

interactions of 2.29 (1) Å for Co(3) and O(7) and 2.43 (1) Å for Co(1) and O(3). These are similar to the long interaction seen in the titanium compound. However, in the more complicated cobalt complex it is more difficult to decide whether or not these close contacts represent real bonds or are just a result of geometric constraints imposed by the ligand.

Another feature of interest in these complexes is the possibility of a host-guest interaction, whereby a small molecule fits inside the cone of the calixarene. The crystal structure of the clathrate *p*-*tert*-butylcalix[4]areneH₄·PhMe has already been reported.²⁸ The cobalt complex **4** crystallizes with five toluene molecules. Two of these are involved in a host-guest interaction. A typical arrangement is shown in Figure 5. The titanium complex **2** crystallizes with three toluenes in the asymmetric unit, and one of these is incorporated into the cone. By contrast, the iron

complex **3** has one and one-half molecules of *n*-hexane in the asymmetric unit and neither of these is found within the cone. The reason for this difference in behavior is not immediately obvious, since the cone opening is both flexible and wide. If one takes the distances between opposing carbons bonded to the *tert*-butyl groups as a measure, the openings are 7.49 × 9.18 Å for **2**, 5.44 × 9.60 Å for **3**, and 7.44 × 9.01 and 7.33 × 9.19 Å for **4**.

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Registry No. 1, 60705-62-6; **2**, 98719-91-6; **3**, 98705-02-3; **4**, 98719-93-8; Fe(N(SiMe₃)₂)₃, 22999-67-3; Co[N(SiMe₃)₂]₂, 18544-54-2.

Supplementary Material Available: Tables of atom coordinates, thermal parameters, complete tables of bond distances and angles, hydrogen coordinates and structure factors (24 pages). Ordering information is given on any current masthead page.

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Highly Reactive Organolanthanides. Systematic Routes to and Olefin Chemistry of Early and Late Bis(pentamethylcyclopentadienyl) 4f Hydrocarbyl and Hydride Complexes

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Abstract: The reaction of the organolanthanide complexes Cp'₂MCl₂·Li(ether)₂⁺, Cp' = η⁵-(CH₃)₅C₅, M = La, Nd, Sm, and Lu, with LiCH[Si(CH₃)₃]₂ provides a straightforward route to the broad class of ether- and halide-free bis(pentamethylcyclopentadienyl) lanthanide alkyls, Cp'₂MCH[Si(CH₃)₃]₂. These complexes were characterized by standard analytical methodology. The M = Nd complex crystallizes in the monoclinic space group P2₁/n with four molecules in a cell of dimensions (-100 °C) a = 11.045 (9) Å, b = 23.554 (7) Å, c = 11.648 (9) Å, and β = 103.10 (6)°. Least-squares refinement led to a value for the conventional R index (on F) of 0.078 for 4287 independent, absorption-corrected reflections having I > 3σ(I). The molecular structure consists of monomeric Cp'₂NdCH[Si(CH₃)₃]₂ units with a "bent-sandwich" Cp'₂Nd configuration: (ring centroid)-Nd-(ring centroid) = 134.4°. The CH[Si(CH₃)₃]₂ fragment is coordinated to the Cp'₂Nd group in a highly unsymmetrical fashion with a Nd-C σ-bond distance of 2.517 (7) Å and a rather short secondary contact to a single methyl carbon atom of 2.895 (7) Å. Spectroscopic data suggest that this interaction is highly metal-to-carbon in character. The Cp'₂NdCH[Si(CH₃)₃]₂ complexes react with H₂ under mild conditions to yield the corresponding hydrides (Cp'₂MH)₂. These complexes are extremely active homogeneous ethylene polymerization catalysts with turnover frequencies exceeding 1800 s⁻¹ (25 °C, 1 atm of ethylene pressure) for M = La. Activities are in the order La ≥ Nd ≫ Lu. The kinetics of this process and the molecular weight characteristics of the resulting polymer are severely limited by mass transport effects; evidence is presented that these are "living" polymers and that chain transfer by β-hydride elimination is not important. For La and Nd, propylene and 1-hexene react rapidly at -10 °C to yield equal quantities of the disproportionation products alkane + metal η³-alkenyl. Butadiene undergoes reaction with these hydrides to yield η³-crotyl complexes, and significant polymerization does not occur. For 1-hexene under low H₂ (or D₂) pressure at room temperature, some formation of 2-methylundecane is also observed. The analogous reaction of cyclohexene with these hydrides is sluggish and appears to produce an η¹-cyclohexenyl complex. There is no evidence for cyclohexene oligomers. Although unreactive toward olefins, Cp'₂NdCH[Si(CH₃)₃]₂ reacts with CO to yield a dimeric dionediolate.

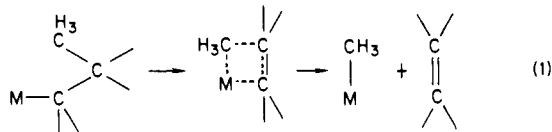
Much of the recent development of early transition- and f-element hydrocarbyl and hydride chemistry can be attributed to the beneficial characteristics of bis(pentamethylcyclopentadienyl) (Cp'₂) supporting ligation.²⁻⁴ However, in contemplating com-

parative studies of isoelectronic, isoleptic 4f/5f systems,^{5,6} it was evident to us that routes to lanthanide Cp'₂MR and (Cp'₂MH)₂

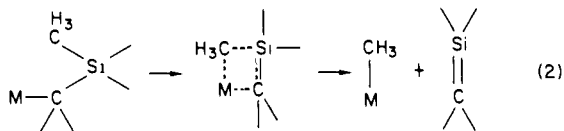
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complexes were circuitous for late lanthanides⁷ and virtually unknown for early (La–Nd) lanthanides.⁸ The latter were of greatest interest to us since U(III)⁶ and Nd(III)⁵ are isoelectronic, because the early organolanthanides have the greatest importance in catalysis⁹ and because, a priori, the early lanthanides might, for a given ligand array, offer the greatest degree of coordinative unsaturation and possibly reactivity. In planning syntheses, the use of highly lipophilic, sterically bulky R functionalities (as in our uranium work⁶) was anticipated so that undesirable coordination to the lanthanide ion of ether or halide ligands (normally present during the preparation of Cp₂MR complexes) could be avoided. In most d-element hydrocarbyl syntheses, the choice of R is also frequently dictated by the desire to avoid destabilizing β-hydrogen atoms. However, it now appears that β-alkyl elimination (e.g., eq 1) may be an equally important decomposition pathway for some organo-f-element complexes and must also be considered in ligand selection.



Ligands such as CH[Si(CH₃)₃]₂(CH(TMS)₂)^{6a,10} offer both the attraction of substantial lipophilic bulk and a lack of β-hydrogen atoms as well as a defense (heretofore largely unrecognized) against β-alkyl elimination since such an extrusion process would produce a relatively high-energy¹¹ Si=C bond (e.g., eq 2).



In the present contribution, we employ this ligand to straight-

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forwardly (i.e., in as little as one "pot") synthesize a broad class of stable Cp₂MR complexes⁵ ranging from the lightest (M = La) to the heaviest (M = Lu) lanthanide.¹² The interesting chemical and unusual structural properties of these molecules are then discussed, including the diffraction-derived crystal structure of Cp₂NdCH(TMS)₂. In addition, hydrogenolysis readily yields the corresponding series of hydrides, (Cp₂MH)₂, from M = La to Lu. The rather extraordinary reactivity of these molecules is demonstrated herein by their very high activity for olefin oligomerization and polymerization. It is thus possible to compare the behavior of early lanthanides with Watson's recent results on Lu.^{4,7c} However, the Cp₂M ligation array may be far from optimum for organolanthanide coordinative unsaturation, and approaches to "opening" as well as immobilizing the supporting ligation are illustrated by a companion chemical/structural study¹³ of organolanthanide hydrocarbyls and hydrides with a chelating X[(CH₃)₄C₅]₂ ligand.¹⁴ In a third contribution,¹⁵ we then focus in detail on the kinetic and mechanistic aspects of olefin hydrogenation by the above two classes of organolanthanides. Remarkably little is known about the nature of such processes for early transition- and f-element homogeneous catalysts, and the present hydrides are of particular interest as some of the most active homogeneous olefin hydrogenation catalysts yet discovered.

Experimental Section

Materials and Methods. All operations were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware in a dual-manifold Schlenk line or interfaced to a high-vacuum (10⁻⁵ torr) system or in a dinitrogen-filled, Vacuum Atmospheres glovebox with a high-capacity atmosphere recirculator. Argon (Matheson, prepurified), ethylene (Matheson, CP), propylene (Matheson, CP), dihydrogen (Linde), and deuterium gas (99.5%, Matheson) were purified by passage through a supported MnO oxygen removal column¹⁶ and a Davison 4A molecular sieve column. Aliphatic hydrocarbon solvents were pretreated with concentrated H₂SO₄, KMnO₄ solution, MgSO₄, and Na + 4A molecular sieves. All reaction solvents were distilled from Na/K/benzophenone under nitrogen and were condensed and stored in vacuo in bulbs on the vacuum line containing a small amount of [Ti(η⁵-C₅H₅)₂Cl]₂ZnCl₂ as indicator.¹⁷ Cyclohexane and heptane were additionally vacuum-transferred onto Na/K and stirred for at least a day before use in catalytic experiments. The olefins 1-hexene (Aldrich Gold Label) and cyclohexene (Aldrich Gold Label) were purified by stirring over Na/K for at least 6 h and were freshly vacuum-transferred. Deuterated solvents were dried over Na/K alloy and vacuum-transferred before use.

Anhydrous lanthanide halides were prepared from the corresponding oxide and ammonium chloride.¹⁸ Pentamethylcyclopentadiene was prepared by the procedure developed in this laboratory.^{14,19} The complexes Cp₂NdCl₂Li(ether)₂²⁰ and Cp₂LuCl₂Li(ether)₂²¹ were prepared by the literature procedures. Bis(trimethylsilyl)methyl lithium (LiCH(TMS)₂) was prepared by the literature procedure.²²

Physical and Analytical Measurements. Proton and carbon NMR spectra were recorded on either a Varian EM-390 (CW, 90 MHz) a JEOL FX-90Q (FT, 90 MHz), or a JEOL FX-270 (FT, 270 MHz)

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spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to TMS ($lw =$ line width). Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer using either Nujol or Fluorolube mulls or KBr pellets sandwiched between KBr plates in an o-ring-sealed, air-tight holder. As a routine precaution, one compound from each class was examined in both KBr and Nujol/Fluorolube to ensure that no reaction was occurring with the dispersing agent. Gas chromatography was performed on a Varian 3700 series instrument with appropriate columns, flame ionization detection, and a Hewlett-Packard 3390A electronic integrator. GC/MS studies were performed with a Hewlett-Packard 5985 instrument and interfaced data system. Deuterium incorporation was measured by using appropriate analytical methodology.²³ We thank Dr. Doris Hung for assistance. Gel permeation chromatography was performed at 135 °C in 1,2,4-trichlorobenzene by using various Waters Assoc. instruments in the Dow Chemical Co. Central Research Laboratory.

Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Syntheses. $Cp'_2LaCl_2Li(ether)_2^+$ (1). A suspension of 2.1 g (8.6 mmol) of anhydrous $LaCl_3$ and 2.44 g (17.2 mmol) of $LiCp'$ in 120 mL of THF was refluxed for 12 h. The solvent was then removed in vacuo, being careful to keep the temperature below 10 °C to avoid formation of a less reactive complex (probably $(Cp'_2LaCl)_2$). The white residue was then extracted with 200 mL of diethyl ether and the mixture filtered, reduced in volume to 30 mL, and slowly cooled to -30 °C. Decantation of the solvent and drying under high vacuum yielded 2.7 g (49.6%) of $Cp'_2LaCl_2Li(ether)_2^+$ as a white, microcrystalline solid:

1H NMR (C_6D_6) δ 3.25 (q, 8 H), 2.17 (s, 30 H), 1.07 (t, 12 H). Anal. Calcd for $C_{27}H_{30}LiLaCl_2O_2$: C, 52.92; H, 7.93. Found: 52.80; H, 7.97.

$Cp'_2LaCH(TMS)_2$ (5). A suspension of 2.6 g (4.1 mmol) of $Cp'_2LaCl_2Li(ether)_2^+$ and 0.68 g (4.1 mmol) of $LiCH(TMS)_2$ in 150 mL toluene was stirred for 12 h at 0 °C. The solvent was then removed in vacuo and the white residue extracted with 100 mL of pentane. The resulting mixture was then filtered, the volume of the filtrate reduced to 30 mL, and the filtrate slowly cooled to -30 °C. Pale-yellow crystals of $Cp'_2LaCH(TMS)_2$ were isolated by decantation and subsequent vacuum drying: yield 1.4 g (60%);

1H NMR (toluene- d_6) δ 1.96 (s, 15 H), 1.91 (s, 15 H), 0.16 (s, 18 H), -0.44 (s, 1 H);

IR (KBr pellet, cm^{-1}) 2950 (s), 2930 (s), 2910 (s), 2860 (s), 2730 (w), 1590 (br, m), 1435 (s), 1380 (s), 1255 (s), 1240 (s), 1145 (w), 1085 (m), 1050 (s), 1018 (m), 955 (w), 945 (m), 855 (s), 820 (s), 750 (m), 740 (m), 680 (m), 650 (m), 595 (w), 565 (m), 370 (m).

Anal. Calcd for $C_{27}H_{49}LaSi_2$: C, 57.02; H, 8.68; Si, 9.88; La, 24.42. Found: C, 56.86; H, 8.70; Si, 9.72; La, 24.63.

