0.26 g, 0.9 mmol) in 10 mL of tetrahydrofuran caused a slow color change from colorless to pink, then to red. The reaction mixture was stirred for 30 min, the volatiles were removed, and the residues were dissolved in toluene. Addition of two drops of pyridine as well as two drops of *N*-methylimidazole to the purple toluene solution gave an orange suspension. Centrifugation followed by cooling of the obtained orange solution to −30 °C resulted in almost complete crystallization of **1**·toluene. Removal of the mother liquor followed by drying under vacuum gave **1** as an orange microcrystalline material (0.45 g, 60%). Analytically pure complex **1** is completely insoluble in hexanes, but soluble in aromatic solvents and in tetrahydrofuran. Anal. Calcd for $C_{37}H_{42}Cl_2N_5Yb$: C, 55.50; H, 5.29; N, 8.75. Found: C, 55.23; H, 5.01, N, 8.54. IR (Nujol): 1702 w, 1522 m, 1422 m, 1280 w, 1238 s, 1167 w, 1108 s, 1084 s, 1062 w, 1026 w, 936 m, 927 m, 847 s, 796 w, 751 w, 738 m, 722 s, 689 w, 658 m, 616 w cm^{-1}. Characterization data for $DmpYb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ (**2**): In the glovebox, addition of a solution of 2,6-dimesitylphenyllithium (0.30 g, 0.9 mmol) in 10 mL of tetrahydrofuran to a colorless suspension of $YbCl_3$ (0.26 g, 0.9 mmol) in 10 mL of tetrahydrofuran followed by addition of 1 equiv $KN(SiMe_3)_2$ (0.16 g, 0.9 mmol) gave an orange solution. The reaction mixture was stirred for 30 min and centrifuged. The solvent was removed, and the residues were dissolved in hexanes and centrifuged. Cooling to −30 °C resulted in complete crystallization of **2**. Removal of the mother liquor followed by drying under vacuum gave **2** as an orange-red microcrystalline material (0.39 g, 50%). Analytically pure complex **2** is slightly soluble in hexanes and well soluble in aromatic solvents. Anal. Calcd for $C_{38}H_{59}Cl_2LiN_5O_2Si_2Yb$: C, 52.53; H, 6.84; N, 1.61. Found: C, 52.34; H, 7.18; N, 1.64. ^7Li NMR (C_6D_6, 155.5 MHz, 25 °C): δ −124.5 (s, $\nu_{1/2}$ = 280 Hz). IR (Nujol): 1910 w, 1611 w, 1540 w, 1244 s, 1168 w, 1094 w, 1071 m, 1045 s, 1013 w, 966 s, 918 w, 870 m, 847 s, 777 w, 754 w, 726 w, 689 w, 666 s, 614 m, 588 w, 547 w cm^{-1}.

(9) Crystal data for $DmpYbCl_2(N\text{-}MeIm)_2(py)$ (**1**)· toluene: triclinic, $P\bar{1}$, $a = 12.4455(2)$ Å, $b = 12.8094(2)$ Å, $c = 15.2558(2)$ Å, $\alpha = 69.9266(8)°$, $\beta = 78.0016(6)°$, $\gamma = 69.7674(4)°$, $V = 2132.37(5)$ Å^3, $Z = 2$, $T = −75(2)$ °C, $D_{calc} = 1.391$ g cm^{-3}, $R(F) = 6.92\%$ for 5481 observed independent reflections ($4° \le 2\theta \le 52°$). Crystal data for $DmpYb[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2$ (**2**): monoclinic, $P2_1/c$, $a = 14.4941(2)$ Å, $b = 12.1560(2)$ Å, $c = 24.1861(4)$ Å, $\beta = 93.2338(7)°$, $V = 4254.58(19)$ Å^3, $Z = 4$, $T = −100(2)$ °C, $D_{calc} = 1.357$ g cm^{-3}, $R(F) = 4.15\%$ for 8375 observed independent reflections ($4° \le 2\theta \le 57°$).

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