close agreement with values expected for geminal hydrogen atoms attached to sp^2-hybridized carbon (typically 0–3 Hz; cf. 12–15 Hz for geminal hydrogens attached to sp^3-hybridized carbon[15]). Finally, an olefinic C–H stretching band at 3055 cm^{-1} is seen in the infrared spectrum (Nujol mull).[16]

The crystal structure of $(C_5Me_3(CH_2)_2)Ta(H)_2(PMe_3)_2$ has been determined in the orthorhombic space group *Pnma*.[17] The molecule is located on the mirror plane that contains the two phosphorus atoms and the tantalum atom and bisects the five-membered ring between the methylene groups (Figure 1). Important distances are shown in the figure caption. The tantalum atom is clearly displaced away from C(31) toward the C(33)–C(33′) edge (0.44 Å from the ring centroid as determined by a normal from the ring plane through the metal atom), presumably due to the additional bonding interactions between the metal atom and the methylene carbon atoms C(36) and C(36′). The Ta–C(36) distance is more than 1 Å shorter than the metal–methyl distance found in $(\eta^5\text{-}C_5Me_5)Ta$ compounds.[19] The methylene carbon atoms, which are closer to the metal atom partially by virtue of the 0.44 Å ring displacement, are also bent below the plane of the ring by 33.4°. Similar bending of a methylene group toward a metal atom has been observed in the molecular structures of related fulvene complexes.[20–24] The inter ring-carbon distance C(31)–C(32) is short at 1.407 (5) Å, while C(33)–C(33′) is relatively elongated at 1.460 (8) Å. Finally, the C(ring)–C(methylene) distances are 1.429 (6) Å, values consistent with coordinated double bonds. Thus, the description of the $C_5Me_3(CH_2)_2$ ligand as an η^4-butadiene/η^3-allyl system would seem most appropriate.

A potentially useful feature of 1 is the retention of the abstracted ring hydrogens within the metal coordination sphere, thus offering an opportunity to exploit reversible metal-to-ring hydrogen migrations for the generation of coordinatively unsaturated, electron-rich metal fragments of tantalum. For example, the migration of both metal hydride hydrogens to the $C_5Me_3(CH_2)_2$ ligand is demonstrated by the reaction of an inert solvent solution of 1 with carbon monoxide resulting in the formation of $Cp^*Ta(PMe_3)_2(CO)_2$ (70% by ^1H NMR), which has been characterized by comparison with data from an authentic sample.[25] Reactivity studies are presently being extended to other substrate molecules, in addition to assessing the mechanism of formation and interrelationship of the tautomers 1 and 2.

Acknowledgment. We wish to thank the Science and Engineering Research Council (U.K.) for grants (to V.C.G. and W.C.) and a studentship (T.P.K.). R.D.S. acknowledges support from the faculty grant-in-aid program at Arizona State. We are grateful to Dr. D. Reed for use of the Edinburgh high-field NMR facility.

Supplementary Material Available: High-field NMR data for compound 1 and tables of positional and anisotropic thermal parameters and bond lengths and angles (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[16] A band at 3040 cm^{-1} was observed for $Cp^*(C_5Me_4CH_2)TiMe$. See ref 4.