$Cp'_2NdCH(TMS)_2$ (6). The above procedure was repeated with 5.1 g (8.0 mmol) of $Cp'_2NdCl_2Li(ether)_2^+$ and 1.32 g (7.9 mmol) of $LiCH(TMS)_2$ in 50 mL of toluene to yield, after workup and recrystallization from pentane, 3.67 g (80%) of $Cp'_2NdCH(TMS)_2$ as blue-green crystals:

1H NMR (C_6D_6 , 20 °C) δ 61.7 (s, 1 H, $lw = 75$ Hz), 8.87 (s, 15 H, $lw = 15$ Hz), 8.73 (s, 15 H, $lw = 15$ Hz), -16.52 (s, 18 H, $lw = 30$ Hz); ^{13}C NMR (67.80 MHz, toluene- d_6 , -5 °C) δ 988.23 (Si_2CH), 307.45 ($Cp'-C$), 320.10 ($Cp-C$), 7.45 ($Si(CH_3)_3$), -15.59 ($Cp-CH_3$), -17.55 ($Cp-CH_3$);

IR (Nujol mull, cm^{-1}) 1250 (s), 1248 (s), 1080 (w), 1030 (m), 1015 (m), 855 (vs), 820 (s), 755 (w).

Anal. Calcd for $C_{27}H_{49}NdSi_2$: C, 56.49; H, 8.60; Nd, 25.12; Si, 9.78; Li, 0.00. Found: C, 56.26; H, 8.79; Nd, 25.13; Si, 9.80; Li, 0.01.

$Cp'_2SmCH(TMS)_2$ (7) (One-Pot Procedure). A mixture of 1.00 g (3.90 mmol) $SmCl_3$ and 1.11 g (7.81 mmol) $LiCp'$ was refluxed in 50 mL of THF for 8 h. The solvent was then removed in vacuo and the residue, together with 0.65 g (3.91 mmol) $LiCH(TMS)_2$, was suspended in 50 mL of toluene at -78 °C. The mixture was allowed to gradually warm to room temperature over the next 12 h, the solvent removed under high vacuum, and the residue extracted with 50 mL of pentane. Subsequent filtration, slow cooling of the filtrate to -78 °C, filtration, and drying produced 0.600 g (27%) of $Cp'_2SmCH(TMS)_2$ as red-brown crystals. An additional 0.400 g (18%) of product can be recovered from the mother liquor (total yield 45%):

1H NMR (toluene- d_6) δ 20.44 (s, 1 H), 0.90 (s, 15 H), 0.78 (s, 15 H), -4.72 (s, 18 H);

IR (KBr pellet, cm^{-1}) 2900 (vs), 1430 (m), 1375 (m), 1235 (s), 1020 (m), 950 (w), 830 (vs), 750 (m), 710 (w), 680 (s), 652 (m), 572 (m), 370 (m), 275 (w).

Anal. Calcd for $C_{27}H_{49}SmSi_2$: C, 55.89; H, 8.51; Sm, 25.91; Si, 9.68. Found: C, 55.86; H, 8.58; Sm, 26.09; Si, 9.55.

$Cp'_2LuCH(TMS)_2$ (8). The aforementioned procedure for $Cp'_2LaCH(TMS)_2$ was carried out with 3.1 g (4.62 mmol) of $Cp'_2LuCl_2Li(ether)_2^+$ and 0.79 g (4.75 mmol) of $LiCH(TMS)_2$ in 150 mL of toluene. The standard workup and pentane recrystallization yielded 1.8 g (64%) of $Cp'_2LuCH(TMS)_2$ as colorless crystals:

1H NMR (C_6D_6) δ 1.95 (s, 15 H), 1.89 (s, 15 H), 0.17 (s, 18 H), -0.02 (s, 1 H);

IR (KBr pellet, cm^{-1}) 2950 (s), 2940 (s), 2900 (s), 2860 (s), 2730 (w), 1600 (br, m), 1440 (s), 1378 (s), 1250 (s), 1235 (s), 1150 (w), 1090 (m), 1050 (m), 1030 (m), 950 (w), 940 (w), 840 (s), 755 (w), 700 (w), 660 (m), 600 (w), 580 (m), 375 (m).

Anal. Calcd for $C_{27}H_{49}LuSi_2$: C, 53.62; H, 8.17. Found: C, 53.55; H, 8.20.

$(Cp'_2LaH)_2$ (10) and $(Cp'_2LaD)_2$. $Cp'_2LaCH(TMS)_2$ (0.200 g, 0.35 mmol) was stirred under an H_2 atmosphere in 50 mL of pentane for 2 h at 0 °C. The resulting colorless precipitate was isolated by filtration, washed with 2×3 mL of pentane, and dried in vacuo to yield 0.14 g (97%) of $(Cp'_2LaH)_n$ as a colorless, microcrystalline solid. The analogous $(Cp'_2LaD)_n$ complex was prepared by using D_2 :

1H NMR (benzene- d_6) δ 10.21 (s, 2 H), 2.06 (s, 60 H);

IR (KBr pellet, cm^{-1}) 2960 (m), 2900 (s), 2850 (s), 2710 (w), 1435 (s), 1380 (m), 1260 (w), 1120 (s, br), 1020 (m), 940 (m), 800 (w), 750 (w, br), 610 (w), 565 (m), 555 (m), 370 (w); for $(Cp'_2LaD)_2$ 2965 (s), 2905 (s), 2850 (s), 2710 (w), 1490 (w), 1435 (s), 1380 (m), 1325 (w), 1080 (m, br), 1020 (m, br), 940 (w), 800 (m, br), 615 (w), 585 (w), 550 (w), 380 (w).

Anal. Calcd for $C_{20}H_{31}La$: C, 58.54; H, 7.61; La, 33.85. Found: C, 58.41; H, 7.83; La, 33.86.

$(Cp'_2NdH)_2$ (11) and $(Cp'_2NdD)_2$. The above procedure was carried out with 1.00 g (1.74 mmol) of $Cp'_2NdCH(TMS)_2$ in 50 mL of pentane. Filtration, washing, and drying yielded 0.600 g (83%) of $(Cp'_2NdH)_2$ as a blue-green, microcrystalline powder. $(Cp'_2NdD)_2$ was prepared via an analogous procedure by using D_2 :

1H NMR (C_6D_6 , 22 °C) δ 1.80 (s, 30 H, $lw = 52$ Hz);

IR (Nujol mull, cm^{-1}) 1250 (w), 1135 (s, br), 1020 (w), 970 (w), 795 (w).

Anal. Calcd for $C_{20}H_{31}Nd$: C, 57.79; H, 7.52; Nd, 34.70; MW, 831 (dimer). Found: C, 57.66; H, 8.03; Nd, 34.27; MW, 883 \pm 25 (cryoscopic in benzene).

$(Cp'_2SmH)_2$ (12). This compound was prepared from $Cp'_2SmCH(TMS)_2$ by using the procedure above for $(Cp'_2LaH)_n$ and was isolated as a pink powder. It exhibited spectroscopic properties identical with those reported in the literature^{8b} except that, in our hands, the Sm-H signal could not be located in the 1H NMR.

$(Cp'_2LuH)_2$ (13) and $(Cp'_2LuD)_2$. These complexes were prepared by the aforementioned procedure for $(Cp'_2LaH)_2$ using either H_2 or D_2 in pentane. With H_2 , the yield of $(Cp'_2LuH)_2$ was 98% of colorless, polycrystalline solid. The NMR spectral data agree well with literature data^{7c,d} for $(Cp'_2LuH)_2$:

1H NMR (cyclohexane- d_{12}) δ 9.11 (s, 1 H), 2.09 (s, 30 H);

Complete IR (KBr pellet, cm^{-1}) 2970 (m), 2910 (s), 2860 (s), 2715 (w), 1440 (s), 1385 (s), 1340 (br, s), 1260 (m), 1155 (m), 1100 (m), 1020 (m), 800 (m), 685 (m), 630 (m, br), 440 (m), 380 (m), 315 (s); for $(Cp'_2LuD)_2$ 2970 (m), 2910 (s), 2860 (s), 2715 (w), 1495 (w), 1440 (s), 1385 (m), 1265 (w), 1155 (br, w), 1100 (w), 1065 (w), 1020 (m), 960 (m), 860 (w), 800 (m), 710 (w), 685 (w), 590 (w), 500 (w), 450 (m), 380 (m), 315 (s).

Anal. Calcd for $C_{20}H_{31}Lu$: MW, 892 (dimer). Found: MW, 710 \pm 60 (cryoscopic in benzene under H_2).

$Cp'_2Nd(\eta^3-C_3H_5)_2$ (15). A solution of $Cp'_2NdCH(TMS)_2$ (1.00 g, 1.74 mmol) in 50 mL of pentane was stirred overnight under an H_2 atmosphere at 0 °C. The resulting precipitate of $(Cp'_2NdH)_2$ was filtered off and washed well with cold pentane. The hydride was then suspended in 50 mL of pentane at -78 °C, and with stirring, a 3-4 M excess of propylene was introduced. The suspension was slowly warmed to -15 °C and then stirred for 3.5 h at this temperature (dissolution of the hydride was visible by -30 °C). At this time, all the hydride had reacted (as evidenced by dissolution), and the excess propylene and pentane were removed in vacuo. The residue was then redissolved in 30 mL of pentane and slowly cooled overnight to -78 °C. The resulting large green-brown crystals were filtered off and washed with cold pentane to yield 0.49 g (62%) of $Cp'_2Nd(\eta^3-C_3H_5)_2$:

1H NMR (toluene- d_6) δ 8.94 (s, 1 H, $lw = 56$ Hz), 6.39 (s, 15 H, $lw = 12$ Hz), 6.95 (s, 15 H, $lw = 12$ Hz), -39.32 (s, 2 H, $lw = 83$ Hz), -51.18 (s, 2 H, $lw = 49$ Hz); IR (KBr pellet, cm^{-1}) 3060 (w), 2960 (s), 2900 (s), 2850 (s), 2720 (w), 1960 (vw), 1535 (m), 1490 (w), 1440 (s), 1378 (s), 1260 (m), 1245 (m), 1149 (w), 1090 (s), 1060 (m), 1018 (s), 945 (w), 865 (w), 799 (m), 769 (s), 708 (w), 665 (m), 615 (w), 592 (m), 545 (vw), 435 (w), 375 (w), 330 (w), 300 (w).

(23) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1860-1869 and references therein.

Anal. Calcd for $C_{23}H_{35}Nd$: C, 60.61; H, 7.74; Nd, 31.65. Found: C, 60.33; H, 8.10; Nd, 31.60.

Olefin Polymerization Experiments. These experiments were conducted in a 500-mL flamed round-bottom reaction flask attached to a high-vacuum line. The flask was fitted with Morton-type indentations and an overhead mechanical stirrer (high speed stirring motor, large Teflon paddle). The shaft of the stirrer could be sealed to allow high-vacuum pump down. The flask was also equipped with two straight-bore high-vacuum stopcocks. In a typical experiment, the exterior connecting tube of one stopcock (ca. 10 mm in length) was sealed with a new serum cap. The reaction vessel was then pumped down for several hours, back-filled with inert gas, the stopcock closed, the flask reevacuated, and a measured quantity of solvent (cyclohexane or heptane) vacuum-transferred into the reaction flask from Na/K. Next, gaseous ethylene or propylene was admitted to the vessel through the gas purification column. The gas pressure was continuously maintained at 1.0 atm with a mercury manometer apparatus. Rapid stirring of the solution was initiated, and after several minutes (to allow saturation of the solvent with olefin), the stopcock was opened and a small aliquot of 5.0 mM catalyst solution in cyclohexane injected by a gastight syringe just above the rapidly stirring solution (the syringe needle had been flattened so that the catalyst solution exited in a fine spray). In the case of ethylene, voluminous quantities of polyethylene formed within seconds. After a measured time interval, the polymerization was then quenched by injecting methanol through the serum cap of the second stopcock. The polymeric product was collected by filtration, washed with methanol, and dried under high vacuum. Identical results were obtained when using toluene as the reaction solvent.

Attempts to polymerize propylene via the above procedure produced only what appeared to be traces of oligomers. Pressurized reactions in cyclohexane solution using a Kontes quartz Worden vessel were no more successful.

For 1-hexene/ethylene copolymerizations, ethylene gas was admitted at various pressures to a stirring solution of the catalyst in 1-hexene. Quenching of the polymerization and product isolation were as described for polyethylene (vide supra).

Reactions with 1-Hexene. By using high-vacuum techniques, approximately 0.25 mmol of $(Cp'_2NdH)_2$ or $(Cp'_2LaH)_2$ was allowed to react with a ca. 10-fold excess of 1-hexene in 10 mL of pentane. The reaction was begun at $-78^\circ C$ and was brought to $-10^\circ C$ over a period of 2–3 h. After several additional hours at $-10^\circ C$, the hydride had dissolved. The solvent and other volatiles were then removed under high vacuum, and the residue was dissolved in cyclohexane- d_{12} . The resulting solution was filtered and then transferred to an NMR tube in the glovebox. Assignments refer to structure **L** in the text.

Nd (17, 25 °C): 1H NMR δ 6.68 (s, 15 H, $lw = 12$ Hz, Cp'), 6.22 (s, 15 H, $lw = 12$ Hz, Cp'), -37.7 (s, 1 H, $lw = 54$ Hz), -32.3 (s, 1 H, $lw = 112$ Hz), -30.5 (s, 1 H, $lw = 85$ Hz).

La (18, 25 °C): 1H NMR δ 1.97 (s, 15 H, Cp'), 1.93 (s, 15 H, Cp'), 6.01 (m, 1 H, H3), 3.33 (m, 1 H, H5), 2.34 (d, 1 H, H1); ^{13}C NMR δ 148.97 (d, $J = 145.0$ Hz, CB), 118.8 (s, Cp'), 117.7 (s, Cp'), 97.09 (d, $J = 139.3$ Hz, CC), 70.69 (dd, $J = 141.1, 155.8$ Hz, CA), 35.40 (t, $J = 126.4$ Hz, CD), 26.4 (partially obscured by solvent, CE?), 14.5 (q, $J = 124$, CF), 11.12 (q, $J = 126.5$ Hz, Cp'), 11.00 (q, $J = 126.5$ Hz, Cp'). Assignments refer to structure **L** in the text.

