

Diene Complex of Lanthanum: The Crystal Structure of a Diene-bridged Dilanthanum Complex, $[\text{LaI}_2(\text{thf})_3(\mu\text{-}\eta^4 : \eta^4\text{-PhCH=CHCH=CHPh})\text{LaI}_2(\text{thf})_3]$

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Reaction of metallic lanthanum with 1,4-diphenylbuta-1,3-diene and iodine in THF results in the formation of the diene-bridged bis(diiodolanthanum) complex, $[\text{LaI}_2(\text{thf})_3(\mu\text{-}\eta^4 : \eta^4\text{-PhCH=CHCH=CHPh})\text{LaI}_2(\text{thf})_3]$ **1**, whose structure was characterized by X-ray crystallography.

The diene dianion is theoretically of great interest in view of its linear 6π system.¹ Recently the counter-cation has been found to be important in controlling the stereochemistry of diene dianions as well as their reactivity.²⁻⁸ The diene complexes of heavier metals of Groups 1-3 have attracted little attention and only a few diene complexes of lanthanides have been prepared,⁷⁻⁹ though the organometallic chemistry of heavier Group 1-3 metals has been developed recently.¹⁰ We have been continuing the synthetic study of organolanthanide complexes by the reaction of metallic lanthanides with π -ligands such as cyclooctatetraene.^{9,11} In this communication, we report on the preparation and structural characterization of a new diene complex of lanthanum.

Treatment of finely divided metallic lanthanum with 1 equiv. of iodine and 0.5 equiv. of 1,4-diphenylbuta-1,3-diene in THF at 50 °C for 48 h (Scheme 1) afforded a deep red solution, from which $[\text{LaI}_2(\text{thf})_3(\mu\text{-}\eta^4 : \eta^4\text{-PhCH=CHCH=CHPh})\text{LaI}_2(\text{thf})_3]$ **1** was obtained as red crystals (14% yield) upon cooling the THF solution. § Complex **1** decomposed rapidly upon exposure to air and moisture, but is stable under inert atmosphere. The structure of **1** was characterized by an X-ray structure determination as well as elemental analysis.

Complex **1** crystallized as a centrosymmetric molecule, as shown in Fig. 1. ¶ Each $\text{LaI}_2(\text{thf})_3$ moiety is related by centrosymmetry and each La atom has a pseudooctahedral six-coordination through one η^4 -interaction with the bridging diene unit. Three THF molecules are found in *mer*-arrangement and two iodo ligands are *trans* to each other. It is of interest that the geometry of complex **1** is similar to that of the dilithium compound of 1,4-diphenylbuta-1,3-diene, $[\text{Li}(\text{tmen})(\mu\text{-PhCH=CHCH=CHPh})\text{Li}(\text{tmen})]$,² which has a diene-bridged structure, and is different from the bridging structure of the dinuclear lanthanum butadiene complex, $[\text{La}(\text{C}_5\text{Me}_5)(\text{thf})(\mu\text{-}\sigma : \eta^3\text{-CH}_2\text{=CHCH=CH}_2)\text{La}(\text{C}_5\text{Me}_5)_2]$.⁷ This is attributed to the isoelectronic relationship between lithium and the LaI_2 moiety. Recently some other examples of an inverse sandwich structure have been prepared for Group 3 and 4 metals, *i.e.* $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-}\eta^8 : \eta^8\text{-C}_8\text{H}_8)\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2]$,¹² $[\{\text{HfI}_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-}\eta^6 : \eta^6\text{-C}_6\text{H}_6)\{\text{HfI}_2(\text{PMe}_2\text{Ph})_2\}]$ ¹³ and $[(\text{C}_5\text{Me}_5)_3\text{Hf}_3\text{Cl}_5(\text{C}_4\text{H}_4)]$.¹⁴

Fig. 2 shows a molecule of **1** viewed down the La-La axis, where iodo ligands are eclipsed as observed for $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-}\eta^8 : \eta^8\text{-C}_8\text{H}_8)\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2]$. The bond distances La-C(1) [2.89(1) Å] and La-C(4) [2.94(1) Å] are longer than those of La-C(2) [2.76(2) Å] and La-C(3) [2.82(2) Å], which are comparable to that (av. 2.805 Å) of the polymeric complex $\text{La}(\text{C}_5\text{H}_5)_3$,¹⁵ but are longer than that (2.627-2.651 Å) of a La-C σ bond.^{7,16} The bond distance C(2)-C(3) [1.49(3) Å] is longer than those of C(1)-C(2) [1.25(2) Å] and C(3)-C(4) [1.25(2) Å], although precise

discussion is difficult due to the disorder of C(2) and C(3) carbons of the diene. This observed trend is in sharp contrast to the fact that diene complexes of early transition metals have the tendency of long-short-long bond distances for the diene