[17] Crystallographic data: $C_{16}H_{33}P_2Ta$, $M_r = 468.3$, orthorhombic, *Pnma*, $a = 11.2309\ (6)$ Å, $b = 11.9809\ (5)$ Å, $c = 14.4881\ (7)$ Å, $V = 1949.5\ (2)$ Å^3, and $Z = 4$, $D_{calcd} = 1.595$ g cm^{-3}. Data were collected on a Siemens AED2 diffractometer in ω/θ scan mode, with Mo Kα radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 60°$, and on-line profile fitting;[18a] $T = 295$ K. A total of 8915 reflections (three equivalent sets) were corrected for Lorentz and polarization effects, absorption ($\mu = 5.73$ mm^{-1}, crystal size 0.25 × 0.3 × 0.3 mm, transmission 0.11–0.16), and intensity drift (ca. 5%) of three standards, to give 2972 unique reflections, 2635 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only, $R_{int} = 0.019$). The structure was solved by heavy-atom methods and refined by blocked-cascade least squares on F with all non-hydrogen atoms anisotropic. Methyl H atoms were constrained to give C–H = 0.96 Å and H–C–H = 109.5°; CH_2 and tantalum-bound H were freely refined; $U(H) = 1.2U_{eq}(C)$ except for the freely refined isotropic U for the hydrides.[18b] Residuals of $R = 0.0253$, $R_w = 0.0193$, and $S = 0.97$ were obtained, with weighting[18c] $w^{-1} = \sigma_c^2(F) + 9 + 29G + 8G^2 - 23S + 19S^2 - 65GS$, where $G = F_o/F_{max}$ and $S = \sin\theta/\sin\theta_{max}$, for 116 refined parameters.

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[19] In normal Cp*Ta complexes the ring-methyl carbon atoms are in excess of 3.5 Å from the metal atom as calculated from the crystallographic data given in the following references: (a) $Cp^*Ta(CHCMe_3)(C_2H_4)(PMe_3)$: Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1691. (b) $Cp^*TaCl_2(PhCCPh)$: Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387. (c) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olson, W. A.; Bercaw, J. E. *Inorg. Chem.* **1983**, *22*, 1149.

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The First Salt- and Solvent-Free Monocyclopentadienyl Lanthanide Dialkyl Complex. X-ray Structure Determinations of $La(\eta^5\text{-}C_5Me_5)[CH(SiMe_3)_2]_2$ and of Its Tetrahydrofuran Adduct: Compounds Containing Agostic Si–C Bonds

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Summary: The synthesis and single-crystal X-ray structure determinations of the first salt- and solvent-free monocyclopentadienyl lanthanide alkyl complex $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$ and of its THF adduct precursor are reported. These complexes contain unusual agostic Si–C bonds that facilitate stabilization of the unsaturated lanthanum center. We also report a novel and simple chemical method to remove coordinated THF from highly reactive, electrophilic organolanthanide complexes.

Olefin polymerization is of considerable commercial interest. We have previously reported[1] the synthesis, characterization, and molecular structures of some mo-

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[1] Van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G., submitted for publication in *Organometallics*.

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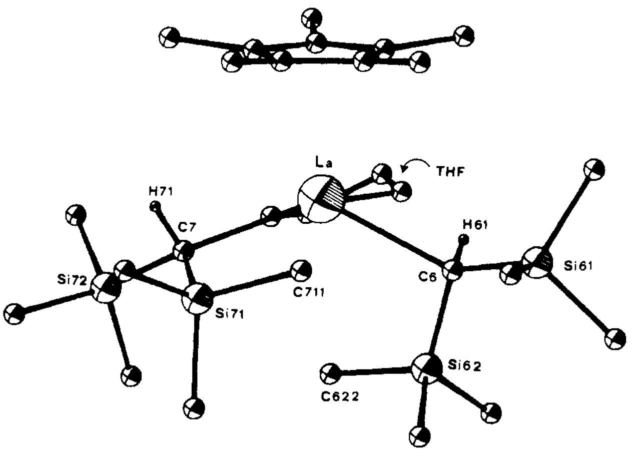

Figure 1. Molecular structure of 1 with hydrogens omitted for clarity: La–C(6) = 2.651 (8) Å, La–C(7) = 2.627 (10) Å, La–O(8) = 2.547 (6) Å, La···C(711) = 3.241 (19) Å, La···C(622) = 3.265 (14) Å, C(6)–La–C(7) = 126.9 (2)°, C(6)–La–O(8) = 92.3 (2)°, C(7)–La–O(8) = 108.1 (3)°, La–C(6)–Si(62) = 102.9 (4)°, La–C(6)–Si(61) = 134.8 (3)°, La–C(7)–Si(72) = 131.1 (5)°, La–C(7)–Si(71) = 103.6 (4)°, La–C(6)–H(61) = 81(5)°, La–C(7)–H(71) = 106 (8)°.

nocyclopentadienyl lutetium alkyl complexes. It was expected that polymerization activity would be severely inhibited, not only by the steric bulk of the alkyl groups but especially by the presence of coordinated THF.