The 1-hexene dimer was prepared by slowly stirring 50 mg of the appropriate $(Cp'_2MH)_2$ complex with 3.0 mL of 1-hexene under 1 atm of D_2 for 1 h. After this time, hexane was removed in vacuo at room temperature and the remaining liquid was vacuum-transferred by using a heat gun. For $M = Lu$, GC/MS showed the product to consist of ca. 99% $C_{12}H_{24}D_2$ with ca. 1% higher oligomers. The total yield of oligomers was approximately 10% for $M = Nd$ and Lu .

Reaction with Butadiene. When the same procedure was used as for 1-hexene above, $(Cp'_2LaH)_2$ was reacted with a ca. 10-fold excess of butadiene in pentane and the product taken up in cyclohexane- d_{12} . **La (14, 25 °C):** 1H NMR δ 1.97 (s, 15 H, Cp'), 1.92 (s, 15 H, Cp'), 6.05 (m, 1 H, H3), 3.27 (m, 1 H, H5), 2.33 (d, 1 H, H1), 1.49 (d, 3 H, CH_3).

Reactions with Cyclohexene. When the procedure described above for 1-hexene was used, cyclohexene was reacted with $(Cp'_2NdH)_2$ and $(Cp'_2LaH)_2$.

Nd (19, 20 °C): 1H NMR δ 5.35 (s, 30 H, $lw = 24$ Hz, Cp'), -55.9 (s, 1 H, $lw = 366$ Hz), -9.12 (s, 2 H, $lw = 33$ Hz), 9.13 (s, 2 H, $lw = 24$ Hz), 11.87 (s, 2 H, $lw = 31$ Hz), 19.22 (s, 2 H, $lw = 43$ Hz).

La (20, 20 °C): 1H NMR δ 4.45 (m, 1 H), 2.48 (m, 2 H), 1.87 (s, 30 H), 1.60 (m, 2 H), 1.51 (m, 1 H); ^{13}C NMR δ 121.0, 120.2, 33.83, 29.35, 25.90, 11.68. This compound was insufficiently stable in cyclohexane- d_{12} for off-resonance decoupling experiments.

$[Cp'_2Nd(CO)_2CH(TMS)_2]_2$ **21.** A solution of 560 mg (0.98 mmol) of $Cp'_2NdCH(TMS)_2$ in 25 mL of pentane was placed under an atmosphere of CO (in excess) and the CO allowed to diffuse into this solution ov-

Table I. Crystallographic Details for $Nd[(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2$

formula	$C_{27}H_{49}NdSi_2$
space group	$P2_1/n$
a , Å	11.045 (9)
b , Å	23.554 (7)
c , Å	11.648 (9)
β , deg	103.10 (6)
volume, Å ³	2951.3
Z	4
density (calcd), g cm ⁻³	1.292
cryst dimensions	$0.5 \times 0.5 \times 0.2$ mm
radiation	Mo K α graphite monochromator
linear absorption coeff, cm ⁻¹	18.6
rel transmission factors	0.73–1.0
temp, °C	-100
scan mode	ω
2θ limit	52.0°
scan range	1.2°
data collected	$+h,+k,+l; +h,+k,-l$
unique data	5721
unique data with $I > 3\sigma(I)$	4287
final no. of variables	352
$R(F)$	0.078
$R_w(F)$	0.106
GO F	3.0

ernight. The resulting dark-red crystals were filtered off, washed with pentane, and dried in vacuo to yield 580 mg (94%) of **21**:

1H NMR (C_6D_6 , $25^\circ C$) δ 8.417 (s, 30 H, $lw = 12$ Hz), -9.00 (s, 18 H, $lw = 12$ Hz) (the methine proton could not be located); IR (KBr pellet, cm⁻¹) 2960 (s), 2903 (s), 2860 (s), 1742 (vw), 1720 (vw), 1708 (vw), 1665 (w), 1660 (w), 1495 (s), 1475 (w), 1440 (m), 1385 (m), 1322 (w), 1270 (m), 1250 (s), 1200 (s), 1075 (m), 1065 (m), 1005 (m), 950 (vw), 915 (m), 865 (m), 845 (s), 835 (s), 780 (vw), 760 (vw), 745 (vw), 690 (m), 642 (m), 572 (m), 535 (w), 482 (m), 465 (vw), 385 (vw), 355 (w), 335 (vw), 295 (m).

Anal. Calcd for $C_{58}H_{98}Nd_2O_4Si_4$: C, 55.28; H, 7.84; Nd, 22.89; M_f , 1260. Found: C, 55.20; H, 7.42; Nd, 23.69; M_f , 1067 (cryoscopic in benzene).

X-ray Crystallographic Study of $Cp'_2NdCH(TMS)_2$ (6).²⁴ Large green prismatic crystals of this complex were grown by slow cooling of a pentane solution to $-30^\circ C$. Crystals suitable for X-ray analysis were cleaved from the larger crystals in a glovebox and sealed in glass capillaries. All diffraction studies were carried out on an Enraf-Nonius CAD4 instrument at $-100^\circ C$. Monoclinic symmetry inferred from the unit cell parameters was confirmed by an analysis of symmetry equivalent intensities. Systematic extinctions were consistent with the space group $P2_1/n$. Accurate unit cell parameters were determined by least-squares refinement of 24 high-angle reflections. Three-dimensional data were collected (5721 independent reflections having $2\theta_{MoK\alpha} < 52^\circ$) using graphite-monochromated Mo radiation and, because of the sizable mosaic spread, ω scans (ω scan width = $1.2^\circ + 0.35 \tan \theta^\circ$). Crystal and/or instrumental instability was monitored through the measurement of six standard reflections that were collected after every 100 min of X-ray exposure time; there was no indication of crystal decomposition. Experimental details are given in Table I.

All calculations were performed on a VAX 11/730 computer with the SDP crystallographic software package²⁵ and programs standard in this laboratory. An empirical absorption correction²⁶ was applied from averaged transmission factors determined from psi scans of nine Bragg reflections. Neutral atom scattering factors²⁷ were used with anomalous dispersion corrections²⁸ being applied to the non-hydrogen atoms.²⁹

The position of the Nd atom was determined from a Patterson summation. Extension of the model was accomplished by using the direct methods program DIRDIF³⁰ and standard Fourier techniques. It was

(24) See paragraph at end of paper regarding supplementary material.

(25) Enraf-Nonius Structure Determination Package.

(26) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(27) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(28) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.

(29) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

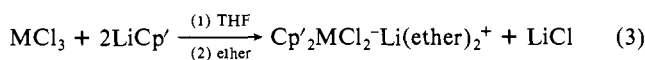
(30) DIRDIF: Direct Methods applied to differences structure factors to strengthen Fourier methods. Beurskens, P. T.; Bosman, W. P.; Doeburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A. J. "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 516.

obvious from the preliminary Fourier syntheses that the Cp' ligands were disordered; two positions of equal height could be located for each Cp' methyl carbon atom. An additional data set was collected on a second crystal at a higher temperature in the hope of finding a higher temperature phase without disorder, but the subsequent structure solution revealed the same characteristic problem. Eventually it was possible to deconvolute the disordered ring atoms. For each Cp' ligand, there are two orientations which are related to each other by a rotation of approximately 36°, i.e., the two ring orientations are staggered relative to each other. In the final disorder model, all Cp' atoms were assigned fixed occupancies of 0.5 (based on the relative heights of the original Fourier calculations), the methyl carbons were refined anisotropically, and the ring carbons were refined isotropically. All other non-hydrogen atoms in the model were refined anisotropically. The large thermal parameters for the C atoms of one of the Si(CH₃)₃ groups may arise from a slight orientational disorder that is caused by the different Cp' orientations.

Hydrogen atom positions were calculated for the methyl carbons of the Si(CH₃)₃ groups assuming idealized staggered configurations. The hydrogen atoms were included in the model as fixed contributors to the structure factors assuming isotropic thermal parameters of 1 Å² greater than that of the atom to which they were attached. The final agreement indexes are given in Table I. The four largest peaks (1.7 (2)–1.9 (2) e/Å³) in the final difference electron density map are located in the vicinity of the Nd atom. An analysis of the data as a function of data collection order, weighting scheme, sin θ/λ, etc., showed no unusual trends.

Results and Discussion

Synthesis. Hydrocarbyls. There are many examples in organolanthanide chemistry⁴ where synthetic approaches and methodology that work well with late lanthanides become increasingly more problematic as the series is traversed to the left. Factors such as charge/ionic radius ratio³¹ are no doubt important. In the present case, the synthesis of Cp'₂MCl₂⁻Li(ether)₂⁺ complexes (eq 3) is straightforward for M = Nd,²⁰ Sm, and Lu,²¹ however,



1, M = La

2, M = Nd

3, M = Sm

4, M = Lu

in the absence of low-temperature workup, this reaction gives far lower yields for La, and an insoluble, rather unreactive complex (probably (Cp'₂LaCl)₂³²) is isolated instead. Alkylation of the above halides proceeds smoothly in nonpolar solvents (eq 4), and crystalline, pentane-soluble hydrocarbyls are obtained in high yields. Unlike Cp'₂MR complexes with smaller alkyl groups,⁴



5, M = La, pale-yellow crystals

6, M = Nd, blue-green crystals

7, M = Sm red-brown crystals

8, M = Lu, colorless crystals

the present compounds do not form complexes with ethers or other Lewis bases. As regards thermal stability, none of the Cp'₂MCH(TMS)₂ complexes visually evidences thermal decomposition in the solid state upon room-temperature storage for several days. The new hydrocarbyls are exceedingly air-sensitive.

¹H and ¹³C NMR spectral data for the various Cp'₂MCH(TMS)₂ complexes are given in the Experimental Section. For 7 and especially 6, the spectra are isotropically shifted and broadened due to the partially filled f shells, but are still readily interpreted. Two diamagnetic examples are shown in Figure 1.

(31) (a) Representative eight-coordinate effective ionic radii:^{31b} La³⁺ (1.160 Å), Nd³⁺ (1.109 Å), Sm³⁺ (1.079 Å), Yb³⁺ (0.985 Å), Lu³⁺ (0.977 Å). (b) Shannon, R. D. *Acta Crystallogr., Sect. A* 1976, *A32*, 751–767.

(32) Lauke, H.; Marks, T. J., unpublished results.

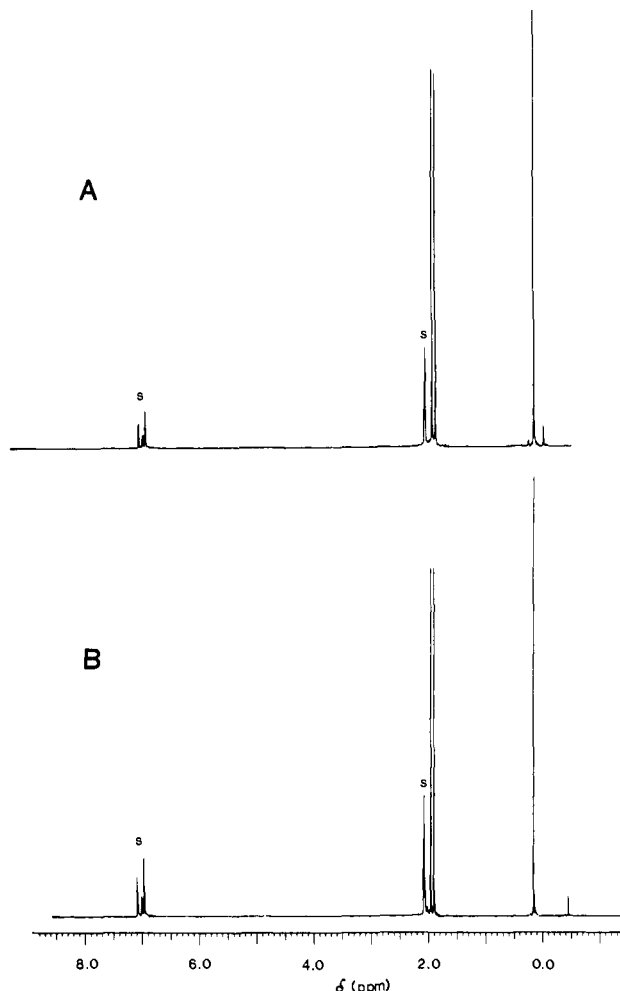
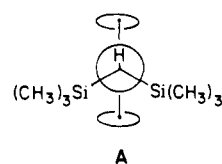


Figure 1. ¹H NMR spectra (270 MHz) of (A) Cp'₂LuCH[Si(CH₃)₃]₂ (8) and (B) Cp'₂LaCH[Si(CH₃)₃]₂ (5), as solutions in toluene-*d*₈. S denotes solvent resonances.

In all cases, the Si–CH₃ groups are magnetically equivalent, but the Cp' rings are nonequivalent, suggestive of a conformation such as A. For Cp'₂NdCH(TMS)₂, which exhibits the largest isotropic



shifts (hence the greatest sensitivity and longest spectral time scale), these relationships persist to –90 °C in toluene-*d*₈. This result will be seen to be of particular significance in light of the diffraction results (vide infra). Also unusual in the NMR spectra are the small magnitudes of ¹J_{C–H} for the methine carbon atoms: e.g., 90.0 Hz in 1. The corresponding ¹J_{C–H} values for the silylmethyl groups (124.5 Hz in 6) are unexceptional. There is nothing in the infrared spectral data (see Experimental Section) which would suggest unusual CH–M interactions.

