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# Synthesis of New Organo Derivatives of Early Lanthanides

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The known chemistry of the lanthanide elements is somewhat limited when compared with the chemistry of the transitional metals, but in recent years the interest in the organometallic chemistry of the lanthanides has expanded rapidly. Most of the work has been centered around the ionic $\pi$-bonded cyclopentadienyl[1,2] and cyclooctatetraenyl[3] ligands, a few indenyl[4] derivatives, and more recently lanthanide(III)-tris(dimethylphosphonium dimethylylide)[5] derivatives (lanthanides = La, Pr, Nd, Sm), and complexes obtained from 1,3-butadienes[6] have also been reported (lanthanides = La, Nd, Sm, Er). With this renewed attention it has also become apparent that metal-to-carbon $\sigma$-bonds constitute a large and important area of lanthanide organometallic chemistry. An extensive synthetic chemistry of cyclopentadienyl[7,8] and homoleptic[7,9,10] alkyls has rapidly developed. There is, however, very little known about the $\sigma$-bonded complexes of the early lanthanides (La, Ce, Pr, Nd).

Recently we communicated our preliminary results in synthesizing the ring-bridged dicyclopentadienyllanthanide chloride $[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]LnCl$ and the corresponding $\sigma$-bonded phenylethynyl complexes $[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]LnC{\equiv}CC_6H_5$ (Ln = La, Ce).[11] These represent the first $\sigma$-bonded derivatives known for lanthanum and cerium. We now wish to report a detailed account of the synthesis and properties of these compounds.

## Experimental Section

All reactions and operations were performed with use of Schlenk techniques or a drybox with an atmosphere of dried, oxygen-free argon. Tetrahydrofuran (THF) and diethyl ether were dried and freed of oxygen by distilling under argon from blue sodium benzophenone ketyl immediately prior to use. Pentane, hexane, and benzene were degassed prior to use and distilled under argon from finely divided lithium aluminum hydride. Anhydrous lanthanide trichlorides were purchased from Alfa-Ventron and were used as received. Melting points were tried in sealed argon-filled capillaries. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

**(1,1′-Trimethylenedicyclopentadienyl)lanthanum Chloride.** Into a pear-shaped Schlenk tube was placed 3.00 g (12 mmol) of lanthanum trichloride, and approximately 150 mL of THF distilled onto the solid. The tube was cooled to 0 °C and a freshly prepared slurry of the disodium salt of 1,3-dicyclopentadienylpropane[12] in THF (12.5 mmol) was added through a Schlenk addition funnel. After stirring at 0 °C for 1 h, the reaction was allowed to warm gradually to room temperature and stirred for 18 h. THF was then removed in vacuo, and the solid was washed with 50 mL of pentane and dried. The solid was extracted twice with 60-mL portions of freshly distilled THF. The reaction mixture was centrifuged, and the THF solution was decanted from the solid. THF was slowly removed in vacuo, giving a pale yellow solid which on drying yielded 1.8 g (44%) of $[Cp(CH_2)_3Cp]LaCl$ (Cp = cyclopentadienyl). Anal. Calcd for $C_{13}H_{14}ClLa$: C, 45.3; H, 4.11, Cl, 10.28; La, 40.31. Found: C, 43.5; H, 5.13; Cl, 10.36; La, 39.67.

**(1,1′-Trimethylenedicyclopentadienyl)(ethynylbenzene)lanthanum.** In a centrifuge Schlenk tube were placed 2.00 g (5.8 mmol) of $[Cp(CH_2)_3Cp]LaCl$ and 0.72 g (5.8 mmol) of (phenylethynyl)sodium.[13] Then, 60 mL of THF, cooled to −78 °C was added to the solids. The resulting suspension was continuously stirred and warmed to room temperature over a 6-h period and overnight. THF was then removed in vacuo, and the resulting solid was washed with 50 mL of pentane and dried. The solid was extracted twice with freshly distilled 50-mL portions of THF. From the combined extracts, THF was slowly evaporated in vacuo to about 5–10 mL. At this point, 50 mL of pentane was added to this concentrated THF solution; a tan solid precipitated. The solid was dried in vacuo for 1 h to give 0.6 g (25%) of $[Cp(CH_2)_3CP][C_6H_5C{\equiv}C]La$ (dec pt 150–200 °C, darkening but no melting). Anal. Calcd for $C_{21}H_{19}La$: La, 33.85. Found: La, 35.51.

