modified MM2 force field designed to model the transition structure[12] indicate that the O=C—O—H torsional angle is 17° and the O=C—C- - -H torsional angle is 118°, whereas these are 0° and 90° in the preferred deprotonation. These deviations from ideality (Figure 4) are predicted to raise the activation energy by 2–4 kcal/mol, reducing the rate by one to two orders of magnitude versus an unstrained model.

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$[Li(Me_2NCH_2CH_2NMe_2)_2][Li_2(Me_2NCH_2CH_2NMe_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}MeC_5H_4)][(\eta^5\text{-}MeC_5H_4)_6U_2(\mu\text{-}Me)]_2$: A Compound with Symmetrically Bridging MeC_5H_4 and Me Groups

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Organometallic compounds of the alkali metals which contain symmetrical bridging cyclopentadienyl groups, i.e., those in which two metal centers are located at equal distance on either side of and on the pseudo C_5-axis of the cyclopentadienyl group, are rare; the only example is the linear zigzag polymeric structure of $[Na(Me_2NCH_2CH_2NMe_2)Cp]$.[1] Symmetrically bridging methyl groups, i.e., those in which the metal–carbon–metal angle is 180° and the carbon atom is an equal distance from the metals, are unknown, though four recent structures have revealed bridging methyl groups in which the angle at carbon is near-linear and the metal–carbon distances are slightly asymmetric[2a] or linear and highly asymmetric.[2b–d] In this communication we describe the synthesis and X-ray crystal structure of $[Li(Me_2NCH_2CH_2NMe_2)_2]\cdot[Li(Me_2NCH_2CH_2NMe_2)]_2[\mu\text{-}MeC_5H_4]\cdot[(MeC_5H_4)_3U]_2[\mu\text{-}Me]$, a compound that contains a MeC_5H_4 group sandwiched between two $Li(Me_2NCH_2CH_2NMe_2)$ fragments and a methyl group that is symmetrically bridging between two $(MeC_5H_4)_3U$ groups.

Jonas has shown that d-transition-metal metallocenes react with lithium alkyls to give compounds in which the alkyl group replaces the cyclopentadienyl group and that this elegant synthetic method leads to many unusual compounds.[3] In the f-transition-metal series, substitution (eq 1 and 2)[4] and addition (eq 3)[4b,c,5] reactions

$$Cp_3M + LiR \rightarrow Cp_2MR + LiCp \qquad (1)$$

$$Cp_3UR' + LiR \rightarrow Cp_3UR + LiR' \qquad (2)$$

$$Cp_3M + LiR \rightarrow LiCp_3MR \qquad (3)$$

have been observed. Addition of 1 molar equiv of methyllithium to $(MeC_5H_4)_3U(thf)$ in diethyl ether in the presence of 1 molar equiv of $Me_2NCH_2CH_2NMe_2$ at −30 °C gives a red precipitate which upon crystallization from diethyl ether gives red crystals which were shown to be $[Li(tmed)_2]\cdot[Li(tmed)]_2[\mu\text{-}MeC_5H_4]\cdot[(MeC_5H_4)_3U]_2[\mu\text{-}Me]$ by X-ray crystallography.[6] The ^1H NMR spectrum of the paramagnetic compound (trivalent uranium has