Molecular Structure Of Nd[(CH₃)₅C₅]₂CH[Si(CH₃)₃]₂ (6). The X-ray structural analysis reveals that single crystals of 6 are composed of monomeric Cp'₂NdCH[Si(CH₃)₃]₂ units as shown in Figures 2 and 3. Final atomic coordinates and anisotropic thermal parameters are given in Tables II and III,²⁴ respectively. Important bond lengths and angles are given with estimated standard deviations in Table IV according to the atom labeling scheme in Figures 2 and 3. Although an orientational disorder of the Cp' rings limits the accuracy of the structure determination, significant conclusions can be drawn about 6. Moreover, these are in complete agreement with the more precise structure of a

Table II. Positional Parameters and Their Estimated Standard Deviations for $\text{Cp}'_2\text{NdCH}[\text{Si}(\text{CH}_3)_3]_2$ (**6**)^a

atom	x	y	z	B(A2)	atom	x	y	z	B(A2)
Nd	0.308 89 (5)	0.145 17 (2)	0.128 33 (4)	2.21 (1)	C(14')	0.623 (2)	0.172 (1)	0.055 (3)	6.5 (6)
Si(1)	0.338 7 (4)	0.144 5 (2)	0.417 7 (3)	3.97 (8)	C(15')	0.648 (3)	0.098 (1)	0.280 (2)	5.4 (7)
C(1)	0.243 (1)	0.102 0 (6)	0.302 (1)	4.6 (3)	C(16')	0.441 (2)	-0.002 (1)	0.220 (3)	5.9 (6)
C(2)	0.438 (1)	0.194 0 (5)	0.350 (1)	4.4 (3)	C(17')	0.289 (2)	0.015 (1)	-0.040 (3)	5.5 (6)
C(3)	0.252 (2)	0.190 2 (9)	0.503 (2)	8.6 (5)	C(23')	0.078 (3)	0.241 (1)	0.217 (2)	6.2 (7)
C(4)	0.453 (2)	0.104 3 (8)	0.528 (1)	7.0 (5)	C(24')	-0.030 (2)	0.145 (1)	0.026 (3)	4.8 (7)
Si(2)	0.133 1 (4)	0.050 6 (2)	0.334 8 (4)	5.76 (9)	C(25')	0.112 (3)	0.155 (1)	-0.184 (2)	6.1 (7)
C(5)	0.211 (2)	-0.007 7 (9)	0.429 (2)	12.1 (7)	C(26')	0.318 (3)	0.256 (1)	-0.115 (3)	6.1 (7)
C(6)	0.043 (2)	0.016 (1)	0.204 (3)	22 (1)	C(27')	0.296 (3)	0.306 (1)	0.131 (3)	6.1 (8)
C(7)	0.019 (2)	0.083 (1)	0.416 (3)	23.3 (8)	C(23)	0.000 (2)	0.205 (1)	0.180 (2)	4.6 (6)
C(8)	0.462 (2)	0.117 (1)	-0.013 (2)	3.1 (4)*	C(24)	-0.015 (3)	0.136 (1)	-0.057 (3)	6.2 (9)
C(9)	0.541 (2)	0.114 3 (7)	0.101 (2)	1.7 (3)*	C(25)	0.179 (4)	0.197 (2)	-0.186 (2)	6.5 (9)
C(10)	0.495 (2)	0.063 8 (8)	0.159 (1)	1.5 (3)*	C(26)	0.339 (2)	0.287 (1)	-0.013 (2)	4.3 (5)
C(11)	0.391 (2)	0.041 4 (8)	0.076 (2)	2.3 (3)*	C(27)	0.218 (2)	0.294 (1)	0.212 (2)	4.2 (6)
C(12)	0.375 (2)	0.073 2 (9)	-0.032 (2)	2.6 (4)*	H(1)	0.388	0.217	0.291	
C(8')	0.440 (2)	0.099 4 (9)	-0.027 (2)	2.8 (4)*	H(2)	0.486	0.218	0.409	
C(9')	0.527 (2)	0.124 (1)	0.058 (2)	3.6 (4)*	H(3)	0.494	0.173	0.315	
C(10')	0.542 (2)	0.090 4 (8)	0.162 (2)	2.0 (3)*	H(4)	0.190	0.213	0.448	
C(11')	0.452 (2)	0.047 2 (8)	0.141 (2)	2.2 (3)*	H(5)	0.210	0.168	0.549	
C(12')	0.383 (2)	0.053 8 (8)	0.020 (2)	2.5 (4)*	H(6)	0.307	0.217	0.551	
C(18)	0.088 (2)	0.209 5 (7)	0.102 (1)	1.6 (3)*	H(7)	0.502	0.080	0.491	
C(19)	0.080 (2)	0.182 (1)	-0.004 (2)	3.2 (4)*	H(8)	0.511	0.130	0.579	
C(20)	0.173 (2)	0.206 1 (9)	-0.058 (2)	3.0 (4)*	H(9)	0.414	0.082	0.577	
C(21)	0.240 (2)	0.247 6 (8)	0.018 (2)	2.2 (3)*	H(10)	0.263	0.007	0.503	
C(22)	0.187 (2)	0.249 5 (9)	0.118 (2)	2.8 (4)*	H(11)	0.155	-0.034	0.450	
C(18')	0.128 (2)	0.228 5 (8)	0.109 (2)	1.9 (3)*	H(12)	0.268	-0.028	0.392	
C(19')	0.083 (2)	0.185 (1)	0.029 (2)	3.3 (4)*	H(13)	-0.003	0.045	0.145	
C(20')	0.143 (2)	0.188 (1)	-0.064 (2)	3.4 (4)*	H(14)	0.094	-0.004	0.158	
C(21')	0.232 (2)	0.229 7 (9)	-0.037 (2)	2.9 (4)*	H(15)	-0.019	-0.009	0.216	
C(22')	0.224 (2)	0.255 (1)	0.073 (2)	3.1 (4)*	H(16)	0.067	0.103	0.488	
C(13)	0.495 (3)	0.156 (1)	-0.111 (2)	4.4 (6)	H(17)	-0.028	0.113	0.370	
C(14)	0.648 (3)	0.146 (1)	0.143 (4)	6.1 (8)	H(18)	-0.033	0.057	0.439	
C(15)	0.553 (3)	0.042 (1)	0.280 (2)	4.7 (6)	C(96)	0.452 8	0.081 9	0.058 2	4*
C(16)	0.315 (3)	-0.011 (1)	0.087 (3)	5.0 (6)	C(97)	0.468 8	0.083 0	0.070 8	4*
C(17)	0.280 (2)	0.058 (1)	-0.146 (2)	4.7 (6)	C(98)	0.153 6	0.218 9	0.035 2	4*
C(13')	0.416 (2)	0.114 (1)	-0.160 (2)	6.0 (5)	C(100)	0.162 0	0.217 2	0.022 0	4*

^aStarred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[(a^2)B(1,1) + (b^2)B(2,2) + (c^2)B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

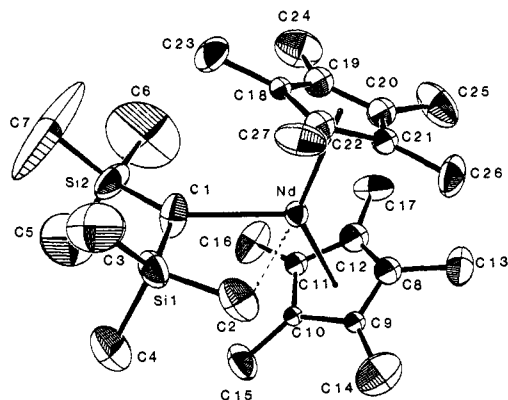


Figure 2. Perspective ORTEP drawing of the non-hydrogen atoms of $\text{Cp}'_2\text{NdCH}[\text{Si}(\text{CH}_3)_3]_2$ (**6**). All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. For clarity, only one orientation of each disordered Cp' ligand has been shown.

ring-bridged analogue, to be discussed in the accompanying contribution.¹³

The coordination pattern for bis(pentamethylcyclopentadienyl) trivalent lanthanides is generally of the pseudotetrahedral $\text{Cp}'_2\text{MX}_2^-$ or $\text{Cp}'_2\text{M}(\text{X})\text{B}$ type (X = uninegative ligand; B = neutrally charged Lewis base)^{4,8b,21,33} with two σ -bonding ligands occupying the "equatorial girdle". To our knowledge, the only exceptions are several recently reported complexes of the small³¹ Lu(III) ion, which are of the $\text{Cp}'_2\text{LuX}$ type^{4b} ($\text{Cp}'_2\text{Lu}(\mu\text{-X})$ -

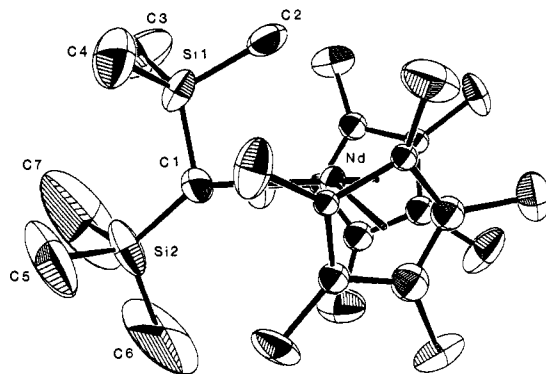


Figure 3. Perspective ORTEP view of the non-hydrogen atoms of $\text{Cp}'_2\text{NdCH}[\text{Si}(\text{CH}_3)_3]_2$ (**6**) approximately perpendicular to the Si1, Si2, C1, Nd plane. All atoms are represented by ellipsoids drawn to encompass 50% of the electron density. For clarity, only one orientation of each disordered Cp' ligand has been shown.

$\text{LuCp}'_2(\text{X})$, X = Cl, CH₃). The coordination geometry of **6** features normal $\text{Cp}'_2\text{M}$ ligation for such types of compounds. For example, the (ring centroid)-Nd-(ring centroid) angle of 134.4° compares favorably with the 135–140° angles reported for several $\text{Cp}'_2\text{YbX}_2^-$ complexes.^{21,33} The present average Nd-C(ring) distance of 2.76 (1, 3, 8, 20) Å³⁴ compares favorably with $\text{Cp}'_2\text{YbX}_2$ data when corrections are made for differing ionic radii.³¹ Although disorder of the Cp' ligands in **6** severely limits

(34) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(33) (a) Tilley, T. D.; Anderson, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856–859. (b) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772–1774.

Table IV. Bond Lengths (Å) and Angles (deg) in Coordination Groups of Cp₂NdCH[Si(CH₃)₃]₂ (**6**)^a

Bond Lengths			
Nd-C1	2.517 (7)	Si1-C4	1.849 (10)
Nd-C2	2.895 (7)	Si2-C5	1.847 (13)
C1-Si1	1.813 (8)	Si2-C6	1.812 (21)
C1-Si2	1.814 (8)		
Si1-C2	1.890 (9)	Si2-C7	1.891 (14)
Si1-C3	1.849 (10)		
Nd-C8	2.700 (20)	Nd-C18	2.825 (11)
Nd-C9	2.755 (11)	Nd-C19	2.780 (20)
Nd-C10	2.770 (11)	Nd-C20	2.748 (15)
Nd-C11	2.722 (12)	Nd-C21	2.157 (12)
Nd-C12	2.783 (12)	Nd-C22	2.791 (13)
Nd-C8'	2.779 (15)	Nd-C18'	2.776 (11)
Nd-C9'	2.760 (20)	Nd-C19'	2.680 (20)
Nd-C10'	2.823 (11)	Nd-C20'	2.740 (20)
Nd-C11'	2.780 (12)	Nd-C21'	2.763 (13)
Nd-C12'	2.713 (12)	Nd-C22'	2.775 (14)
C8-C9	1.417 (21)	C18-C19	1.536 (19)
C8-C12	1.386 (21)	C18-C22	1.422 (18)
C8-C13	1.565 (22)	C18-C23	1.480 (19)
C9-C10	1.515 (17)	C19-C20	1.445 (25)
C9-C14	1.395 (22)	C19-C24	1.518 (27)
C10-C11	1.422 (17)	C20-C21	1.413 (22)
C10-C15	1.497 (18)	C20-C25	1.516 (23)
C11-C12	1.437 (18)	C21-C22	1.417 (19)
C11-C16	1.507 (18)	C21-C26	1.536 (18)
C12-C17	1.536 (19)	C22-C27	1.502 (20)
C8'-C19'	1.339 (24)	C18'-C19'	1.402 (24)
C8'-C12'	1.416 (22)	C18'-C22'	1.379 (21)
C8'-C13'	1.550 (20)	C18'-C23'	1.509 (20)
C9'-C10'	1.425 (21)	C19'-C20'	1.393 (25)
C9'-C14'	1.569 (23)	C19'-C24'	1.552 (25)
C10'-C11'	1.405 (17)	C20'-C21'	1.382 (21)
C10'-C15'	1.600 (20)	C20'-C25'	1.567 (23)
C11'-C12'	1.447 (19)	C21'-C27'	1.432 (20)
C11'-C16'	1.500 (19)	C21'-C26'	1.585 (22)
C12'-C17'	1.445 (20)	C22'-C27'	1.517 (20)
Bond Angles			
Nd-C1-Si1	98.44 (31)	C1-Si2-C5	112.37 (55)
Nd-C1-Si2	140.15 (43)	C1-Si2-C6	113.03 (65)
Si1-C1-Si2	121.27 (44)	C1-Si2-C7	112.67 (64)
Nd-C2-Si2	84.84 (27)	C5-Si2-C7	105.92 (102)
C1-Si1-C2	109.25 (33)	C5-Si2-C6	104.93 (94)
C1-Si1-C3	115.25 (48)	C6-Si2-C7	107.34 (128)
C2-Si1-C4	103.56 (44)	Cg-Nd-Cg ^b	134.4
C3-Si1-C4	106.27 (54)		

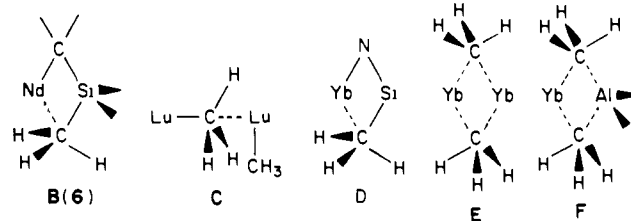
^aThe two different (CH₃)₂C₅ rotamers are differentiated by primed and unprimed metrical parameters. ^bCg = ring centroid.

the metrical precision, the internal Cp' dimensions in **6** appear to be unexceptional.^{4,21,33,35} Thus, the average C-C = 1.42 (2, 3, 11, 20) Å and the average C-CH₃ = 1.52 (2, 4, 13, 20) Å for the two pairs of rings.³⁴ What is unusual about **6**, which is unaffected by the Cp' disorder, and which is essentially duplicated in the more precise, ordered structure of (CH₃)₂Si[(CH₃)₄C₅]₂-NdCH[Si(CH₃)₃]₂¹³ (**9**), is the very unsymmetrical coordination of the σ-bonded alkyl ligand in this unsaturated, formally Cp'₂NdX configuration.

