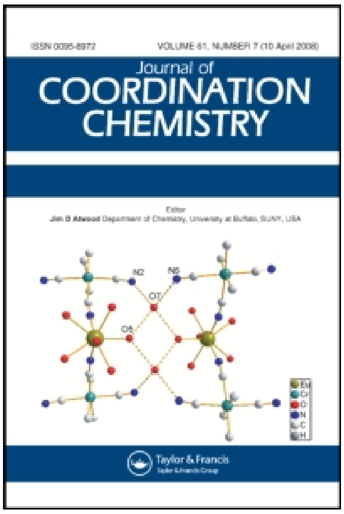

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SYNTHESIS OF NEW ORGANODERIVATIVES OF LOWER LANTHANIDES

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The synthesis of a new class of trimethylene bridged biscyclopentadienyl derivatives of lanthanum(III) and cerium(III) with chloride and pentyethynyl ligands is reported.

In the past few years, interest in the chemistry of organic derivatives of the lanthanide metals has been expanding rapidly. Until relatively recently, little has been known about the structural chemistry of the 14 lanthanide elements, which exist predominantly in the +3 oxidation state. While most of the work has been centered around the ionic π-bonded cyclopentadienyl[1,2] and cyclo-actatetraenyl[3] ligands, a few indenyl[4] derivatives and more recently lanthanide (III)-tris(dimethyl-phosphonium-bis methyl lid)[5] derivatives (lanthanide = La, Pr, Nd, Sm), and complexes obtained from 1,3-butadienes[6] have also been reported (lanthanide = La, Nd, Sm, Er). The present renaissance of interest in the organometallic chemistry of lanthanide elements is partly due to a great deal of focus being placed on σ-bonded complexes.[7] The list of available σ-bonded organolanthanides has been further expanded by the preparation of tris-(trimethylsilyl-methyl)erbium,[8] bis(phenylethynyl)-ytterbium,[9] complexes containing covalent bonds between the lanthanide element (er, Yb) and germanium or tin of the type $(C_5H_5)_2Ln{-}M(C_6H_5)_3$,[10] and homoleptic tert-butyl lanthanide derivatives.[11] To date, however, no stable σ-bonded complexes of lower lanthanides (La, Ce, Pr, Nd) have been reported. The inability to prepare such complexes could possibly be linked to the deficiency of 4f electrons in the lower lanthanides. If so, f-orbital electrons may be playing some subtle role in stabilizing the σ-bonded derivatives. One possible synthetic approach for these complexes could be the use of ligands which have not only electron donar ability but also are bulky to offset the lanthanide contraction effect – thus satisfying the coordinate saturation.

We wish to report the synthesis of a new class of stable σ-bonded organolanthanide complexes the ring-bridged biscyclopentadienyl lanthanide chloride $[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]LnCl$ and the corresponding σ-bonded phenylethynyl complexes $[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]Ln{-}C{\equiv}C{-}C_6H_5$ (Ln = La and Ce). These are the first σ-bonded derivatives known for lanthanum and cerium, though phenylethynyl complexes of higher lanthanides are well known.[7b,e] Also since the preparation of tricyclopentadienyl cerium in 1954,[1a] we believe these are the only other modified biscyclopentadienyl cerous derivatives which have been reported so far.

The 1,1′-trimethylene biscyclopentadienyl lanthanide chloride were prepared in a 50% yield by the reaction anhydrous lanthanide chloride (Ln = La and Ce) and the disodium salt of 1,3-bis-(cyclopentadienide) propane[12] in THF at room temperature, giving a colored solution indicative of trivalent lanthanide ion and a precipitate consisting of NaCl and unreacted $LnCl_3$. The complexes were purified by several extractions with THF. The phenylethynyl complexes were prepared as shown in Eq. (1) by the reaction of the 1,1′-trimethylene bis-cyclopentadienyl lanthanide chloride with phenylethynyl sodium[13] in THF at 0°C.

$$[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]LnCl + Na{-}C{\equiv}C{-}C_6H_5 \xrightarrow[0^\circ C]{THF} NaCl + [1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]La{-}C{\equiv}C{-}C_6H_5 \tag{1}$$

The complexes were precipitated from the reaction solution by concentrating the solution *in vacuo* and by the subsequent addition of pentane. These complexes decompose rapidly upon exposure to oxygen and moisture but their thermal stability is illustrated by the fact that none of these complexes decompose or melt below 100°C in sealed argon filled capillaries.

