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Cyclooctatetraenyl complexes of the early transition metals and lanthanides

X. [1] The first organometallic triple decker sandwich complexes of the lanthanides

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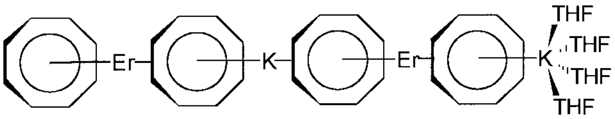
Abstract

Treatment of anhydrous lanthanide trichlorides with $Li_2C_8H_6(SiMe_3)_2$-1,4 in a 2:3 molar ratio affords the first well-defined organolanthanide triple decker sandwich complexes. The compounds $Ln_2[C_8H_6(SiMe_3)_2\text{-}1,4]_3$ (**2**–**4**; Ln = Ce, Nd, Sm) were characterized by elemental analyses and spectroscopic methods. An alternative preparation of **2** involves a ligand redistribution reaction between $CeCl_3$ and the anionic sandwich complex $[Li(THF)_4][Ce\{C_8H_6(SiMe_3)_2\text{-}1,4\}_2]$ (**5**). © 1998 Elsevier Science S.A.

Keywords: Triple-decker sandwich complexes; Organolanthanides; Cyclooctatetraenyl complexes; Cerium; Neodymium; Samarium

1. Introduction

Triple decker sandwich complexes are known since 1970 [2–7]. Typical ligands suitable for the synthesis of such binuclear complexes with parallel rings are among others the cyclopentadienide anion, arenes, boron-containing heterocycles, P_6 units, and the dianion of cyclooctatetraene [8–13]. The first paramagnetic representatives of this interesting class of compounds were reported by Siebert et al. [14,15]. In organolanthanide chemistry, triple decker sandwich complexes with parallel rings are unknown [16,17], although a triple-decker structure has been postulated for materials of the composition $[Ln_2(C_8H_8)_3]$ [18,19]. These compounds are the initial products from cocondensation reactions of lanthanide vapors with cyclooctatetraene. They are insoluble in non-coordinating solvents but react with THF under formation of the bent binuclear complexes $[Ln(C_8H_8)(THF)_2][Ln(C_8H_8)_2]$ [18,19]. Especially the large, flat cyclooctatetraenyl ligand appears to be ideally suited for the construction of multidecker sandwich complexes of the lanthanide elements as exemplified by the unusual erbium compound **1** [20]:



However, multidecker complexes such as **1** are thus far not accessible through rational syntheses. For example, complex **1** was obtained serendipitously by the reaction of the benzylcyclopentadienyl complex $[(C_5H_4CH_2Ph)ErCl_2(THF)_3]$ with $K_2C_8H_8$ in a 1:1 molar ratio [20]. Yet another unusual triple decker containing the related element scandium was recently reported by Cloke et al. [21]. Cocondensation of electron beam vaporized scandium with an excess of $tBuC{\equiv}P$ unexpectedly afforded the binuclear complex $[\{(\eta^5\text{-}P_3C_2tBu_2)Sc\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_3C_3tBu_3)]$, albeit in low yield (5–10%). This formal scandium (I) complex contains a bridging 1,3,5-triphosphabenzene ring.

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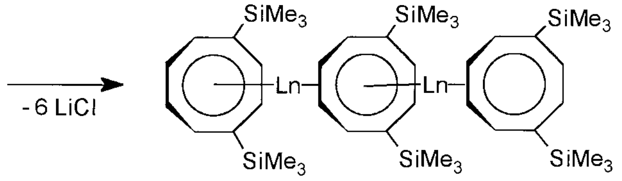
[1] For Part IX see Ref. [1].

2. Results and discussion

As mentioned above, solubility problems have prohibited a full characterization of the complexes $[Ln_2(C_8H_8)_3]$ [18,19]. It should be possible to circumvent such problems by introducing suitable substituents in the cyclooctatetraenyl rings. Indeed, we have now found that by using the bulky 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand [22,23] soluble, well-defined organolanthanide triple-deckers are readily accessible (Eq. (1)). For the success of these preparations, it is important to mix the reagents in the exact stoichiometry of 2:3. Otherwise the products will be contaminated with the anionic sandwich complexes $[Li(THF)_4][Ln\{C_8H_6(SiMe_3)_2\text{-}1,4\}_2]$ [1].