Analysis of the metrical data indicates that atoms Nd, C1, Si1, and Si2 are coplanar to within 0.02 (1) Å. Furthermore, the interaction of the CH(TMS)₂ fragment with the Cp'₂Nd fragment is highly unsymmetrical, with ∠Nd-C1-Si1 = 98.4 (3)° and ∠Nd-C1-Si2 = 140.2 (4)° (adding ∠Si2-C1-Si1 = 121.3 (1)° to these gives a total of 359.9°). The Nd-C1 σ bond distance in **6** is found to be 2.517 (7) Å. Correcting for differences in Nd³⁺ and Lu³⁺ eight-coordinate radii,³¹ the terminal metal-CH₃ distance in Cp'₂Lu(μ-CH₃)LuCp'₂(CH₃)^{4b} becomes 2.476 (12) Å, (2.344 (12) Å actual). The only available metrical data for a lanthanide-

ide-CH(TMS)₂ complex are for pseudotetrahedral Yb(CH(TMS)₂)₃Cl⁻ (Yb-C = 2.373 (24), 2.372 (16), and 2.391 (20) Å).³⁶ Assuming for the moment that this complex is formally eight-coordinate, corrected distances of 2.497 (24), 2.496 (16), and 2.515 (20) Å are calculated for eight-coordinate Nd³⁺, while assuming that formal Yb six-coordination yields eight-coordinate Nd³⁺ distances of 2.615 (24), 2.613 (16), and 2.632 (20) Å. Thus, the present Nd-C1 distance is not unusual. As regards the TMS groups, the average Si-CH₃ distance of 1.856 (17, 23, 44, 6) Å³⁴ compares favorably with similar distances in a number of trimethylsilyl compounds.³⁷ The Si1-C2 contact of 1.890 (9) Å is probably longer than the average Si-CH₃ distance, but this is on the edge of statistical significance (the corresponding difference in **9** is significant¹³). The C1-Si1 and C1-Si2 distances of 1.813 (8) and 1.814 (8) Å, respectively, are slightly shorter than the corresponding distances of 1.889 (4) Å in H₂C[Si(CH₃)₃]₂^{37d} and 1.888 (6) Å in HC[Si(CH₃)₃]₃.^{37d} In common with **6**, the appreciable steric congestion gives rise to relatively large Si-C-Si angles of 123.2 (9)° and 116.3 (4)°, respectively, in the latter two compounds.

In addition to the Nd-C1 σ bond, the unsymmetrical CH(TMS)₂ coordination involves a rather short, ostensibly nonbonding Nd-C2 contact of 2.895 (7) Å—only 0.378 Å longer than Nd-C1. This contact is significantly shorter than the sum of the CH₃ van der Waals radius (2.0 Å)^{38a} and either the Nd single bond radius (1.6 Å),^{38b} metallic radius (1.8 Å),^{38b} or even eight-coordinate ionic radius (1.108 Å).³¹ It is not obvious from inspecting Figures 2 and 3 that the unsymmetrical CH(TMS)₂ coordination is a direct consequence of intramolecular nonbonded repulsions, and it will be seen to be even less so in **9**¹³ where the (CH₃)₄C₅ ligands are "pulled back". From the structure of **9** and also by implication, **6**, it will be seen that the disposition of the α-hydrogen atom (bent toward the metal) is also not an obvious source of the distortion. Rather, it appears that the Nd-C₂ interaction is a consequence of the marked electron deficiency at the metal center and represents one of several recent 4f examples (the only one for an early lanthanide) where some degree of three-center two-electron bridging alkyl group interaction exists (e.g., **B**). Other examples include Cp'₂Lu(μ-CH₃)LuCp'₂(CH₃) (**C**),^{4b} Yb(N(TMS)₂)₂-2-(dmpe) (**D**, dmpe = bis(dimethylphosphino)ethane),³⁹ [Cp'₂M(μ-CH₃)₂ (M = Y, Yb (**E**),⁴⁰ and Cp'₂M(μ-CH₃)₂Al(CH₃)₂ (M = Y, Yb (**F**)).⁴¹ In cases **D**, **E**, and **F**, the multicenter interaction



is Al₂(CH₃)₆-like⁴² in that it does not involve exclusive ("agostic") C-H...M interaction,⁴³ but rather C...M interaction. This will be reinforced for **6** in the structural discussion of **9**¹³ in which the

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(39) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, 104, 3725-3727.

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(41) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45-54.

(42) (a) Huffman, J. C.; Streib, W. E. *Chem. Commun.* **1971**, 911. (b) O'Neill, M. E.; Wade, K. In ref 2c, Chapter 1.

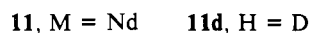
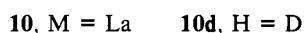
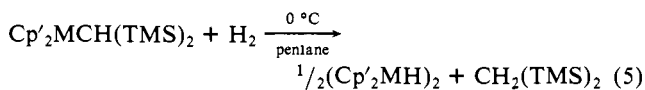
(43) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, 250, 395-408 and references therein.

(35) (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, 250, 237-246. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1981**, 103, 2206-2220. (c) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, 102, 5393-5396.

CH₃ hydrogen atoms have been located and found to conform to the dispositions in **D** and **E** (the latter inferred from the analogous **Y** structure).

To compare the Yb–C distance of 3.04 Å in **D** with that in **6**, an assumed Yb²⁺ six-coordination^{31b} was converted to eight-coordinate Nd³⁺, giving a hypothetical Nd–C distance of 3.13 Å—clearly longer than the 2.895 (7) Å in **6**. Correcting the fully bridging 2.511 (35) Å, (av) Yb–CH₃ distance of **E** in a similar manner yields Nd–C = 2.635 (35) Å, while that in **E** (2.60 (2) Å (av)) becomes 2.73 (2) Å; both contacts are somewhat shorter than in **6**. Although the structure of **6** evidences considerable distortion, it is important to note that in common with **D** and **F**, the distortion does not lie in a deep potential well, and at room temperature, bridge and terminal methyl groups are undergoing rapid intramolecular permutation. Only in the case of **F**⁴¹ is the barrier large enough to allow observation of the instantaneous structure in the low-temperature solution ¹H NMR. As already noted, Si1–C2 may be longer than Si–CH₃ (av), but for the present structure determination, this difference is not statistically significant. This is not the case in the more precise structure determination for **9**,¹³ where the analogous difference is statistically significant. This result, the close Nd–C2 contact, and the approximately eclipse relationship of the C1–Nd and Si1–C2 vectors are reminiscent of syn-periplanar reaction coordinates for β-hydride elimination and suggest that the geometry in **6** is a plausible conformation for incipient β-methyl elimination (eq 1). In the present case, however, elimination would create a high-energy Si=C functionality,¹¹ which appears to be energetically inaccessible (thermolysis in toluene-*d*₈ yields CH₂(TMS)₂ as the major CH(TMS)₂-derived product).

Synthesis. Hydrides. As we first discovered in 1978,⁴⁴ lanthanide-to-carbon σ bonds suffer hydrogenolysis to yield the corresponding hydrides.^{4,45} In the present case (eq 5), reaction is complete within minutes at 0 °C, and the sparingly soluble hydrides **10–13** are isolated in virtually quantitative yields.



Complex **11** was shown to be dimeric in benzene by cryoscopy while **13** is significantly dissociated. Alternative procedures have also been employed for the synthesis of **12**^{8b} and **13**.^{7cd} ¹H NMR data for **10–13** are given in the Experimental Section. In our hands, the hydride functionality undergoes rapid exchange with the deuteria of C₆D₆ in the approximate order Lu ≳ Sm ≳ La. Thus, the hydride signal in **13** could only be located in C₆D₁₂, while that in **10** (Figure 4) is visible for hours in C₆D₆. The low-field shift of the La–H resonance is characteristic of d⁰ and f⁰ systems;⁴⁵ it is also observed in f⁴ **13**. Presumably as a consequence of the slow electron spin–lattice relaxation time, the hydride signals in **11** and **12** could not be located. Complete infrared data for **10–13** and the analogous prepared with D₂ (**10d–13d**) are set out in the Experimental Section. Several representative spectra are shown in Figure 5. M–H modes can be identified by subtracting readily identified Cp'-centered transitions⁴⁵ and by reference to the deuterium-substituent analogues. However, the latter spectra are complicated somewhat by significant scrambling of the label into the Cp' ligands. From the data, it can be seen that the infrared spectra of **10**, **11**, and **12** are essentially superimposable and differ distinctly from that of **13**. Although the hydrogen atoms were not located,^{8b} a structure such as **G** seems probably for **12**, while

(44) Fagan, P. J.; Grynkewich, G. W.; Marks, T. J., unpublished results on [Er(CH₂C₃H₄)₂CH₂Si(CH₃)₃]₂ hydrogenolysis, quoted in ref 2b.

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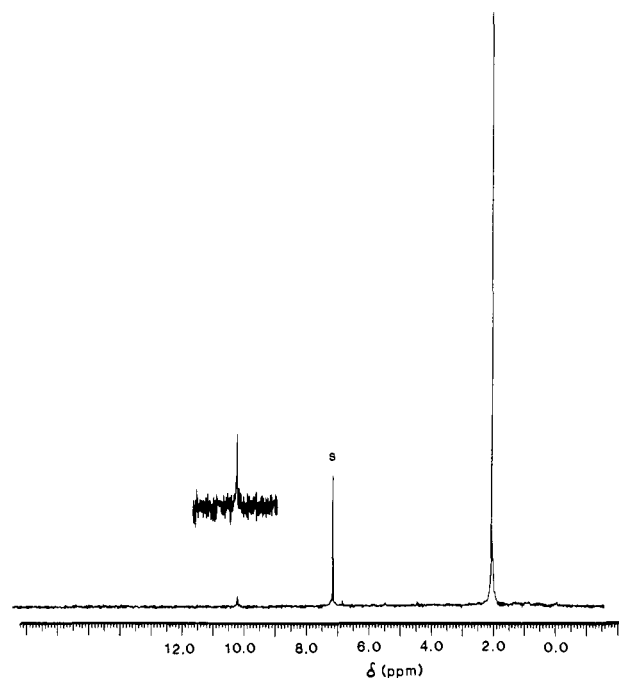


Figure 4. ¹H NMR spectrum (270 MHz) of (Cp'₂LaH)₂ (**10**) as a solution in C₆D₆. S denotes traces of C₆D₅H.

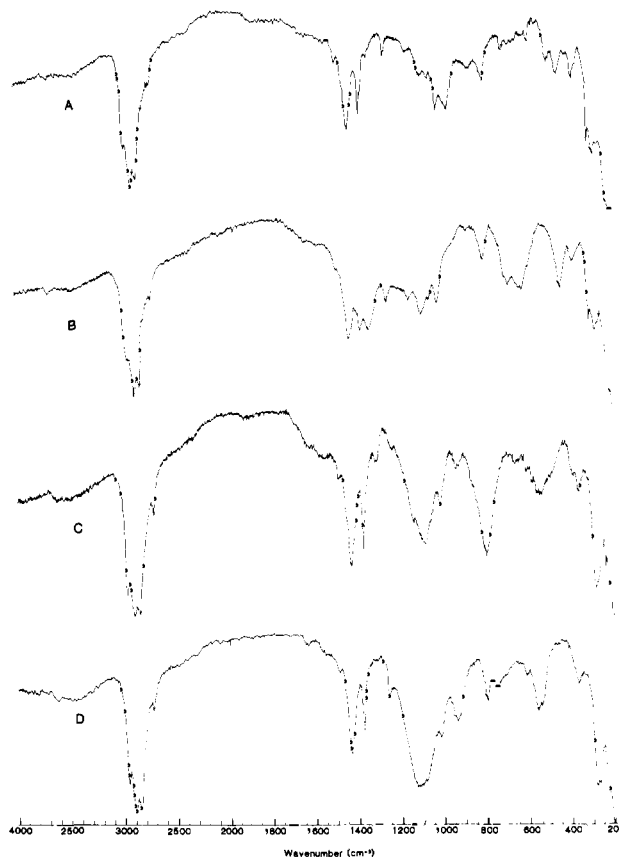


Figure 5. Solid-state infrared spectra as KBr disks of (A) (Cp'₂LuD)₂ (**13d**), (B) (Cp'₂LuH)₂ (**13**), (C) (Cp'₂LaD)₂ (**10d**), and (D) (Cp'₂LaH)₂ (**10**).

a configuration such as **H** has been proposed for **13** for basis of NMR data.^{7c} The core structure of (Cp'₂Th(μ-H)H)₂ is similar