The composition of these complexes has been verified by complete elemental analysis for the chloride derivatives and metal analysis for the phenylethynyl series.[14]

The infrared spectra of these complexes are mostly identical.[15] The phenylethylnyl complex of lanthanum exhibits a sharp C≡C stretch at 2052 cm^{-1} but corresponding cerium complex exhibits only a broad bond at 2050 cm^{-1}. Both of these values are lower than the corresponding value for phenylacetylene (2112 cm^{-1}).[16] Besides the strong bands at 668 and 760 cm^{-1} which are indicative of a mono substituted phenyl group, the bands at 2934 to 2867 cm^{-1} may be assigned to the methylene groups. The bands at 3080, 1045, 1024 and 857 cm^{-1} are attributable to the π-bonded cyclopentadienyl moiety.[17]

Ultraviolet and visible spectra were obtained in a THF solution. The spectra of the phenylethynyl complexes contain a charge-transfer band originating in the U.V. and tailing into the visible region which in some cases has been implicated to indicate some interaction other than a strictly ionic one between the ligand and the metal.[3b,7e]

The magnetic susceptibility of the 1,1′-trimethylene biscyclopentadienyl cerium chloride measured at variable temperature from 48.84°K to 306.23°K is in the range of 1.684 to 2.005 (B.M.). These magnetic susceptibility values are lower than the values calculated for the tripositive state of the metal[18] but are comparable to that reported for cerium cyclooctatetraenyl complexes[3b,19] measured at ambient temperature. Although this variance of magnetic susceptibility is comparable to some cyclopentadienyl lanthanide alkyl and aryl derivatives[7c,e] but in general this is in contrast to all of the other cyclopentadienyl lanthanide complexes. The Cp_3Ln[1b] (Cp + cyclopentadienyl ligand; Ln = Ce, Pr, Sm, Eu, Gd. Dy, Ho, Er, Yb), Cp_2LnCl[2a] (Ln = Sm, Gd, Dy, Ho, Er, Yb), and $CpLnCl_2 \cdot 3THF$[2b] (Ln = Eu, Dy, Er, Yb) complexes have effective magnetic moments which are invariant with temperature.

The 'H NMR spectra was obtained in THF and deutorochloroform in the normal region using a Varian T-Go MNz spectrometer. In case of cerium complexes, isotropic shifts are minimal[20] but the absorption peaks were too broad to be meaningful. For lanthanum complexes the signals at $\delta = 7.57$ and $\delta = 7.74$[21] have relative integrated intensity of 8 and are assigned to the protons of Cp groups. The broad peaks at $\delta = 4.24$ and $\delta = 4.54$ integrate to 6 and are due to the methylene protons. From the lanthanum phenylethynyl complex the signal at $\delta = 8.92$ which integrates to 5 is assigned to phenyl protons.

This work demonstrates that the σ-bonded derivatives of lower lanthanides can be synthesized and our reaction scheme appears to be a general one and should work for other ligands, as well with lower lanthanide elements. Further studies in this area are under investigation.

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13. Prepared from the reaction of ardium metal and elbynyl benzene in ethyl ether.
14. Elemental analyses were preformed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Anal. Calcd. (chloride) for $C_{13}H_{14}LaCl$: C, 45.3; H, 4.11; La, 40.31; Cl, 10.28. Found: C, 43.5; H. 5.13; La, 39.67; Cl, 10.31. Calcd. for $C_{13}H_{14}CeCl$: C, 45.15; H, 4.08; Ce, 40.52; Cl, 10.25. Found: C, 43.5; H, 5.16; Ce 39.18; Cl 10.74. Calcd. (phenyl ethynyl) for $C_{21}H_{19}La$: La, 33.85. Found: 35.66. Calcd. for $C_{21}H_{19}Ce$: Ce, 34.05. Found: 34.71.
15. For example $[1,1'(CH_2)_3(\eta^5\text{-}C_5H_4)_2]La{-}C{\equiv}C{-}C_6H_5$: Ir (Nujol, cm^{-1}) 3080 (s) 2934 (s), 2867 (s), 2052 (s), 1061 (br), 1045 (s), 1024 (m), 1003 (m), 945 (m), 857 (m), 760 (s), 668 (s).
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