We report here the synthesis and molecular structures of La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$ and of its THF adduct precursor La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$(THF). The removal of coordinated THF is achieved by a novel and potentially general, yet simple chemical method which leaves the highly reactive, electrophilic organolanthanide complex intact.

Reaction of La(η^5-C_5Me_5)I_2(THF)$_3$[2] with 2 equiv of KCH($SiMe_3$)$_2$ in hexane/diethyl ether affords salt-free La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$(THF) (1)[3] in 50–60% recrystallized yield. The ^{13}C NMR spectrum for 1 recorded at −20 °C indicated that the two methyne carbons are equivalent and the four $SiMe_3$ groups are equivalent, at δ = 46.3 ppm [^1J(CH) = 92 Hz] and δ = 4.1 ppm [^1J(CH) = 117 Hz], respectively. In ^1H NMR and ^{13}C NMR spectra recorded at −90 °C the C_5Me_5 resonances remain sharp but *two* methyne resonances are observed.[3] The molecular structure[4] of 1 is shown in Figure 1. The coordination sphere around the lanthanum atom resembles a flattened three-legged piano stool [C(6)–La–C(7) = 126.9 (2)°, C(6)–La–O(8) = 92.3 (2)°, C(7)–La–O(8) = 108.1 (3)°]. *Both* bis(trimethylsilyl)methyl (disyl) ligands are significantly distorted, in a manner that has been observed previously for the monoalkyl complexes M(η^5-C_5Me_5)$_2$CH($SiMe_3$)$_2$ (M = Y,[5] Nd[6]) and is also seen for 2.

As well as being exceedingly air- and moisture-sensitive, La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$(THF) also displays a concentration-dependent decomposition rate in cyclohexane-d_{12} at 25 °C. At 40 mM the half-life is ca. 2 h, and La(η^5-C_5Me_5)$_2$CH($SiMe_3$)$_2$ and (Me_3Si)$_2CH_2$ are observed in 25% and 75% yields, respectively, together with a yellow precipitate. The mechanism and factors influencing this apparent pentamethylcyclopentadienyl migration are unknown. The lack of deuterium incorporation from the solvent or from coordinated THF[7] suggests the possible involvement[8,9] of (η^5-C_5Me_5) C–H bonds.

We sought to develop a strategy whereby the THF ligand could be removed cleanly from 1 despite the high reactivity and electrophilicity of 1. Cyclic ethers are known to undergo electrophilic attack, with ring opening, by trimethylsilyl iodide.[10] We postulated that reaction of Me_3SiI with the THF ligand[11] in 1 would lead to the formation of $Me_3SiO(CH_2)_4I$, which would be too sterically hindered to coordinate to the lanthanum center in putative, THF-free La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$. This proved to be the case. Treatment of 1 with 6–10 equiv[12] of Me_3SiI in toluene at 0 °C does indeed afford salt- and solvent-free La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$ (2)[13] in 60% yield, with concomitant formation of $Me_3SiO(CH_2)_4I$. However, complexes 1 and/or 2 are decomposed by Me_3SiI to give {La(η^5-C_5Me_5)I_2}$_n$. In order to achieve rapid separation of 2, this transformation was attempted heterogeneously by using a $-CH_2SiMe_2I$-substituted Merrifield polymer[14] and a $-SiMe_2I$-substituted polystyrene.[15] These methods were somewhat successful; however, we were unable to purify the prepared polymers sufficiently to prevent decomposition of 1 and/or 2.