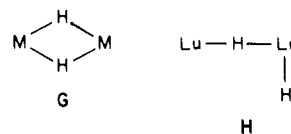


Table V. Ethylene Polymerization by (Cp'₂MH)₂ Compounds^a

entry	compd	M=	concn, μM	temp, °C	time, s	N ₁ , s ⁻¹	efficiency, g/ (mmol min atm)	10 ³ \bar{M}_n	10 ³ \bar{M}_w	10 ³ \bar{M}_z	\bar{M}_w/\bar{M}_n	chains/M
1	La		26	25	5	1450	2440	428	843	1,405	1.97	0.43
2	La		27	25	10	690	1160	227	1,463	5,077	6.42	0.85
3	La		13	25	5	1800	3040	676	1,371	2,552	2.03	0.37
4	Nd		11	25	10	1120	1888					
5	Nd		22	25	10	640	1080					
6	Nd		22	25	5	1360	2280	590	1,070	1,649	1.81	0.32
7	Nd		60	25	10	380	640	233	1,034	2,450	4.46	0.46
8	Nd		60 ^b	25	10	420	705					
9	Nd		60 ^b	25	30	337	567					
10	Nd		60 ^b	25	60	230	386					
11	Nd		60 ^b	25	180	82	138					
12	Nd		60 ^c	54	10	619	1040					
13	Nd		22	-78	600	5.2	8.7	648	1,264	2,589	1.95	0.13
14	Lu		25	25	45	97	162	250	377	472	1.50	0.49
15	Lu		13	25	60	95	157	361	605	817	1.68	0.44
16	Lu		140	25	20	100	167	96	132	151	1.37	0.58

^aAll reactions carried out in 140 mL of cyclohexane except where indicated. ^bCarried out in 40 mL of cyclohexane. ^cCarried out in 88 mL of cyclohexane.

to **G** and exhibits, consistent with local C₂ symmetry, infrared-active antisymmetric (1215 and 1114 cm⁻¹) and symmetric (844 and 650 cm⁻¹) stretching modes.⁴⁵ Depending on the local symmetry, **G** could exhibit two (D_{2h}), three (D₂), or four (C₂) M-H stretching transitions (assuming all are resolved and of detectable intensity). As exemplified by **10** (Figure 5, C, D), **G**-type molecules exhibit a strong, broad transition at ca. 1120 cm⁻¹ which shifts to ca. 800 cm⁻¹ in **10d**⁴⁶ ($\nu_{M-H}/\nu_{M-D} = 1.40$). Furthermore, there appear to be weaker transitions at ca. 940 and 750 cm⁻¹, which shift to ca. 660 ($\nu_{M-H}/\nu_{M-D} = 1.42$) and ca. 510 cm⁻¹ (shoulder, $\nu_{M-H}/\nu_{H-D} \sim 1.47$), respectively, upon deuteration. The spectrum of **13** is somewhat less straightforward to interpret (Figure 5). Relatively strong, non-Cp' features are observed at 1345 (br), 1100 (br), and 650 cm⁻¹ (br or split), which shift to ca. 970 ($\nu_{M-H}/\nu_{M-D} = 1.39$), ca. 860? ($\nu_{M-H}/\nu_{M-D} \sim 1.30$), and ca. 420? cm⁻¹ (very br, $\nu_{M-H}/\nu_{M-D} \sim 1.55$).

Reaction Chemistry with Olefins, Ethylene. As early as 1978, we noted⁴⁷ that solutions of (Cp'₂UH)₂ and photolyzed solutions of Cp'₂U[CH₂Si(CH₃)₃]₂ were active, apparently homogeneous catalysts for ethylene polymerization. The polymer produced was of relatively high molecular weight, high melting point, low branching ratio, and low polydispersity (\bar{M}_w/\bar{M}_n).⁴⁸ Subsequent attempts to unambiguously determine whether trivalent (Cp'₂UH)₂ and Cp'₂UR species served as catalysts (initiators) were frustrated by the high oxidation state lability of these systems (complex mixtures of U(III) and U(IV) compounds were invariably evident in the ¹H NMR spectra⁴⁹). In contrast, the isoelectronic Nd(III) system is expected to be oxidation-state-stable and along with the La(III) analogue offers an intriguing early lanthanide comparison to recent late lanthanide olefin polymerization chemistry^{4b,7b,50} (as well as results on more conventional polymerization catalysts⁵¹).

(46) From the residual intensity of the ca. 1100-cm⁻¹ band in **10d**, it is obvious that exchange with a hydrogen source has occurred. A species such as



is a likely product.

(47) (a) Berlin, J. R.; Fagan, P. J.; Marks, T. J., unpublished results. (b) *Chem. Eng. News*, July 31, 1978, 24. This account contains several unfortunate typographical/journalistic errors.

(48) Berlin, J. R., report submitted in fulfillment of the BA/MS requirements, Northwestern University, June 1978.

(49) Suzuki, H.; Marks, T. J., unpublished results.

(50) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337-339. (b) Ballard, D. G. H.; Curtis, A.; Holton, J.; McMeeking, J.; Pearce, R. J. *Chem. Soc., Chem. Commun.* **1978**, 994-995.

As described in the Experimental Section, all polymerization chemistry was carried out under rigorously anaerobic, high vacuum line conditions. At room temperature and 1 atm of ethylene pressure, the Cp'₂MCH(TMS)₂ complexes (M = La, Nd, and Lu) failed to react with ethylene over the course of several hours. Although the absence of migratory insertion is rationalizable on steric grounds, it should be noted that the same complexes undergo rapid M-CH(TMS)₂ bond hydrogenolysis and migratory CO insertion (vide infra). In contrast to the Cp'₂MCH(TMS)₂ complexes, the corresponding (Cp'₂MH)₂ complexes undergo extremely rapid reaction with ethylene to produce voluminous quantities of polyethylene within seconds of contacting the two reagents.

Data pertaining to the polymerization experiments are set out in Table V. A number of points are noteworthy. First, it is evident that chain propagation is extremely rapid. The approximate order of reactivity follows decreasing ionic radius: La ≥ Nd > Lu. Furthermore, the early lanthanide systems display maximum activities comparable to or in excess of those reported for the most active "homogeneous" ethylene polymerization catalysts discovered to date^{7b,52,53} as well as those for most homogeneous organometallic molecule/inorganic support systems.^{51,54} Indeed, (Cp'₂MH)₂ activities appear to approach those of heterogeneous "third generation" Ziegler-Natta catalysts.^{51,55} The present compounds also exhibit measurable activity even at -78

(51) (a) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In ref 2c, Chapter 22.5. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99-149. (c) Pino, P.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857-875. (d) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979. (e) Yamamoto, A.; Yamamoto, T. *J. Polym. Sci. Macromol. Rev.* **1978**, *13*, 161-218. (f) Chien, J. C. W., Ed. "Coordination Polymerization"; Academic Press: New York, 1975. (g) Choi, K.-Y.; Ray, W. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1985**, *C25*, 1-56, 57-97.

(52) (a) Kaminsky, W.; Lüker, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 225-228 and references therein. (b) Deuschke, J.; Kaminsky, W.; Lüker, H. In "Polymer Reaction Engineering"; Reichert, K. H., Geiseler, W., Eds.; Hanser Publishers: Munich, 1983; pp 207-220.

(53) Kaminsky's molecular/oligomer catalyst Cp₂Zr(CH₃)₂/Al(CH₃)₃O_n⁵² is reported to be the most active "homogeneous" system discovered to date. At 90 °C, it has a reported efficiency (in a specially designed reactor) of 4700 g of polymer/(mmol of catalyst min atm). This catalyst is completely inactive at -78 °C.

(54) (a) Some typical efficiencies (g of polymer/(mmol of precatalyst min atm)) at 80 °C are as follows: Zr(benzyl)₄/Al₂O₃, 33;^{54b} Cr(allyl)₃/SiO₂, 31;^{54c} Zr(allyl)₄/Al₂O₃, 5.8.^{54c} (b) Ballard, D. G. H. *J. Polym. Sci. Chem. Ed.* **1975**, *13*, 2191-2212. (c) Yermakov, Yu. I.; Zakharov, V. A. In ref 51f, pp 91-133.

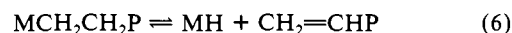
(55) (a) Some typical efficiencies (g of polymer/(mmol of precatalyst min atm)) at 80 °C are as follows: CrO₃/SiO₂, 33;^{51b} TiCl₃/AlCl₃/SiO₂, 250;^{54c} TiCl₄/AlX₃/R_{3-n}/Mg(OH)Cl, 170;^{51b} TiCl₃/AlCl₃/magnesium compounds, 3300.^{54c} Only the latter two systems are formally "third generation" catalysts.^{55b} (b) Galli, P.; Luciani, L.; Cecchin, G. *Angew. Makromol. Chem.* **1981**, *94*, 63-89 and references therein.

°C (entry 13) and are active at room temperature for periods of at least 2 weeks. Modest heating (+54 °C) increases turnover frequency as well as catalyst efficiency (entry 12).

The $(\text{Cp}'_2\text{MH})_2$ /ethylene turnover frequencies and catalyst efficiencies were estimated by quenching the polymerization reaction after measured time intervals and weighing the quantity of polyethylene produced. As such, these estimates are clearly lower limits to the reactivities of the most active La and Nd catalysts. Important questions arise concerning the intrusion of mass-transport effects as well as possible effects of poisoning due to residual traces of air, water, impurities, etc. Information can be obtained by studying reaction rates as a function of catalyst quantity and concentration (is ethylene "starvation" occurring? is a certain quantity of catalyst serving a sacrificial role in scavenging impurities?), reaction time (is the precipitating polyethylene impeding ethylene diffusion to the catalyst centers?), and contrasting behavior of the more active (La, Nd) and less active (Lu) catalysts. Relevant data are presented in Table V. When identical reaction procedures are carried out for Nd with an increased quantity of catalyst at identical overall concentration, the apparent turnover frequency and catalyst efficiency appears to fall (entries 7 and 8), implicating inadequate monomer delivery to the reaction solution¹⁵ (probably due to inadequate stirring¹⁵) and arguing that little of the catalyst serves a sacrificial role. A general pattern of decreasing N_t and decreasing efficiency is also observed for La and Nd with increasing catalyst concentration (entries 1 and 3 and 4 and 5). This could also be attributed to mass-transport effects, although any kinetically important equilibrium involving $(\text{Cp}'_2\text{MH})_2$ dissociation would introduce qualitatively similar behavior. The rates of dimer dissociation, chain initiation, and chain propagation in these systems are not known. The highly active La and Nd catalysts also exhibit a pattern of decreasing turnover frequency and decreasing efficiency with increasing reaction time (entries 1 and 2, 5 and 6, and 8–11). This behavior appears to reflect restricted ethylene diffusion to the entrained catalyst centers as increasing quantities of solid polymer accumulate.^{56a,b} In contrast to the above result for the La and Nd catalyst, the far less active $(\text{Cp}'_2\text{LuH})_2$ system exhibits N_t and efficiency parameters which are relatively insensitive to catalyst concentration and reaction times (entries 14–16). It is entirely reasonable that mass-transport effects should be less important for the less active catalyst.^{56c}

The foregoing conclusions are supported and additional information is provided by the GPC data (Table V). For a completely homogeneous, kinetically well-behaved (propagation as described by k_p remains constant throughout the polymerization), irreversible polymerization in which termination (described by k_t), chain transfer (described by k_{ct}), and poisoning are insignificant, and in which initiation is instantaneous, a Poisson molecular weight distribution is expected for high degrees of polymerization.⁵⁷ That is, the polymer (a "living polymer") should be virtually monodisperse; i.e., $\bar{M}_w/\bar{M}_n = 1.0$. Under similar constraints but admitting the operability of termination and chain transfer (and assuming k_p , k_t , and k_{ct} remain constant throughout the polymerization), the "most probable" molecular weight distribution is expected; i.e., $\bar{M}_w/\bar{M}_n = 2.0$.^{57,58} We suspect that the living polymer regime is operative for the present systems (in accord with the long time periods over which activity was measurable), modified principally by possible mass-transport and heterogeneity effects. In regard to irreversibility, the polymerization is far from thermoneutral ($\Delta H \approx -26$ kcal/mol)^{59a} and in

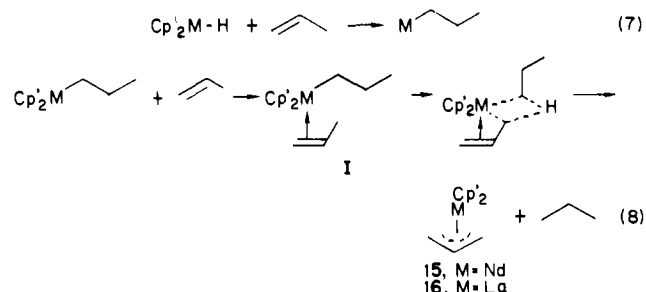
regard to termination/chain-transfer processes, thermochemical data⁵⁹ and experiments with 1-hexene (vide infra) argue that β -hydride elimination (eq 6) should be quite endothermic for a straight-chain primary alkyl. The operability of other termination



P = polymer chain

(e.g., Cp' H atom abstraction), chain-transfer, or impurity-related processes is more difficult to assess (reproducibility and entries 4, 5, and 8 in Table V argue against the intrusion of the latter). Nevertheless, the data in Table V generally support the living polymer hypothesis. The least active, least mass-transport-influenced Lu system exhibits polydispersities consistently below 2.0. For the more active La- and Nd-based catalysts, polydispersity is low for short reaction times and increases with increasing reaction times. This would be in accord with increasing heterogeneity of the system and an increasing diversity of diffusion-influenced propagation rates as the quantity of solid polymer rapidly built up. Indeed, typical heterogeneous Ziegler-Natta catalysts generally exhibit high polydispersities.⁵¹ The data for the -78 °C experiment in Table V argue that temperature effects on termination processes such as β -H elimination are probably not important under the present conditions.⁶⁰ Thus, eq 6 is likely to have a large, positive entropy of reaction,^{59a} and if the position of this equilibrium controlled \bar{M}_w/\bar{M}_n , then a greater sensitivity to temperature might be expected. Such is not the case. Finally, data in Table V showing polymer chains produced per lanthanide atom are informative. That the ratios are never greater than 1.0 argues against extensive chain transfer. That they are consistently less than 1.0 could arise from mass transport or rate-limiting initiation effects, and the data are not extensive enough to draw a clear-cut distinction. However, the foregoing discussion, the near independence of this ratio on the quantity or concentration of organolanthanide (i.e., none serves a sacrificial role), and the increase of M_n with increasing reaction time argues, for the less mass-transport-limited Lu system, that poisoning effects are not competing with polymerization. Rather, it appears that a process such as initiation-limiting dissociation of the $(\text{Cp}'_2\text{MH})_2$ dimer combined with entrainment of partially or unreacted hydride in the growing polymer mass is operative. Further information on stoichiometric $(\text{Cp}'_2\text{MH})_2$ -olefin reactivity will be presented in the following section and in the contribution on catalytic hydrogenation.¹⁵ Efforts to better characterize the lifetimes and temperature dependence of the $(\text{Cp}'_2\text{MH})_2$ -initiated polymerization are continuing.