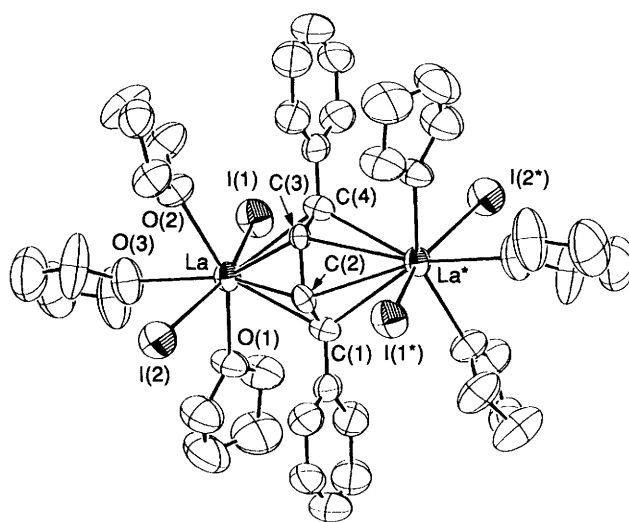


Fig. 1 An ORTEP drawing of complex **1** with the numbering scheme. Central carbons of diene moiety are disordered and the half of them is omitted for clarity. Hydrogen atoms and a solvated THF molecule were also omitted for clarity. Selected bond lengths (Å) and angles (°): La-I(1) 3.176(1), La-I(2) 3.170(1), La-O(1) 2.530(8), La-O(2) 2.509(8), La-O(3) 2.602(9), La-C(1) 2.89(1), La-C(2) 2.76(2), La-C(3) 2.82(2), La-C(4) 2.94(1), C(1)-C(2) 1.25(2), C(2)-C(3) 1.49(3), C(3)-C(4) 1.25(2); I(1)-La-I(2) 159.50(4), I(1)-La-O(1) 83.5(2), I(1)-La-O(2) 80.6(2), I(1)-La-O(3) 80.6(2), I(2)-La-O(1) 89.3(2), I(2)-La-O(2) 86.4(2), I(2)-La-O(3) 79.0(2), O(1)-La-O(2) 150.0(3), O(1)-La-O(3) 75.9(3), O(2)-La-O(3) 74.1(3).

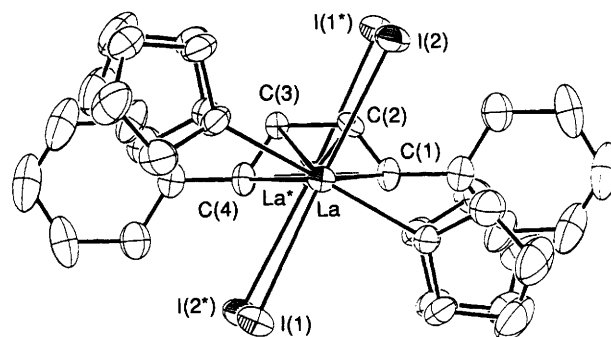
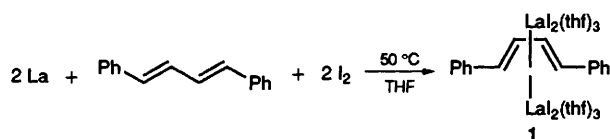


Fig. 2 An ORTEP drawing of complex **1** along with the La-La vector. Two THF molecules are omitted for clarity.



Scheme 1

moiety. For $(C_5H_5)_2Hf(1,3\text{-diene})$, a metallacyclopent-3-ene structure has been proposed.¹⁷ A naphthalene complex of lutetium, $(C_5H_5)Lu(\eta^4-C_{10}H_8)(dme)$, has been reported to contain a η^4 -diene unit coordinated to $Lu(C_5H_5)$ moiety, in which the tendency of long–short–long bond distances for the diene moiety has been noted.^{8b}

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Footnotes

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§ Preparation of 1. To a mixture of 1,4-diphenylbuta-1,3-diene (55 mg, 0.27 mmol) and finely divided lanthanum metal (74 mg, 0.53 mmol) in THF (5 ml) was added iodine (138 mg, 0.54 mmol) diluted in THF (5 ml). After the reaction mixture was stirred for 2 days at 50 °C, the resulting deep red solution was separated from the residual iodolanthanum compounds and lanthanum metal. The solution was evaporated to give a highly coloured solid. Recrystallization from THF (40 ml) afforded compound 1 (53 mg, 14% yield) as red crystals.

When this reaction (0.5 mmol scale) was carried out in a mixture of THF (20 ml) and pyridine (1 ml), complex 1 (18% yield) was obtained, mp 98–106 °C (decomp.). Satisfactory elemental analysis was obtained.

¶ Crystal data for 1: $C_{44}H_{70}La_2O_7$, $M = 1496.46$, crystal size $0.2 \times 0.2 \times 0.6$, triclinic, space group $P\bar{1}$, $a = 12.573(3)$, $b = 12.707(4)$, $c = 8.673(2)$ Å, $\alpha = 99.55(3)$, $\beta = 98.07(2)$, $\gamma = 81.97(2)^\circ$, $V = 1343.4(7)$ Å³, $Z = 1$, $d_c = 1.850$ g cm⁻³, 5518 reflections ($2\theta_{max} = 55.2^\circ$, $2\theta-\omega$ scan, 23 °C) collected on a Rigaku AFC-5R diffractometer using Mo-K α radiation. During the data collection, the standards decreased by -28.9% and thus a linear correction factors was applied to the data to account for this decay. Data were also corrected for Lorentz and polarization effects, and an empirical absorption correction was applied based on an azimuthal scan of a reflection having χ near 90°. Structure was solved by the direct method (SHELX 86) and refined by full-matrix least squares (TEXSAN package of Molecular Structure Corporation) to $R = 0.045$, $R_w = 0.044$ for 2303 reflections with $I > 3\sigma(I)$ and 264 parameters. H-atoms were located at the calculated positions and not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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