$[2LnCl_3 + 3Li_2C_8H_6(SiMe_3)_2\text{-}1,4]$



2-4, Ln = Ce, Nd, Sm

(1)

Due to the presence of six trimethylsilyl substituents in the molecules the intensely colored complexes are readily soluble in THF, diethylether, acetonitrile, or toluene. Solutions in toluene exhibit the deep colors of the solid materials, while solutions in coordinating solvents are much lighter in color (yellow), indicating the formation of weakly bonded adducts. Evaporation of such solutions to dryness immediately gives back the original unsolvated complexes. The triple decker sandwich structure of **2**–**4** can be deduced unambiguously from the analytical and spectroscopic data. Elemental analysis (C, H, and Ln) and ^1H NMR spectra reveal that all three compounds are unsolvated. Despite the presence of paramagnetic central ions the NMR spectra exhibit relatively sharp signals in the case of the selected lanthanide elements cerium, neodymium, and samarium [24]. Especially useful are the ^{29}Si NMR spectra, which show only two signals for the trimethylsilyl groups in accordance with the triple decker sandwich structure. Also, very informative are the mass spectra of **2**–**4**. In all three cases, they exhibit the molecular ion with the correct isotopic pattern. No peaks at higher masses are observed. Unfortunately, the complexes resisted numerous attempts to grow single crystals for an X-ray crystallographic study. The complexes crystallized from various solvents in the form of very thin needles unsuitable for X-ray diffraction.

The tendency to form the new binuclear complexes is surprisingly high. For example, it was discovered that the cerium complex **2** is also accessible by a ligand redistribution reaction between the anionic sandwich complex $[Li(THF)_4][Ce\{C_8H_6(SiMe_3)_2\text{-}1,4\}_2]$ (**5**) [1] and anhydrous cerium trichloride in THF solution (65% yield):

$$3\underset{5}{[Li(THF)_4][Ce\{C_8H_6(SiMe_3)_2\text{-}1,4\}_2]} + CeCl_3$$

$$\rightarrow 2\underset{2}{Ce_2[C_8H_6(SiMe_3)_2\text{-}1,4]_3} + 3LiCl$$

3. Experimental

All reactions were carried out under rigorous exclusion of air and moisture using standard Schlenk line and dry-box techniques. Solvents were carefully dried over Na/benzophenone and freshly distilled under N_2 prior to use. IR spectra: Perkin–Elmer spectrometer 180 and Bio-Rad FTS 7, Nujol mulls between KBr disks. ^1H NMR spectra: Bruker WP 80 SY and Bruker AM-250 (250 MHz, TMS ext., 25°C). ^{29}Si NMR spectra: Bruker AM-250 (79.460 MHz, TMS, 25°C). Elemental analyses: Analytical laboratory of the Department of Inorganic Chemistry, University of Göttingen. The starting materials $1,4\text{-}(Me_3Si)_2C_8H_8$ (COT* = η^8-$C_8H_6(SiMe_3)_2$-1,4) [23] and $LnCl_3$ [25] were prepared according to literature procedures.

3.1. General procedure for the preparation of 2–4

To a solution of 9.0 mmol $Li_2C_8H_6(SiMe_3)_2$-1,4 [22,23] in 80 ml THF are added 6.0 mmol of anhydrous $LnCl_3$ (Ln = Ce, Nd, Sm) and the resulting mixture is stirred for 48 h at room temperature. All volatiles are removed in vacuo and the residue is extracted with 200 ml of boiling toluene. After filtration through a thin layer of Celite filter aid the clear filtrate is concentrated to a total volume of 30 ml. Crystallization at −20°C (24 h) affords the analytically pure product.

3.2. Tris[1,4-bis(trimethylsilyl)cyclooctatetraenyl]-dicerium(III) (2)

Yield: 1.93 g (63%), blue–green crystals, mp > 360°C. Calcd.: C, 49.18; H, 7.08; Ce, 27.32%. $C_{42}H_{72}Ce_2Si_6$ (1025.78) found: C, 47.79; H, 7.81; Ce, 26.35%. IR (KBr) (cm^{-1}) 1403 (m), 1248 (vs), 1214 (m), 1094 (s, br), 1048 (s), 1031 (s, sh), 907 (m), 839 (vs), 808 (s), 783 (m), 751 (vs), 733 (vs), 687 (m), 548 (m), 391 (m). ^1H NMR (C_6D_6, 250 MHz, 25°C): $\delta = 5.63$ (br, 4 H, ring-H), 5.36 (br, $\nu_{1/2} = 28$ Hz, 20 H, 2 ring-H + 2 $SiMe_3$), 2.97 (br, 4 H, ring-H), 2.74 (br, $\nu_{1/2} = 17$ Hz, 40 H, 4 ring-H + 4 $SiMe_3$), 2.47 (br, 4 H, ring-H). ^{29}Si NMR (C_6D_6, 79 MHz): $\delta = -6.0$ (s, SiMe$_3$), -4.1 (s, SiMe$_3$). EI MS (70 eV): m/z (%): 1026 (63) [M^+], 1009 (2) [M$^+$–CH$_3$], 636 (4) [(COT*)$_2$Ce$^+$], 388 (100) [(COT*)Ce], 160 (5) [(COT*)$^+$–SiMe$_4$], 73 (16) [SiMe$_3^+$].