A synthetically superior approach was discovered. Reaction of La(η^5-C_5Me_5)I_2(THF)$_3$[2] with Me_3SiI afforded THF-free {La(η^5-C_5Me_5)I_2}$_n$.[16] Treatment with KCH($SiMe_3$)$_2$ (2 equiv) in ether gave 2 in 75% yield. Reaction of 2 with THF (1 equiv in C_6D_{12}) regenerates 1 quantitatively. Unexpectedly, 2 exhibits considerably greater thermal stability than 1. This behavior may be analogous to the increased ionic character and reactivity shown by lithium alkyls[17] on coordination of a donor ligand. At 25 °C, the ^{13}C NMR spectrum of 2 exhibits resonances at δ = 58.35 ppm [^1J(CH) = 100 Hz] and δ = 3.62 ppm for the CH($SiMe_3$)$_2$ groups, indicative of a symmetrical time-averaged trigonal-planar structure with equivalent trimethylsilyl groups. At −90 °C, *two* different quaternary

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(2) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23.

(3) ^1H NMR (C_6D_6, 25 °C): δ 3.55 (THF), 2.018 (C_5Me_5), 1.35 (THF), 0.276 ($SiMe_3$), −0.85 ppm (CH). ^{13}C NMR (C_7D_8, −90 °C): δ 119.0 (s, C_5Me_5), 68.2 (THF), 45.2 (br, CH), 40.5 (br, CH), 23.7 (THF), 10.85 (s, C_5*Me*$_5$), 5.2 (br, $SiMe_3$), 3.3 ppm (vbr, $SiMe_3$).

(4) Crystal data for La(η^5-C_5Me_5){CH($SiMe_3$)$_2$}$_2$(THF) (1): $C_{28}H_{61}O$-Si_4La, M_n 664, monoclinic, space group $P2_1/n$, a = 17.056 (3) Å, b = 13.200 (2) Å, c = 16.873 (4) Å, β = 106.17 (2)°, U = 3648.7 Å^3, Z = 4, D_{calcd} = 1.20 g cm^{-3}, F(000) = 1288 electrons, T = 233 K, graphite monochromated Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 13.2 cm^{-1}; current R = 4.4, R_w = 5.2, S = 0.86 for 4439 independent reflections with $I > 3\sigma(I)$.

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(7) Decomposition of La(η^5-C_5Me_5)[CH($SiMe_3$)$_2$]$_2$(THF-d_8) yields only (Me_3Si)$_2CH_2$.

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(10) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.

(11) It seems unlikely that 1 is in equilibrium with 2 and free THF. However, free THF does exchange with coordinated THF.

(12) Excess Me_3SiI is necessary for conversion to 2 at a rate greater than the decomposition of 1.

(13) ^1H NMR (C_6D_6, 25 °C): δ 1.997 (C_5Me_5), 0.263 ($SiMe_3$), −0.75 ppm (CH).

(14) $-CH_2SiMe_2I$-functionalized polystyrene was prepared by treatment[14a] of the Merrifield polymer (Fluka) with Mg(anthracene)(THF)$_3$ in THF, followed by quenching with Me_2SiCl_2. After filtration, washing with toluene, and drying, chloride–iodide exchange was achieved with BI_3 in toluene.[14b] (a) Itsuno, S.; Darling, G. D.; Stover, H. D. H.; Frechet, J. M. J. *J. Org. Chem.* **1987**, *52*, 4645. (b) Wolfsberger, W.; Schmidbaur, H. *J. Organomet. Chem.* **1971**, *28*, 301.

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(16) Anal. Calcd for $C_{10}H_{15}I_2La$: C, 22.73; H, 2.84; I, 48.07: La, 26.33. Found: C, 22.54; H, 2.76; I, 48.24; La, 26.35.