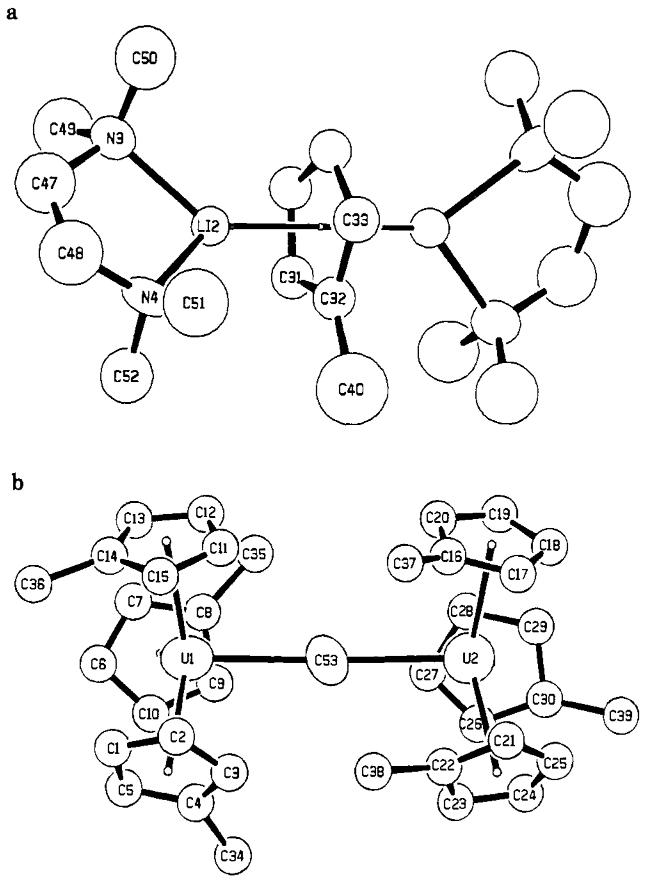

Figure 1. (a) ORTEP drawing of $[Li_2(Me_2NCH_2CH_2NMe_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}MeC_5H_4)]$ fragment: Li–C(av) = 2.31 (3) Å, Li–N(av) = 2.09 (1) Å, N(3)–Li–N(4) = 86.7 (22)°, N–Li–ring centroid(av) = 136°. (b) ORTEP drawing of $[(\eta^5\text{-}MeC_5H_4)_6U_2(\mu\text{-}Me)]$ fragment: U–C(CP)(av) = 2.82 (4) Å, U–ring centroid(av) = 2.57 Å, U–C(53)(av) = 2.72 (1) Å, U–C(53)–U = 176.9 (11)°, ring centroid–U–C(53)(av) = 100°, ring centroid–U–ring centroid(av) = 117°.

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(6) (a) Methyllithium (1.7 mL of a 0.97 M diethyl ether solution, 1.7 mmol) was added to $(MeC_5H_4)_3U(thf)$ (0.91 g, 1.7 mmol) in diethyl ether (30 mL) and $Me_2NCH_2CH_2NMe_2$ (0.25 mL, 1.7 mmol) at −30 °C. The red precipitate was stirred at −30 °C for 30 min and then warmed to −10 °C, the volatile material was removed at −10 °C, and then the solid was exposed to a vacuum for 1 h at room temperature. The red solid was extracted with diethyl ether (100 mL) and filtered, and the filtrate was concentrated to ca. 80 mL and then cooled to −20 °C. The red crystals (0.20 g, 19%) were collected, mp 81–85 °C. Additional crops of crystals may be obtained on concentration and cooling the mother liquors [Anal. Calcd for $C_{104}H_{161}Li_3N_8U_4$: C, 50.0; H, 6.50; N, 4.49. Found: C, 49.4; H, 7.26; N, 6.49. ^1H NMR (C_7D_8, −70 °C) δ 14.4 (12 H), 6.17 (2 H), 3.21 (1.5 H), 2.63 (4 H), 2.35 (4 H), 2.10 (12 H), 1.50 (12 H), −8.08 (18 H), −18.7 (12 H), −284.7 (3 H)]. The resonances at δ +14.4 and −18.7 are tentatively assigned to the ring methine protons and the resonance at δ −8.08 to the ring methyl protons of the $(MeC_5H_4)U$ fragment. The resonance at −284.7 is due to the bridging methyl group. The ring methine and methyl group resonance on the $(MeC_5H_4)Li$ fragment are assigned to the resonances at δ 6.17 and 3.21, respectively. The other resonances are due to the $Me_2NCH_2CH_2NMe_2$ protons. The line width, $\nu_{1/2}$, of all the resonances is ca. 10–15 Hz, except that of the resonance at δ −284.7 which is 30 Hz. (b) *X-ray Crystallography* (see Supplementary Material).

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an f^3 electronic configuration) contains four broad features ($\nu_{1/2} \sim 100$ Hz) at 30 °C at δ 6.11, 2.23, −5.42, and −10.8 in approximate area ratio of 1.5:3:1:1 though at −70 °C all the resonances in the spectrum may be assigned based upon the crystallographic result.[6] Most importantly, the $U_2(\mu\text{-Me})$ resonance at δ −284.7 (−70 °C) follows Curie law, and the extrapolated chemical shift at +30 °C is δ −185, in the region of uranium methyls.[4b,7]