**(1,1′-Trimethylenedicyclopentadienyl)cerium Chloride.** In a pear-shaped Schlenk tube was placed 6.2 g (25 mmol) of cerium trichloride, and approximately 150 mL of THF was distilled over the solid. The tube was cooled to 0 °C, and a freshly prepared slurry of the disodium salt of 1,3-bis(cyclopentadienyl)propane in THF (25 mmol) was added through a Schlenk addition funnel. After stirring for 1 h, it was allowed to warm gradually to room temperature in 5–6 h and stirred for an additional 18 h. THF was then removed in vacuo, and the solid was washed with 50 mL of pentane and dried. The solid was extracted twice with 60-mL portions of THF. The solid byproducts were removed by centrifugation, and THF was slowly evaporated in vacuo. A greenish brown crystal-type solid was obtained, which on drying yielded 4.8 g (55.5%) of $[Cp(CH_2)_3Cp]CeCl$. Anal. Calcd for $C_{13}H_{14}ClCe$: C, 45.15; H, 4.08; Cl, 10.25; Ce, 40.52. Found: C, 43.5; H, 5.16; Cl, 10.74; Ce, 39.18.

**(1,1′-Trimethylenedicyclopentadienyl)(ethynylbenzene)cerium.** In a centrifuge Schlenk tube were placed 2.00 g (5.8 mmol) of $[Cp(CH_2)_3Cp]CeCl$ and 1.2 g (9 mmol) of (phenylethynyl)sodium. Then, 60 mL of THF cooled to −78 °C was added to the solids. The resulting suspension was allowed to stir with gradual warming to room temperature in 6–8 h and stirred overnight. THF was removed in vacuo, and the solid was washed with 50 mL of pentane and dried. The solid residue was extracted twice with fresh 50-mL portions of THF. From the combined extracts, the THF solution was concentrated in vacuo to about 15 mL, and then 50 mL of pentane was added to the solution, precipitating a brown solid. The mixture was centrifuged, pentane was decanted, and the solid was dried in vacuo for 1.5 h to give 0.65 g (27%) of $[Cp(CH_2)_3Cp][C_6H_5C{\equiv}C]Ce$ (dec pt 150 °C, color darkens but no melting). Anal. Calcd for $C_{21}H_{19}Ce$: Ce, 34.05. Found: Ce, 34.71.

**Instrumental Measurements.** Visible and ultraviolet spectra were recorded on a Beckman Model 24 spectrophotometer. Solutions were kept in a special 1-cm quartz cuvette which had been fused to a Schlenk

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adaptor so that the solutions could be maintained under an inert atmosphere.

Infrared spectra were recorded on a Beckman IR-8 or Perkin-Elmer Model 727 spectrophotometer as Nujol and Fluorolube mulls and examined between NaCl plates. The mulls were prepared in the drybox with use of dry, degassed Nujol or Fluorolube which had been deoxygenated and dried.

Proton NMR spectra of the complexes were recorded at room temperature on a Varian T-60 spectrometer. Spectra were obtained in THF and deuteriochloroform solutions. Mass spectrum was recorded with a Hewlett-Packard Model 5980Å gas chromatograph quadrapole mass spectrometer at ionizing voltages of both 15 and 70 eV and coupled to a computer data system. Magnetic susceptibility was measured by the Faraday method using $Hg[Co(SCN)_4]$ as a standard. The instrument was tied into a computer data system which gave continuous readouts of $\chi$, $\chi_M$ and $\mu_{eff}$ as the temperature was varied.

The X-ray photoelectron spectra were obtained on a Hewlett-Packard 5950Å ESCA spectrometer using an Al X-ray anode. The typical residual pressure in this system was in the $10^{-9}$-torr range. Charging effects were neutralized by using an electron flood gun. Since the spectra were obtained by digital accumulation, it was possible to verify that no photodecomposition took place during acquisition of the spectra. The binding energy scale was chosen for the C (1s) level arising from the ligand or surface contamination and was assumed to be 284.8 eV.