3.3. *Tris[1,4-bis(trimethylsilyl)cyclooctatetraenyl]dineodymium(III) (**3**)*

Yield: 0.93 g (30%), green crystals, mp > 340°C (dec.). Calcd.: C, 48.79; H, 7.02; Nd, 27.90%. C$_{42}$H$_{72}$Nd$_2$Si$_6$ (1034.03) found: C, 48.99; H, 8.06; Nd, 26.83%. IR (KBr) (cm^{-1}) 1262 (s), 1245 (vs), 1207 (m), 1048 (vs), 1039 (s, sh), 978 (m), 932 (m), 899 (m), 835 (vs, br), 813 (s, sh), 794 (m), 750 (s), 738 (s), 635 (m), 380 (s), 350 (s). ^{1}H NMR (C$_6$D$_6$, 250 MHz, 25°C): $\delta = 3.13$ (br, $\nu_{1/2} = 35$ Hz, 18 H, SiMe$_3$), 0.49 (br, $\nu_{1/2} = 36$ Hz, 36 H, SiMe$_3$), $-9{,}58$ (br, $\nu_{1/2} = 98$ Hz, 12 H, ring-H), -13.76 (br, $\nu_{1/2} = 106$ Hz, 6 H, ring-H). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): $\delta = -5.2$ (s, SiMe$_3$), -51.6 (br, $\nu_{1/2} = 24$ Hz, SiMe$_3$). EI MS (70 eV): m/z (%): 1028 (8) [M$^+$], 779 (2) [(COT*)$_2$Nd$_2^+$], 390 (4) [(COT*)Nd$^+$], 209 (100) [(COT*)$^+$–C$_3$H$_4$], 73 (36) [SiMe$_3^+$].

3.4. *Tris[1,4-bis(trimethylsilyl)cyclooctatetraenyl]disamarium(III) (**4**)*

Yield: 0.85 g (27%), orange–brown crystals, mp > 330°C (dec.). Calcd.: C, 48.22; H, 6.94; Sm, 28.74%. C$_{42}$H$_{72}$Si$_6$Sm$_2$ (1046.27) found: C, 47.68; H, 7.28; Sm, 28.00%. IR (KBr) (cm^{-1}) 1261 (s), 1247 (vs), 1208 (m), 1093 (s, sh), 1080 (s), 1048 (vs), 1031 (s, sh), 978 (m), 933 (m), 836 (vs), 800 (s, sh), 779 (m), 749 (m), 727 (vs), 693 (m), 635 (m), 554 (m), 511 (m), 370 (s), 340 (vs). ^{1}H NMR (C$_6$D$_6$, 250 MHz, 25°C): $\delta =$ 13.20–12.62 (m, 18 H, Ring-H), 2.44 (br, $\nu_{1/2} = 89$ Hz, 36 H, SiMe$_3$), 2.24 (s br, $\nu_{1/2} = 28$ Hz, 18 H, SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79 MHz): $\delta = -5.2$ (s, $\nu_{1/2} = 7$ Hz, SiMe$_3$), -5.7 (s, $\nu_{1/2} = 2$ Hz, SiMe$_3$). EI MS (70 eV): m/z (%): 1046 (4) [M$^+$], 1031 (1) [M$^+$–CH$_3$], 797 (24) [(COT*)$_2$Sm$_2^+$], 649 (1) [(COT*)$_2$Sm$^+$], 400 (7) [(COT*)Sm$^+$], 248 (15) [(COT*)$^+$], 160 (31) [(COT*)$^+$–SiMe$_4$], 73 (100) [SiMe$_3^+$].

3.5. *Alternative preparation of **2***

A mixture of 0.78 g (0.8 mmol) [Li(THF)$_4$][Ce{C$_8$H$_6$(SiMe$_3$)$_2$-1,4}$_2$] (**5**) [1] and 0.65 g (2.4 mmol) anhydrous CeCl$_3$ in 80 ml THF is heated under reflux for 48 h and the resulting clear yellow solution is evaporated to dryness. The residue is extracted with 80 ml of boiling toluene and filtered through a thin layer of Celite filter aid. Concentration of the blue–green filtrate to ca. 10 ml followed by crystallization at -20°C (24 h) affords 0.55 g (65% based on **5**) of **2** as intensely blue–green crystals.

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