(17) RLi(solvent) complexes may simply be more reactive than (RLi)$_n$ because they are less highly associated. Decomposition of 1 occurs by loss of $CH_2(SiMe_3)_2$ and formation of a pale, yellow-colored material which has broad ^1H NMR resonances for the (η^5-C_5Me_5) and CH($SiMe_3$)$_2$ groups.

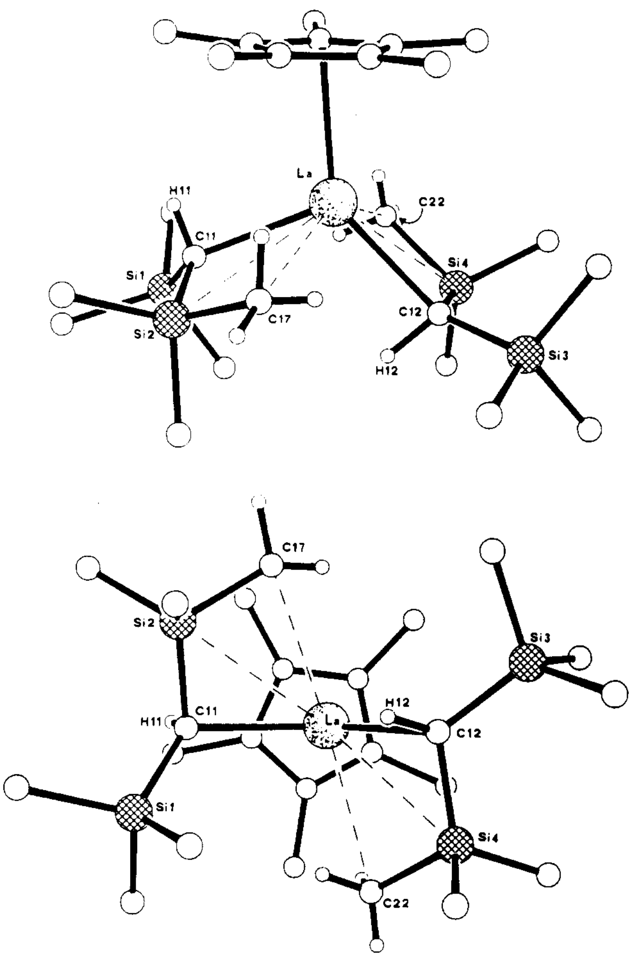

Figure 2. Alternative perspective views of the molecular structure of 2. Methyl group hydrogens except those on C(17) and C(22) have been omitted for clarity: La···C(17) = 2.978 (6) Å, La···C(22) = 2.988 (6) Å, La···Si(2) = 3.353 (2) Å, La···Si(4) = 3.400 (2) Å; La···H(11) = 2.64 (5)°, La···H(12) = 2.75 (5)°, La–C(11)–Si(1) = 126.4 (4)°, La–C(11)–Si(2) = 99.6 (3)°, La–C(12)–Si(3) = 129.6 (3)°, La–C(12)–Si(4) = 98.8 (3)°.

C_5Me_5 resonances are observed at δ = 120.85 ppm and δ = 119.91 ppm in ca. 2:3 ratio, as well as two methyne resonances at δ = 59.3 ppm and δ = 54.3 ppm, together with inequivalent trimethylsilyl groups. The different quaternary resonances are possibly indicative of two isomers. Hindered rotation in an yttrium-bound $CH(SiMe_3)_2$ group has been studied.[5]

The structure determination[18] of $La(\eta^5\text{-}C_5Me_5)[CH(SiMe_3)_2]_2$ (Figure 2) was undertaken to define the structural consequences of removal of the THF ligand. The geometries of 1 and 2 differ primarily in the conformations of the disyl ligands and in the pyramidalization of the $La(\eta^5\text{-}C_5Me_5)[CH(SiMe_3)_2]_2$ fragment in 1 which results from THF coordination. Small changes in La–C σ-bond lengths are observable, and in the La···Si and La···C secondary interactions, which are uniformly weaker in the more saturated THF adduct than in 2.