## Results and Discussion

In the course of our studies with the newly synthesized complexes of early lanthanides it became apparent the choice of ring-bridged dicyclopentadienyl ligand may have some effect in stabilizing these complexes. Due to methylene-bridge, electron-donating properties of Cp rings are enhanced to match the more electropositive character of early lanthanide elements. Also the bridged ligand occupies the large coordination site of these lanthanides which, in effect, provides a much needed congestion around the metal sphere, an important contribution for the stability of a complex.

**Synthesis.** The new organolanthanide complexes were prepared according to reactions 1 and 2. The complexes were

$$[1,1'\text{-}(CH_2)_3(\pi^5\text{-}C_5H_4)_2]^{2-}2Na^+ + LnCl_3 \xrightarrow{THF} [1,1'\text{-}(CH_2)_3(\pi^5\text{-}C_5H_4)_2]LnCl + 2NaCl \quad (1)$$

$$[1,1'\text{-}(CH_2)_3(\pi^5C_5H_4)_2]LnCl + NaC{\equiv}CC_6H_5 \xrightarrow[0\ °C]{THF} NaCl + [1,1'\text{-}(CH_2)_3(\pi^5\text{-}C_5H_4)_2]LnC{\equiv}CC_6H_5 \quad (2)$$

purified by extraction. In the solid state, all of them appear to be stable indefinitely in an atmosphere of argon. Though these complexes are air sensitive, their thermal stability is quite high; all are stable to at least 100 °C in sealed argon-filled capillaries.

The infrared spectra of these complexes are mostly identical.[14] The phenylethynyl complex of lanthanum exhibits a sharp C≡C stretch at 2052 $cm^{-1}$, but the corresponding cerium complex exhibits only a broad band at 2050 $cm^{-1}$. Both of these values are lower than the corresponding value for phenylacetylene (2112 $cm^{-1}$).[15] Besides the strong bands at 668 and 760 $cm^{-1}$ which are indicative of a monosubstituted phenyl group, the bands at 2934–2867 $cm^{-1}$ may be assigned to the methylene groups. The bands at 3080, 1045, 1024, and 857 $cm^{-1}$ are attributable to the $\pi$-bonded cyclopentadienyl moiety.[16]

Ultraviolet and visible spectra were obtained in a THF solution. The spectra of the phenylethynyl complexes contain a charge-transfer band originating in the UV 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,8e]

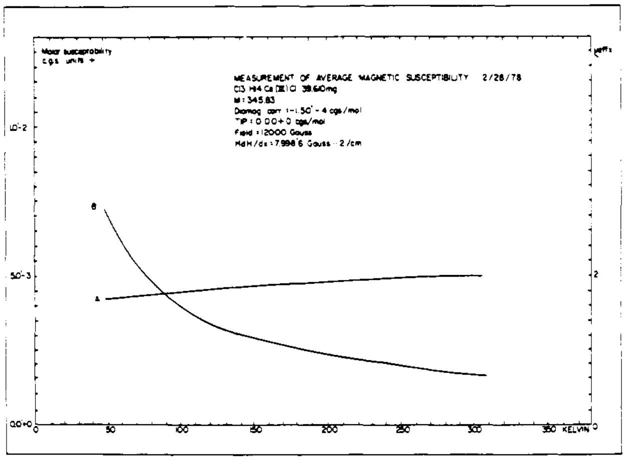

**Figure 1.** Magnetic susceptibility of $[Cp(CH_2)_3Cp]CeCl$: A, magnetic moment ($\mu_{eff}$); B, molar susceptibility ($\chi_M$).

**Table I.** Proton NMR of $[Cp(CH_2)_3Cp]LaCl$ and $[Cp(CH_2)_3Cp]CeCl^{a,b}$

| compd | signal$^c$ | proton shift | assignt |
|---|---|---|---|
| $[Cp(CH_2)_3Cp]LaCl$ | s | 7.57,$^d$ 7.58$^e$ (4) | α-Cp |
| | s | 7.74,$^d$ 7.77$^e$ (4) | β-Cp |
| | m | 4.24,$^e$ 4.54$^e$ (6) | $CH_2$ |
| $[Cp(CH_2)_3Cp]CeCl$ | bm | 7.44,$^d$ 8.39$^e$ (8) | Cp |
| | bm | 3.99, 4.54$^e$ (6) | $CH_2$ |

$^a$ NMR data in ppm based on upfield THF peak occurring at δ 1.79. $^b$ All data at 25 °C. $^c$ s = singlet, m = multiplet, bm = broad multiplet. $^d$ In THF. $^e$ In deuteriochloroform.