Reaction Chemistry with Olefins. Propylene, 1-Hexene, Butadiene, and Cyclohexene. The reaction of $(\text{Cp}'_2\text{LaH})_2$ (**10**) or $(\text{Cp}'_2\text{NdH})_2$ (**11**) solutions with propylene at atmospheric pressure yields η^3 -allyl complexes. In situ monitoring of the reaction by 270-MHz ¹H NMR reveals that 1.0 (1) equiv of propane is formed per equivalent of η^3 -allyl produced, suggesting the insertion/intramolecular allylic C-H activation sequence in eq 7 and 8. Allyl



compound **15** could be made on a preparative scale and charac-

(56) (a) More accurate rates could be obtained under flow conditions,^{56b} operating in the regime in which propagation does not proceed beyond the soluble oligomer stage. (b) Schnell, D.; Fink, G. *Angew. Makromol. Chem.* **1974**, *39*, 131–147 and references therein. (c) It is not clear what effect the differing structure of the $(\text{Cp}'_2\text{LuH})_2$ dimer will have on the ethylene polymerization reactivity (if any).

(57) (a) Peebles, L. H., Jr. "Molecular Weight Distributions in Polymers"; Interscience: New York, 1971. (b) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 81–86.

(58) (a) Soga, K.; Izumi, K.; Ikeda, S.; Keii, T. *Makromol. Chem.* **1977**, *178*, 337–342. (b) Doi, Y.; Kinoshita, J.; Morinaga, A.; Keii, T. *J. Polym. Sci. Chem. Ed.* **1975**, *13*, 2491–2497.

(59) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Marks, T. J.; Morss, L. R. *Organometallics* **1985**, *4*, 352–355. (c) Sonnenberger, D. C.; Schock, L. E.; Marks, T. J., unpublished results.

(60) (a) This is probably not the case at temperatures appreciably above 25 °C.^{51,52,60b} (b) Mauermann, H.; Marks, T. J., unpublished results.

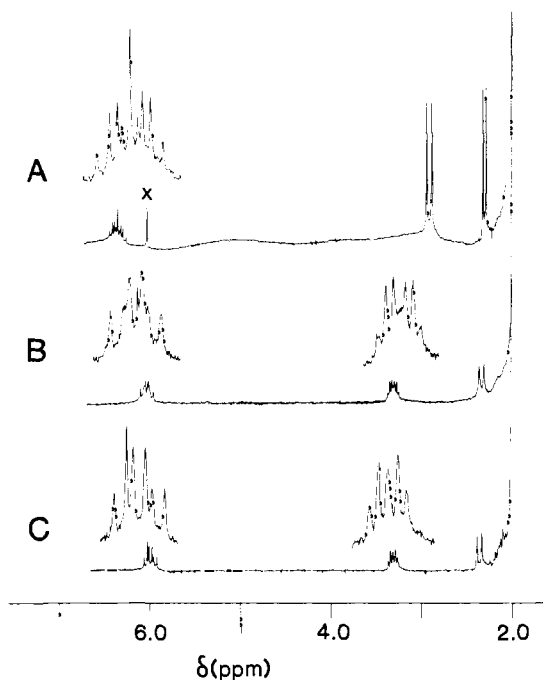
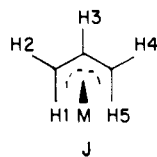
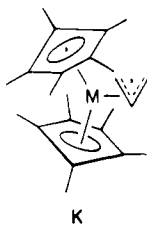


Figure 6. ^1H NMR spectra (270 MHz) in C_6D_{12} of (A) $\text{Cp}'_2\text{La}(\eta^3\text{-allyl})$, (B) $\text{Cp}'_2\text{La}(\eta^3\text{-crotyl})$, and (C) $\text{Cp}'_2\text{La}(\eta^3\text{-hexenyl})$. x denotes a trace of impurity.

terized by standard methodology (see Experimental Section for details). The η^3 coordination geometry is established by ^1H NMR data which exhibit the characteristic AM_2X_2 pattern.⁶¹ Indeed, chemical shifts and coupling constants for **16** (Figure 6A, structure J) are reminiscent of early transition-metal η^3 -allyl data^{61b,c} with



δ_{H_3} 6.35, $\delta_{\text{H}_{1,5}}$ 2.91, $\delta_{\text{H}_{2,4}}$ 2.30, and $J_{\text{H}_3-\text{H}_{2,4}} = 9.2$ Hz (syn coupling), and $J_{\text{H}_3-\text{H}_{1,5}} = 15.5$ Hz (anti coupling). That the bound allyl exhibits C_s symmetry and the Cp'_2 rings are magnetically nonequivalent support conformation K. In addition to the NMR



data, infrared spectra reveal characteristic η^3 -allyl C-C modes and the absence of $\nu_{\text{C}=\text{C}}$ diagnostic of an η^1 -allyl.^{62,63} Magnetization-transfer experiments reveal that **15** is static up to +90 $^\circ\text{C}$, giving no evidence for $\eta^3 \rightleftharpoons \eta^1$ interconversion^{61,63} nor rotation of the η^3 -allyl moiety. Further support for this chemical/structural picture follows from experiments with butadiene and 1-hexene

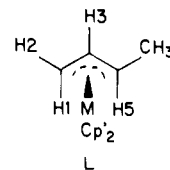
(61) (a) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71-80 and references therein. (b) Hoffmann, E. G.; Kallweit, R.; Schroth, G.; Sevogel, K.; Stempfle, W.; Wilke, G. *J. Organomet. Chem.* **1975**, *97*, 183-202 and references therein.

(62) Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977; pp 263-276.

(63) (a) Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 702-710. (b) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529-5539. (c) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 259-261. (d) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *156*, 108-160.

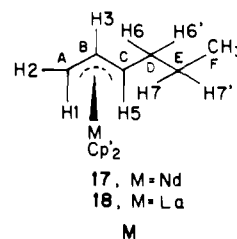
(vide infra). Watson has observed similar allyl formation for $\text{M} = \text{Lu}$; however, a mechanism has not been suggested, and the allyl is reported to be either η^3 - or η^1 -coordinated and fluxional.^{4c,7c} Reaction 8 also produces small quantities of propylene oligomers, similar to the Lu case.⁷ We suggest that allyl formation and oligomerization via migratory insertion may proceed from the same precursor, I. Stirring either **15** or **16** under an atmosphere of D_2 yields propane which is $\geq 95\%$ d_3 by GC/MS.

Unlike the case of many organolanthanides,⁹ the reaction of $(\text{Cp}'_2\text{LaH})_2$ (**10**) with butadiene does not yield polybutadiene. Rather, an η^3 -crotyl complex is produced. The assignment of structure L with the methyl group in the syn position follows from ^1H NMR data (Figure 6B and Experimental Section). Thus,



H_3 (δ 6.05) appears as a sextet, with $J_{\text{H}_3-\text{H}_{1,5}} = 13.5$ Hz (δ_{H_1} 2.33, δ_{H_5} 3.27) and $J_{\text{H}_3-\text{H}_2} \sim 9.5$ Hz. We assign the H_2 resonance as being obscured by the Cp' absorption since irradiation in this region collapses the H_3 signal to a triplet ($J = 13.5$ Hz). Irradiation at H_5 collapses H_3 to a doublet of doublets, with $J = 9.5$ and 12.9 Hz. Furthermore, irradiation at H_3 collapses the H_1 resonance to a singlet and the H_5 resonance to a quartet. We assign the crotyl methyl resonance to a doublet ($J = 5.9$ Hz) at δ 1.49. Irradiation at this signal collapses H_5 to a doublet ($J = 13.5$ Hz). As in the allyl complexes, the Cp' ligands are magnetically nonequivalent.

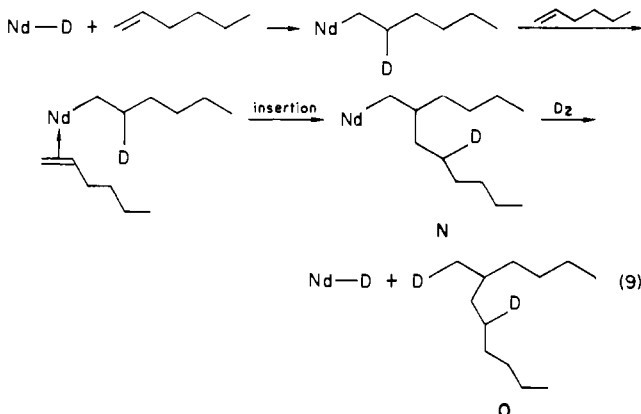
The reaction of 1-hexene with $(\text{Cp}'_2\text{LaH})_2$ (**10**) and $(\text{Cp}'_2\text{NdH})_2$ (**11**) was also investigated by NMR. At probe temperatures as low as -78 $^\circ\text{C}$ in toluene- d_8 , complete consumption of hydride by excess 1-hexene occurs within a few hours. At room temperature, the reaction is essentially instantaneous. A single organometallic product is observed (no intermediates were visible) along with an approximately equal quantity of *n*-hexane. If the reaction is carried out at -10 $^\circ\text{C}$, the volatiles are pumped off, and the product is dissolved in cyclohexane- d_{12} , similar but better quality (due to the absence of interfering organics) spectra could be obtained. In the case of Nd, the ^1H NMR spectrum of the product is reminiscent of that of $\text{Cp}'_2\text{Nd}(\eta^3\text{-C}_3\text{H}_5)$, with magnetically nonequivalent Cp' rings and allylic resonances having similar isotropic shifts (see Experimental Section for details). This suggests structure M; the aliphatic protons could not be definitively



assigned and were possibly obscured by residual hexane. Reaction of this compound with D_2O yields 1-hexene which was $\geq 95\%$ hexene- d_1 by GC/MS. The reaction of $(\text{Cp}'_2\text{LaH})_2$ with 1-hexene also yields an allylic product, which could be characterized by ^1H (Figure 6C) and ^{13}C NMR, and the similarity of the spectral parameters to those of $\text{Cp}'_2\text{La}(\eta^3\text{-allyl})$ and $\text{Cp}'_2\text{La}(\eta^3\text{-crotyl})$. Thus, we assign H_3 at δ 6.01, H_1 at δ 2.34, δ H_5 at 3.33, and δ H_2 as obscured by the Cp' resonances. These assignments were verified by decoupling experiments, which yielded the parameters $J_{\text{H}_3-\text{H}_1} \sim 14.5$ Hz, $J_{\text{H}_3-\text{H}_2} \sim 8.6$ Hz, and $J_{\text{H}_3-\text{H}_5} \sim 13.8$ Hz. The methyl resonance is readily assigned to a triplet at δ 0.68, $\text{H}_{7,7'}$ to a multiplet at ca. δ 1.29 (irradiation collapses the δ 0.68 signal to a singlet), and H_6 and H_6' probably to two multiplets at δ 1.87 and 2.07 (coupling to H_5 is ca. 5.9 and 6.3 Hz, respectively). Irradiation of either of the $\text{H}_{6,6'}$ multiplets results in some simplification of the H_5 resonance. Again, the Cp' ligands are

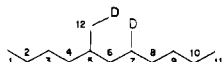
magnetically nonequivalent. The ^{13}C NMR data (see Experimental Section) are in accord with these assignments. Reaction of the La hexenyl complex with D_2O yielded 1-hexene which was $\geq 95\%$ hexene- d_1 by GC/MS. Furthermore, stirring this complex in pentane under D_2 yielded *n*-hexene which was $\geq 95\%$ hexane- d_3 by GC/MS.

Rapidly stirring any of the $(\text{Cp}'_2\text{MH})_2$ complexes with 1-hexene under 1 atm of H_2 (or D_2) reveals that they are extremely active hydrogenation catalysts (N_1 values are as high as $120\,000\text{ h}^{-1}$).⁵ The details of the catalytic hydrogenation chemistry will be presented in the following contribution.¹⁵ It suffices here to state that for 1-hexene, the sequence involves (i) addition of metal hydride to olefin to produce a hexyl complex and (ii) hydrogenolysis of the metal-carbon bond to yield alkane (hexane-1,2- d_2 using D_2) and to regenerate the metal hydride. More interesting in the present context is the result in *neat* 1-hexene at room temperature under conditions where D_2 introduction is mass-transport-limited (e.g., stirring is inadequate). In this case, besides hexane- d_2 , smaller, nearly equal quantities of hexane- d_1 and hexane- d_3 are also observed¹⁵ along with small quantities of a hexene dimer (vide infra). This observation agrees with the scenario depicted in eq 7 and 8: with Nd-D/ D_2 , 1:1 alkane- d_1 /alkane- d_3 is predicted. At room temperature in *neat* 1-hexene under an even greater deficiency of D_2 , the hexene dimer $\text{C}_{12}\text{H}_{12}\text{D}_2$ is obtained in significant quantities along with traces ($\leq 1\%$) of a dideuterated trimer (ca. 10% of the hexene is oligomerized, the remainder being converted to hexanes). On the basis of ^1H and ^{13}C NMR data^{24,64} and experiments using H_2O^{64} and MS data,⁶⁵ this hydrocarbon is assigned structure **O**, and the probable mechanism is shown in eq 9. That a hydrogenolytic environment



is required to obtain oligomers suggests that species such as **N** do not readily suffer β -hydride elimination (to regenerate hydride for further oligomerization catalysis) and also that the η^3 -allyl is not an important precursor for 1-hexene oligomers under these conditions. Qualitatively, it appears that increasing temperatures ($-10 \rightarrow +30\text{ }^\circ\text{C}$) favor olefin insertion into the metal-carbon σ bond over competing allylic C-H activation and η^3 -allyl formation.