In complex 2 the disyl ligands are bound to lanthanum primarily by La–C σ-bonds [La–C(11) = 2.537 (5) Å, La–C(12) = 2.588 (4) Å, cf. La–C(6) = 2.651 (8) Å, La–C(7) = 2.627 (10) Å in 1] and adopt conformations such that the α-CH groups are endo and exo with respect to the C_5Me_5 ligand. This quasi-trigonal geometry at lanthanum is distorted from regularity, having cp–La–C(11) = 109.2°, cp–La–C(12) = 141.1°, and C(11)–La–C(12) = 109.7° (where cp is the centroid of the C_5 ring); these angles sum to 360.0°. The coordinative unsaturation at lanthanum in 2 (as in 1) is relieved by a variety of secondary interactions. A $La(\eta^5\text{-}C_5Me_5)$ dialkyl moiety has four available acceptor orbitals of mainly 5d character; thus two α-C–H and two β-C–Si interactions are possible in 2. In 1, one of these orbitals is used by the THF ligand and this may explain the large difference in La–C_α–H_α angles observed in the solid-state structure of 1. Hence in 2, the α-CH bonds show strong distortions, having substantially reduced La–C–H angles [La–C(11)–H(11) = 86 (3)°, La–C(12)–H(12) = 85 (3)° and La···H(11) = 2.64 (5) Å, La···H(12) = 2.75 (5) Å; cf. La–C(6)–H(61) = 81 (5)°, La–C(7)–H(71) = 106 (8)° in 1]. In both 1 and 2 the disyl groups are distorted so that each has one Si–Me group in close proximity to the lanthanum atom. The resultant La···Si and La···C contacts are well within the sum of van der Waals radii and imply favorable interactions with the lanthanum center [La···Si(2) = 3.353 (2) Å, La···Si(4) = 3.400 (2) Å, La···C(17) = 2.978 (6) Å, and La···C(22) = 2.988 (6) Å, cf. La···C(622) = 3.265 (14) Å and La···C(711) = 3.241 (19) Å in 1]. The conformations of the disyl ligands in both 1 and 2 have their La–C_α–Si–Me systems essentially planar with torsion angles La–C(11)–Si(2)–C(17) = 8.2° and La–C(12)–Si(4)–C(22) = −9.5°; cf. 12.3° and 14.3° in 1. Surprisingly, the methyl group hydrogens on C(17) and C(22) in 2 are *not* oriented so as to place one hydrogen close to the lanthanum atom, in marked contrast to agostic β- and γ-CH systems, in which one C–H bond is invariably directed toward the metal (methyl hydrogens were not located for 1). Similar distortions and conformations for β-Si–Me groups have been observed by X-ray diffraction in $[TiCp_2C({=}CMePh)SiMe_3]^+$,[19] $Nd(\eta^5\text{-}C_5Me_5)_2CH(SiMe_3)_2$,[6] $Nd[(\eta^5\text{-}C_5Me_4)_2SiMe_2]CH(SiMe_3)_2$,[20] and $Y(\eta^5\text{-}C_5Me_5)_2CH(SiMe_3)_2$[5] and, by ab initio calculations, for $[TiCl_2C(CH_2)SiH_2Me]^+$.[21] However, only in one case[20] did the structural data indicate a β-Si–Me interaction rather than a γ-C–H–metal interaction.[22] The best description of these interactions in 2 is of an agostic Si–C–metal bond, although there appears to be only a marginal lengthening of the interacting β-Si–C bond compared with the other Si–Me bonds [Si–C(622) = 1.910 (11) Å, Si(71)–C(711) = 1.945 (13) Å; cf. mean Si–Me = 1.907 Å in 1; Si–C(17) = 1.897 (8) Å, Si–C(22) = 1.900 (7) Å; cf. mean Si–Me = 1.874 (4) Å in 2]. These species may be viewed as models for the early stages of the β-methyl elimination reaction,[23] analogous to β-C–H agostic species which model the β-hydride elimination reaction. The near planarity of the La–C–Si–Me system is reminiscent of the planar four-center intermediates postulated and observed[24] in β-hydride elimination.