**Table II.** Proton NMR of $[Cp(CH_2)_3Cp]LaC{\equiv}CPh$ and $[Cp(CH_2)_3Cp]CeC{\equiv}CPh^{a,b}$

| compd | signal$^c$ | proton shift | assignt |
|---|---|---|---|
| $[Cp(CH_2)_3Cp]LaC{\equiv}CPh$ | s | 8.92 (5) | Ph |
| | m | 7.31 (4) | α-Cp |
| | s | 7.49 (4) | β-Cp |
| $[Cp(CH_2)_3Cp]CeC{\equiv}CPh$ | s | 9.16 (5) | Ph |
| | m | 7.29–7.59 (8) | Cp |

$^a$ NMR data in ppm based on upfield THF peak occurring at δ 1.79. $^b$ All data at 25 °C. $^c$ s = singlet, m = multiplet.

The magnetic susceptibility of the (1,1′-trimethylenedicyclopentadientyl)cerium chloride measured at variable temperature from 48.84 to 306.23 K is in the range of 1.684–2.005 $\mu_B$. The results are plotted in Figure 1. These magnetic susceptibility values are lower than the values calculated for the tripositive state of the metal[17] but are comparable to that reported for cerium cyclooctatetraenyl complexes[3b,18] measured at ambient temperature. Although this variance of magnetic susceptibility is comparable to some cyclopentadienyllanthanide alkyl and aryl derivatives,[8c,e] in general this is in contrast to all of the other cyclopentadienyllanthanide 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 $^1H$ NMR spectra were obtained in THF and deuteriochloroform in the normal region with use of a Varian T-60 MHz spectrometer and are listed in Tables I and II. In the

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(14) For example, IR (Nujol) for $[1,1'\text{-}(CH_2)_3(\eta^5\text{-}C_5H_4)_2]LaC{\equiv}CC_6H_5$: 3080 (s), 2934 (s), 2867 (s), 2052 (s), 1061 (br), 1045 (s), 1024 (m), 1003 (m), 945 (m), 857 (m), 760 (s), 668 (s) $cm^{-1}$.

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Table III. Binding Energies (BE) for Cl (2p) and La (3d) Photoelectron Lines[a, b]

| compd | BE | | |
|---|---|---|---|
| | La (3d) | Cl ($2p_{1/2}$) | Cl ($2p_{3/2}$) |
| $LaCl_3$ | 835.0 | 197.6 | 197.0 |
| $[Cp(CH_2)_3Cp]LaCl$ | 833.0 | 198.8 | 197.6 |
| $Cp_3La$ | 831.0 | NO[c] | NO[c] |

[a] All values in electronvolts (eV). [b] Binding energy scale was chosen for $C_{1s}$ peak–284.8 eV. [c] Not observed.

case of cerium complexes, isotropic shifts are minimal,[19] but the absorption peaks were too broad to be meaningful. For lanthanum complexes the signals at $\delta$ 7.57 and 7.74 have a relative integrated intensity of 8 and are assigned to the protons of the Cp groups. The broad peaks at $\delta$ 4.24 and 4.54 integrate to 6 and are due to the methylene protons. For the lanthanum phenylethynyl complex the signal at $\delta$ 8.92, which integrates to 5, is assigned to phenyl protons.

In the mass spectrum of $[Cp(CH_2)_3Cp]CeCl$, the parent ion is only 0.6% as abundant as the most prominent peak at $m/e$ 91, and the cerium isotopes are not abundant in the spectrum either. The peak at $m/e$ 72 may be formed from the chlorine isotopes or as a residue of the ligand. The lowest intensity peaks were not displaced in the computer output because of the normalization procedure. The most probable fragmentation path appears to be the breaking of the cerium–cyclopentadienyl bonds and the bridge carbon bonds, resulting in seven carbon membered ions ($m/e$ 91 and 92). The remaining fragments of this complex at $m/e$ 77–80 also appears in the spectrum. Another fragmentation pattern at $m/e$ 171, 172, and 173 appears to be the splitting of the Ce–Cl group. Further degradation is indicated by mass peaks at intervals of 14 mass units, indicating the loss of $CH_2$ groups.