The crystal structure (Figure 1) contains one molecule each of $Li(tmed)_2$ (not shown in Figure 1 but see Supplementary Material) and $[Li(tmed)_2[\mu\text{-}MeC_5H_4]$, and two molecules of $[(MeC_5H_4)_3U]_2[\mu\text{-Me}]$. The Li(tmed) fragments are not unusual in any way.[8] In the bridging MeC_5H_4 fragment, the average Li–C distance of 2.31 ± 0.03 Å and the Li–ring centroid distance of 2.00 Å are in the range found in $[(Me_3Si)_3C_5H_2]Li(tmed)$[9a] of 2.33 ± 0.03 Å and in $Me_3SiC_5H_4Li(tmed)$[9b] of 2.28 ± 0.01 Å. The Li–ring centroid–Li angle is 175°; the MeC_5H_4 group is the perpendicular bisector of the Li···Li vector, and the two Li(tmed) fragments are oriented perpendicular to each other. The bonding in this inverted sandwich fragment may be viewed in the following way. Each lithium atom in the LiN_2^+ fragment can use a s- and two p-orbitals for four electrons in bonding to the tmed ligand. The empty sp^2-hybridized orbital of σ-symmetry on each LiN_2^+ fragment can interact with the filled σ-symmetry orbital on the $MeC_5H_4^-$ anion forming bonding, antibonding, and nonbonding combinations. The two electrons are located in the bonding molecular orbital; this description is the familiar one given for three-center two-electron bonding. The filled, π-symmetry orbitals on the $MeC_5H_4^-$ fragment can act as π-donors toward the empty, unhybridized, orthogonal p-orbitals on each $Li(tmed)^+$ fragment, accounting for the perpendicular orientation of the two $Li(tmed)^+$ fragments. On the other hand, the perpendicular orientation minimizes the repulsion between the Me_2N groups across the MeC_5H_4 ring, and steric rather than electronic factors may be responsible for the observed geometry.

The other fascinating feature of the molecule is the geometry of the anion with the U–C(53)–U angle of 176.9 (11)° and U–C(53) distances of 2.71 (3) and 2.74 (2) Å. The hydrogen atoms on the bridging methyl groups were not located in the X-ray study[6b] though the symmetry requires that the idealized geometry at carbon is apparently trigonal-bipyramidal, similar to that found for the benzyl group in tetrameric $PhCH_2Na(tmed)$,[10a] a geometry that has fascinated theoreticians.[10] The location of C(53) equidistant from the two uranium atoms could be due to disorder between two equivalent positions with unequal U–C distances. Unfortunately, all of the crystals fracture on cooling though efforts to obtain a better data set are continuing. The U–C(53) distance is long relative to $Cp_3U(n\text{-Bu})$[11] of 2.43 (2) Å and $[Cp_3U(n\text{-Bu})]^-$ of 2.56 (1) Å[4c] as expected since linear bridge bonds are ca. 10% longer than terminal ones in $(Me_5C_5)_2Lu(\mu\text{-Me})Lu(Me)(C_5Me_5)_2$.[2c] The average U–C(cp) distance of 2.82 ± 0.04 Å and the ring centroid–U–ring centroid angle of 117° are identical with those found in $Cp_3U(n\text{-Bu})$[11] and $Cp_3U(n\text{-Bu})^-$.[4c] It is difficult to describe the bonding in the anion, since the idealized C_{3v} symmetry $(MeC_5H_4)_3U$ fragment has many orbitals (s, p, d, f) of σ-symmetry, though the following description appears to be reasonable. The D_{3h} symmetry methyl anion is formed from s- and two p-orbitals giving a sp^2-hybridized set that contains six electrons for the C–H bonds and an unhybridized p-orbital with its two electrons that can be used in bonding with the σ-orbitals on the Lewis acid, $(MeC_5H_4)_3U$.

The bridging cyclopentadienyl and methyl groups described in this note may be viewed as models for the bimolecular transition state in electrophilic substitution at unsaturated and saturated carbon centers.[12]

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Supplementary Material Available: A listing of positional parameters, thermal parameters, bond lengths and angles, distance restraints, least-squares planes, ORTEP view of the unit cell, and method of solution of X-ray data (14 pages). Ordering information is given on any current masthead page.

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Acyclic Tertiary and Quaternary Carbon Stereocontrol via New Aldol Equivalent Reactions of Optically Active (*E*)-Enol Ethers

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The development of enantioselective methodologies for acyclic multiple stereocontrol continues to represent an important challenge for synthetic chemists.[1] Optically active 2-ethenyl-1,3-dioxolanones, available in one step from acrolein or methacrolein and lactic acid, mandelic acid, or hexahydromandelic acid,[2] are of interest in this regard as a new class of enal equivalent for stereocontrolled synthesis. We have recently developed several new methodologies for the conversion of these materials into the corresponding (*E*)-enol ethers, including (Scheme I) (a) nickel- and palladium-catalyzed conjugate addition of organoborates,[3] (b) Lewis acid-catalyzed addition of trimethylsilyl ketene acetals and thiophenols,[4] and (c) nickel-mediated homoenolate coupling reactions with halocarbons.[2]

We now report that the optically active enol ethers so obtained undergo highly diastereoselective reactions with a variety of aliphatic and aromatic acetals to give the protected aldol products **1**, several of which have been reductively deprotected to afford the corresponding alcohols **2** (Scheme II, Table I).[5–7]

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