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[18] Crystal data for $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$ (2): $C_{24}H_{53}Si_4La$, M_r 593.04, hexagonal, space group $P6_3$ (No. 173), a = 18.543 (5) Å, c = 16.039 (4) Å, U = 4776 (2) Å^3, Z = 6, D_{calcd} = 1.24 g cm^{-3}, $F(000)$ = 1860 electrons, T = 200 K, monochromated Mo Kα X-radiation, λ = 0.71069 Å, μ(Mo Kα) = 15.04 cm^{-1}; R = 0.026, R_w = 0.032, S = 1.63 for 2722 unique, observed reflections with $I > 3\sigma(I)$. All hydrogen atoms were constrained to idealized geometries except those on C(11), C(12), C(17), and C(22) which were allowed to refine freely.

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[22] Similar distortions have been observed for lanthanide $N(SiMe_3)_2$ structures.[5] See also: (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725. (c) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575. (d) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205

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Supplementary Material Available: Experimental, analytical, spectroscopic, and crystal data, tables of positional parameters and anisotropic thermal parameters, and full listings of bond distances and angles (22 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

Synthesis of New Monomeric Zirconium and Hafnium Hydride Butadiene Complexes. The X-ray Structure of (η^5-Cyclopentadienyl)(η^4-butadiene)[1,2-bis(dimethylphosphino)ethane]hydridozirconium

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Summary: Room-temperature reaction of CpM(dmpe)(η^4-butadiene)Cl (**1**) [M = Zr, Hf; dmpe = 1,2-bis(dimethylphosphino)ethane] with $NaH_2Al(OCH_2CH_2OCH_3)_2$ [Red-Al] led to the new zirconium and hafnium hydrides CpM(dmpe)(η^4-butadiene)H [M = Zr (**2a**), 60%; M = Hf (**2b**), 57%] as pale yellow crystals. **2a** is monoclinic, space group $P2_1/n$, with a = 8.175 (2) Å, b = 15.706 (3) Å, c = 15.516 (2) Å, β = 99.41 (1)°, V = 1965.4 (7) Å^3, and Z = 4. Fast insertion reactions of CH_2CHR (R = H, Me, Et; 26 °C, 1 atm) into the Zr–H bond led to the formation of the corresponding alkyl derivatives CpM(dmpe)(η^4-butadiene)R [R = Et (**3**); R = n-Pr (**4**); R = n-Bu (**5**)] in good yield and crystalline form.

The chemistry of the M–H bond is continually receiving a great deal of attention in view of its involvement in many fascinating chemical processes.[1] In the chemistry of group IVB (group 4) metals, the synthesis and the reactivity of this functionality are well established for the bis(cyclopentadienyl)titanium and -zirconium derivatives,[2] while the analogous hafnium congeners remain much less characterized.[3] However, apart from these systems, this literature is surprisingly poor and limited to only two reports.[4] We now report the synthesis and characterization of the novel zirconium and hafnium hydrides CpM(dmpe)(η^4-butadiene)H [M = Zr (**2a**); M = Hf (**2b**)] together with a preliminary study on their reactivity with α-olefins.