The X-ray photoelectron spectra (ESCA) of $LaCl_3$, $[Cp(CH_2)_3Cp]LaCl$, and $Cp_3La$ were measured. Cl 2p and La 3d photoelectron lines of these three compounds are summarized in Table III. The binding energies of both the Cl $2p_{1/2}$ and Cl $2p_{3/2}$ photopeaks increase slightly as the number of chlorine ions in the molecule are reduced from 3 in $LaCl_3$ to 1 in $[Cp(CH_2)_3Cp]LaCl$. The 0.6-eV increase in binding energy of the Cl $2p_{3/2}$ photopeak in $[Cp(CH_2)_3Cp]LaCl$ relative to $LaCl_3$ is miniscule but important and could be interpreted as a very small decrease in the electronic charge density located in chlorine ions in going from $LaCl_3$ to $[Cp(CH_2)_3Cp]LaCl$. In the case of La $3d_{5/2}$ signals, strong satellite peaks were observed on both sides of the parent peaks which, in general, has been the subject of long debate.[20] These satellites which occur at a 3–6 eV higher energy region than that of main peaks have been attributed to charge-transfer shake-up from occupied orbital(s) (L → "4f")[21] If the L → "4f" transition causes the satellite peak, the intensity would be reduced as the number of "f" electrons is constantly increased. This is supported by the observation that the satellite lines of any lanthanum complex are much more intense than in any of the rest of the 14 lanthanide elements. In fact, it is not even observed following cerium in the lanthanide series of the periodic table.

The configuration of these complexes as monomeric or polymeric is still unresolved. Because of their low solubilities the molecular weights have not yet been determined, even though, when freshly prepared, solubilities of these complexes seem to be better. This can be seen; when first synthesized, these complexes are monomeric but slowly changing after a period of time. So that this question may be settled, the complete structure elucidation will shortly be done by X-ray diffraction analysis.

There seems to be no doubt that big anionic ligands can greatly stabilize lanthanides toward $\sigma$-bond formation. Here it appears both electronic properties and steric rigidity are operating together. These newly synthesized complexes bridge a gap of the missing dicyclopentadienyl derivatives of the early lanthanides, which in turn eventually will be used for the synthesis of a series of $\sigma$-bonded complexes for all the lanthanide elements.

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**Registry No.** $[Cp(CH_2)_3Cp]LaCl$, 75857-12-4; $[Cp(CH_2)_3Cp]LaC{\equiv}CPh$, 75861-71-1; $[Cp(CH_2)_3Cp]CeCl$, 75861-70-0; $[Cp(CH_2)_3Cp]CeC{\equiv}CPh$, 75861-72-2; $LaCl_3$, 10099-58-8; $Cp_3La$, 1272-23-7.

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# Chemistry of the $\mu_2$-Alkyne Ligand in $(\eta^5\text{-}C_5H_5)_2Ni_2(RC{\equiv}CR)$

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An understanding of the chemistry of bridging alkyne ligands in polynuclear metal complexes is important to the overall development of organocluster chemistry. In recent years, we have studied the chemistry of bridging $\mu_x$ ($x \geq 2$) alkyne ligands in dinuclear[1,2] and polynuclear[3,4] metal complexes with special emphasis on three types of reactions: (i) alkyne exchange between free and bound alkyne to gain a measure of alkyne–$M_x$ bond strengths and of dynamic features of these complexes; (ii) hydrogen addition reactions to assess alkyne reduction tendencies and also the tendency of the polynuclear complex to fragment into smaller species; (iii) catalytic hydrogenation of alkynes (selectivity). Described below is such a study of $(\eta^5\text{-}C_5H_5)_2Ni_2(\mu_2\text{-}\eta^2\text{-}RC{\equiv}CR)$ complexes.

## Experimental Section

**Reagents and Procedures.** Solvents were dried by refluxing over sodium and distillation prior to use. Diphenylacetylene purchased from Aldrich Chemical Co. was used without any purification. Di-*p*-tolylacetylene,[5-7] $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$,[8] $(C_5H_5)_2Ni_2(C_7H_7C_2C_7H_7)$,[8] and $(CH_3C_5H_4)_2Ni_2(C_6H_5C_2C_6H_5)$[8] were prepared by literature procedures.

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