(64) (a) The structure of and labeling pattern in this hydrocarbon follow from high-field $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C data and $\Delta\text{C}(\text{D})$ parameters derived therefrom.^{64b-d} The spectrum is shown in the Supplementary Material.²⁴ Assignments are reported below. δ 14.12 (q, $J_{\text{C-H}} = 124.0\text{ Hz}$, C1), 23.14 (t,

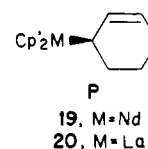


$J_{\text{C-H}} = 124.0\text{ Hz}$, C2), 29.46 (t, $J_{\text{C-H}} = 122.1\text{ Hz}$, C3), 36.89 (t, $J_{\text{C-H}} = 122.1\text{ Hz}$, C4), 32.76 (d, $J_{\text{C-H}} = 119.4\text{ Hz}$, C5), 37.11 (t, $J_{\text{C-H}} = 123.4\text{ Hz}$, C6), 26.75 (t, d, $J_{\text{C-H}} = 124.3$, $J_{\text{C-D}} = 18.9\text{ Hz}$, C7), 29.72 (t, $J_{\text{C-H}} = 123.5\text{ Hz}$, C8), 32.05 (t, $J_{\text{C-H}} = 123.8\text{ Hz}$, C9), 22.79 (t, $J_{\text{C-H}} = 126.0\text{ Hz}$, C10), 14.17 (q, $J_{\text{C-H}} = 124.3\text{ Hz}$, C11), 19.45 (t, t, $J_{\text{C-H}} = 122.6$, $J_{\text{C-D}} = 19.0\text{ Hz}$, C12). (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley: New York, 1980; pp 50-53. (c) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 259-261. (d) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *156*, 108-160.

(65) Stenhagen, E.; Abrahamson, S.; McLafferty, F. W. "Register of Mass Spectral Data"; Wiley: New York, 1974; Vol. 1, p 585.

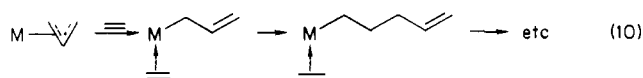
Consideration of the sterically congested structure of **N** indicates why subsequent 1-hexene insertions are unfavorable. It will be seen that the "opened" $\text{Me}_2\text{SiCp}'_2\text{M}$ ($\text{Cp}' = \eta^5\text{-(CH}_3)_4\text{C}_5$) environment can alter this situation to a significant degree.¹³ The reason why propylene oligomerization is less effective in these experiments presumably reflects the lower concentrations of the gaseous olefin which were achievable under 1 atm of pressure.

As monitored by ^1H NMR spectroscopy, the reaction of either $(\text{Cp}'_2\text{LaH})_2$ or $(\text{Cp}'_2\text{NdH})_2$ with cyclohexene at room temperature is orders of magnitude slower than with 1-hexene. For each metal, one major organometallic product is detected. The ^1H NMR spectra of the La and Nd products (see Experimental Section) are rather complex and bear little resemblance to those of the previously discussed η^3 -allyls; interestingly, the Cp' ligands are magnetically equivalent in these complexes. When D_2O is added to these products, the only detectable C_6 species is cyclohexene, which is $\geq 96\%$ cyclohexene- d_1 by GC/MS. The proton spectra reveal no evidence of the slowing of a dynamic process down to $-85\text{ }^\circ\text{C}$. From these results, we tentatively assign the η^1 -allyl structure **P** (possibly fluxional) to the cyclohexene reaction products. An η^3 -allyl coordination mode is presumably desta-

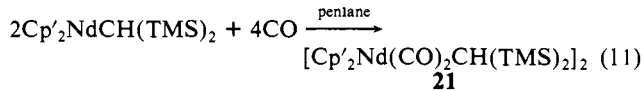


bilized by the steric bulk of the cyclohexenyl fragment. There is no evidence for the formation of cyclohexene oligomers in these reactions. It will be seen in the discussion of catalytic cyclohexene hydrogenation¹⁵ that some lanthanide cyclohexyl complexes readily undergo β -hydride elimination.

Copolymerizations. As already noted, the $\text{Cp}'_2\text{M}$ coordination sphere is apparently too constricted (cf., eq 9) to support the rapid polymerization of olefins bulkier than ethylene (few homogeneous catalysts are effective⁵¹). However, it was found in exploratory studies that hexene could be copolymerized with ethylene by stirring hexene solutions of $(\text{Cp}'_2\text{NdH})_2$ under an ethylene atmosphere at various pressures. This process presumably involves ethylene at the insertion step of eq 9. Since the $(\text{Me}_2\text{SiCp}'_2\text{MH})_2$ complexes were found to be more active catalysts, discussion of this chemistry is deferred to the next paper in this issue.¹³ It was also found that $\text{Cp}'_2\text{Nd}(\eta^3\text{-allyl})$ was effective in initiating ethylene polymerization. Such a process may involve the monohapto form of the allyl (eq 10).



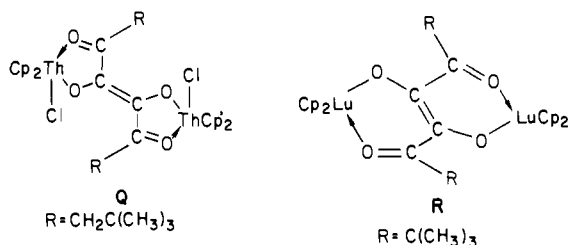
Reaction Chemistry with Carbon Monoxide. It was also of interest, for comparative purposes, to briefly survey the insertion chemistry of the $\text{Cp}'_2\text{MCH}(\text{TMS})_2$ complexes with CO. Under 1 atm of CO, $\text{Cp}'_2\text{NdCH}(\text{TMS})_2$ reacts according to eq 11 to yield the deep-red complex **21**. On the basis of elemental analysis,



molecular weight data, ^1H NMR/IR spectroscopy, and characteristic color, a dionediolate structure is inferred. Such complexes are known for both actinides^{35c,66} (structure **Q** has been crystallographically identified) and lanthanides⁶⁷ (structure **R** has been crystallographically identified). On the basis of the present spectroscopic data, it is not possible to unambiguously distinguish between structures **Q** and **R**.

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Discussion

The synthetic chemistry presented here offers straightforward, general routes to a broad family of ether- and halide-free bis-(pentamethylcyclopentadienyl)lanthanide alkyls and hydrides. The hydrides are of course greatly desirable synthetic targets for catalytic studies but are equally valuable precursors for numerous types of ether- and halide-free lanthanide hydrocarbyls and other derivatives.⁴ One result of this work is thus a readily accessible, homologous series of tractable, thermally stable, very electrophilic (for which there is structural evidence), and very highly reactive lanthanide alkyl/hydride pairs which span the 4f block from the lightest (4f⁰) to the heaviest member (4f¹⁴). In chemistry involving olefins, significant reactivity differences are observed between light (La, Nd) and heavy (Lu) lanthanides. For example, the light members appear to be the most active "homogeneous" ethylene polymerization catalysts prepared to date. For bulkier olefins, allylic C-H activation and η^3 -allyl formation are found to compete

with olefin insertion into the metal-carbon σ bond. This fine structure is by no means predicted and will be explored further in our following discussions of Me₂SiCp''₂ lanthanide chemistry¹³ and organolanthanide-catalyzed olefin hydrogenation chemistry.¹⁵

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Registry No. 1, 98720-34-4; 2, 78128-14-0; 3, 98720-35-5; 4, 78128-06-0; 5, 98720-36-6; 6, 93383-00-7; 7, 98720-37-7; 8, 98720-38-8; 10, 98720-39-9; 10d, 98720-41-3; 11, 93303-98-1; 11d, 98720-42-4; 12, 84751-30-4; 12d, 98720-43-5; 13, 98720-40-2; 13d, 98720-48-0; 14, 98720-49-1; 15, 98720-52-6; 16, 98720-50-4; 17, 98735-43-4; 18, 98720-44-6; 19, 98720-45-7; 20, 98720-46-8; 21, 98720-47-9; LaCl₃, 10099-58-8; LiCp', 51905-34-1; (Cp'₂LaCl₂)₂, 98735-44-5; LiCH(TMS)₂, 41823-71-6; SmCl₃, 10361-82-7; C₆D₆, 1076-43-3; propylene, 115-07-1; ethylene, 74-85-1; polyethylene, 9002-88-4; 1-hexene, 592-41-6; butadiene, 106-99-0; cyclohexene, 110-83-8; 5-deuterio-7-(deuteriomethyl)-undecane, 98720-51-5; 1-hexene/ethylene copolymer, 25213-02-9.

Supplementary Material Available: Table of anisotropic thermal parameters for non-hydrogen atoms (Table III) and listing of observed and calculated structure factors from the final cycle of least-squares refinement and ¹³C NMR spectra of the 1-hexene dimer C₁₂H₂₄D₂ (51 pages). Ordering information given on any current masthead page.

Highly Reactive Organolanthanides. Synthesis, Chemistry, and Structures of 4f Hydrocarbyls and Hydrides with Chelating Bis(polymethylcyclopentadienyl) Ligands

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Abstract: This contribution discusses lanthanide hydrocarbyl and hydride chemistry based upon Me₂SiCp''₂ supporting ligation (Cp'' = η^5 -(CH₃)₄C₅). The reaction of MCl₃, M = Nd, Sm, or Lu, with Me₂Si(Cp''Li)₂ yields the precursor complexes Me₂SiCp''₂MCl₂Li(ether)₂⁺. A slightly different workup procedure yielded (Me₂SiCp''₂NdCl)₂Cl⁻Li(THF)₂⁺, which crystallizes in the monoclinic space group P2₁/n with two molecules in a unit cell of dimensions (-133 °C) a = 11.666 (3) Å, b = 12.585 (3) Å, c = 17.765 (6) Å, and β = 94.91 (2)°. Least-squares refinement led to a value for the conventional R index (on F) of 0.045 for 3231 independent reflections having I > 3 σ (I). The structure consists of two Me₂Si(η^5 -Cp'')₂Nd units bridged by a chloride ion and an Nd-Cl⁻Li⁺Cl⁻-Nd linkage. The Nd-Cl distances are 2.802 (1) and 2.754 (2) Å, and \angle Cl-Nd-Cl = 97.1 (1)°. The (ring centroid)-Nd-(ring centroid) angle is 121.3°. The Nd-C(ring) distances vary from 2.647 (7) to 2.815 (7) Å, with the shorter distances being to those carbon atoms closest to the Me₂Si bridge. The Me₂SiCp''₂MCl₂ compounds react with LiCH[Si(CH₃)₃]₂ to yield ether- and halide-free Me₂SiCp''₂MCH[Si(CH₃)₃]₂ derivatives. The M = Nd compound crystallizes in the monoclinic space group P2₁/n with four molecules in a cell of dimensions (-125 °C) a = 10.229 (2) Å, b = 15.623 (3) Å, c = 19.687 (3) Å, and β = 105.41 (2)°. Least-squares refinement led to a value of the conventional R index (on F) of 0.044 for 3407 independent, absorption corrected reflections having I > 3 σ (I). The molecular structure consists of monomeric Me₂SiCp''₂NdCH[Si(CH₃)₃]₂ units with η^5 -Cp'' coordination, and \angle (ring centroid)-Nd-(ring centroid) = 121.6°. The CH[Si(CH₃)₃]₂ fragment is coordinated to the Me₂SiCp''₂Nd center in a highly unsymmetrical fashion with a Nd-C σ -bond distance of 2.506 (7) Å and a secondary interaction to one methyl group of Nd-C = 2.862 (8) Å. The Si-C distance to this carbon atom is significantly longer than the other Si-CH₃ contacts. Approximate hydrogen atom locations argue against an important M...HC(methyl) interaction and reveal a bending of the hydrogen atom on the σ -bonded carbon atom toward the metal with \angle Nd-C-H ~ 76°. Reaction of the Me₂SiCp''₂MCH[Si(CH₃)₃]₂ complexes with H₂ yields the corresponding hydrides, which are formulated as Me₂SiCp''₂M(μ -H)₂MCp''₂SiMe₂ dimers. These compounds are active agents for the polymerization of ethylene as well as for the oligomerization of propylene and 1-hexene. For a constant lanthanide ion, a (Me₂SiCp''₂MH)₂ hydride is an ca. 10 times more active for this reaction than the corresponding (Cp'₂MH)₂ hydride. Deprotonation of Me₂SiCp''₂LuCH(TMS)₂ with *t*-BuLi/TMEDA leads to a metallacycle formulated as Li(TMEDA)₃⁺-Me₂SiCp''₂LuCH₂Si(CH₃)₂C(H)Si(CH₃)₃⁻.

In the previous paper in this issue,² we describe general, straightforward synthetic approaches to and chemical/physico-

chemical properties of the 4f hydrocarbyls and hydrides Cp'₂MR (Cp' = η^5 -(CH₃)₅C₅, R = CH[Si(CH₃)₂]₂) and (Cp'₂MH)₂, where