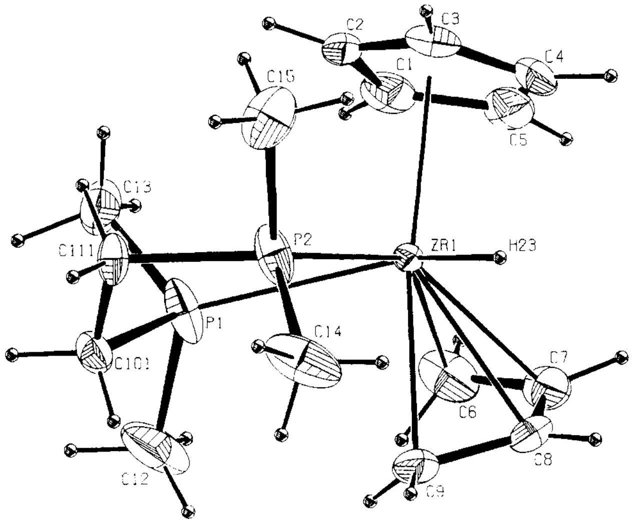

Figure 1. ORTEP drawing of CpZr(dmpe)(η^4-butadiene)H, independent molecule 1, showing the labeling scheme. Selected bond distances (Å) and angles (deg): Zr(1)–H(23) = 1.80 (5); Zr(1)–C(6) = 2.418 (3); Zr(1)–C(7) = 2.421 (3), Zr(1)–C(8) = 2.440 (3); Zr(1)–C(9) = 2.443 (3); Zr(1)–P(1) = 2.725 (1); Zr(1)–P(2) = 2.704(1); C(8)–C(9) = 1.430 (5); C(7)–C(8) = 1.382 (5); C(6)–C(7) = 1.425 (6); P(1)–Zr(1)–P(2) = 71.55 (3); C(6)–C(7)–C(8) = 119.1 (3); C(7)–C(8)–C(9) = 118.8 (3).

The compounds CpM(dmpe)(η^4-butadiene)Cl (M = Zr, Hf) (1)[5,6] react with $NaH_2Al(OCH_2CH_2OCH_3)_2$ (Red-Al) in toluene to give light brown solutions which, when cooled, produce pale yellow-crystals of 2 (Zr, 60%; Hf, 57%).

$$\underset{\mathbf{1}}{\text{CpM(dmpe)}(\eta^4\text{-butadiene})\text{Cl}} \xrightarrow[\text{toluene}]{NaH_2Al(OCH_2CH_2OCH_3)_2} \underset{\mathbf{2a}:\ M = Zr \quad \mathbf{2b}:\ M = Hf}{\text{CpM(dmpe)}(\eta^4\text{-butadiene})\text{H}} \quad (1)$$

An X-ray analysis carried out on a single crystal of **2a** reveals the unit cell composed of discrete monomeric units.[7] The geometry around zirconium is distorted octahedral (Figure 1) with the Cp ring centroid on the apical vertex and the dmpe ligand on two equatorial positions. The *s-cis*-butadiene ligand is symmetrically η^4-bonded to the metal with the two terminal carbon atoms C(6) and C(9) occupying respectively one equatorial and the second apical position [Cp(centroid)–Zr–C(6) = 104.9 (1)°; Cp(centroid)–Zr–C(9) = 167.6 (9)°]. No significant differences have been found between the Zr–C(diene) distances [ranging from 2.418 (3) to 2.440 (3) Å], suggesting an almost perfect η^4-mode of coordination for this fragment. This bonding mode, which is common for the late transition metals,[8] has never been observed for the group IVB metals, the distortion around the coordinated butadiene being explained in terms of high contribution of σ complex character.[9] The hydride, which occupies the fourth

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(7) **2a** is monoclinic in the space group $P2_1/n$. Cell data: a = 8.175 (2) Å, b = 15.706 (3) Å, c = 15.516 (2) Å, β = 99.41 (1)°, V = 1965.4 (7) Å^3, Z = 4, R = 0.034, R_w = 0.036, and GOF = 1.430 for a fit of 407 variables to 4156 observations. Structure was solved by standard Patterson methods; hydrogen atom positions were located and refined isotropically. Supplementary material contains full details on structure determination.

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