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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

S.D. Stults, R.A. Andersen, and A. Zalkin

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A Compound with Symmetrically Bridging MeC_5H_4 and Me Groups

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Abstract

Reaction of eqimolar amounts of MeLi and $(MeC_5H_4)_3U(thf)$ in $Me_2NCH_2CH_2NMe_2$ and diethyl ether gives red crystals of $[Li(Me_2NCH_2CH_2NMe_2)_2]$ $[Li_2(Me_2NCH_2CH_2NMe_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}MeC_5H_4)][(\eta^5\text{-}MeC_5H_4)_6U_2(\mu\text{-}Me)]_2$ in 19% yield. Single crystal X-ray crystallography; monoclinic, $C_{2/C}$, a=18.093(4) Å, b=21.706(6) Å, c=27.233(6) Å, β=97.53(3)°, Z=4, R=0.053 [2165 data, $F^2>3\sigma(F^2)$], shows that the compound is composed of two cationic fragments, $[Li(Me_2NCH_2CH_2NMe_2)_2]$ and $[Li_2(Me_2NCH_2CH_2NMe_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}MeC_5H_4)]$, the latter of which contains two Li(tmed) units on opposite sides of the planar MeC_5H_4 ring, i.e., an inverted sandwich structure, and the anion portion contains a symmetrically bridging methyl group sandwiched between two $(MeC_5H_4)_3U$ units so that the methyl group has D_{3h} symmetry. Solution ^1H NMR studies are consistent with the X-ray structural result.

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 zig-zag 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 note 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, an inverse sandwich compound, and a methyl group that is linear, symmetrically bridging between two $(MeC_5H_4)_3U$ groups, i.e., the methyl group is sandwiched between two $(MeC_5H_4)_3U$ fragments.

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 (eqs. 1 and 2)[4] and addition (eq. 3)[4b,c,5] reactions have been observed.

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

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

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

Addition of one molar equivalent of methyllithium to $(MeC_5H_4)_3U(thf)$ in diethyl ether in the presence of one molar equivalent 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 $[Li(tmed)_2]\cdot[Li(tmed)]_2[\mu MeC_5H_4]\cdot[(MeC_5H_4)_3U]_2[\mu\text{-}Me]$ by X-ray crystallography.[6] The ^{1}H-NMR spectrum of the paramagnetic compound, trivalent uranium has an f^3 electronic configuration, contains for broad features ($\nu_{\frac{1}{2}}$ ~ 100 Hz) at 30° C at δ6.11, 2.23, -5.42, and -10.8 of approximate area ratio of 1.5:3:1:1 though at -30° 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 (-30°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) contains one molecule each of $Li(tmed)_2$ (not shown in the Figure 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 averaged 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 bisection 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, anti-bonding, and a non-bonding

combination. 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 geometry at carbon is trigonal bipyramidal, similar to that found for the benzyl group in tetrameric $PhCH_2Na(tmed)$,[10a] a geometry that has fascinated theoreticians.[10] 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 averaged U-C(cp) distance of 2.82±0.04 Å and the ring centroid-U-ring centroid angle of 117° are identical to 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. Table of positional parameters, thermal parameters, bond lengths and angles, distance restraints, least-squares planes, and ORTEP view of the unit cell.

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6. (a) Methyllithium (1.7 mL of a 0.97M diethyl ether solution, 1.7 mmol) was added to $(MeC_5H_4)_3U(thf)$ (0.91g, 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 then warmed to -10° C and the volatile material was removed at -10° C then the solid was exposed to a vacuum for 1 h at room temperature. The red solid was extracted with diethyl ether (100 mL), filtered, and the filtrate was concentrated to ca. 80 mL, then cooled to -20° C. The red crystals (0.20g, 19%) were collected, m.p. 81-85° C. Additional crops of crystals may be obtained on concentration and cooling the mother liquors. Anal. Calcd for $C_{104}H_{161}Li_3N_8U_3$: C, 50.0; H, 6.50; N, 4.49. Found: C, 49.4; H, 7.26; N, 6.49. ^{1}HNMR (C_7D_8, -70° C): δ14.4(12H), 6.17(2H), 3.21(1.5H), 2.63(4H), 2.35(4H), 2.10(12H), 1.50(12H), -8.08(18H), -18.7(12H), -284.7(3H). The line width, $\nu_{\frac{1}{2}}$, 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. The compound crystallizes in the monoclinic space group $C_{2/c}$ with cell dimensions a = 18.093(4) Å, b = 21.706(6) Å, c = 27.233(6) Å, β = 97.53(3)°, V = 10602.9 Å^3, Z = 4, d(calcd) = 1.56 g cm^{-3}, and μ = 58.17 cm^{-1}. A modified Picker FACS-1 automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator was used. A set of θ-2θ scan data was collected and corrected for absorption (analytical method)[6c] and Lorenz and polarization effects. The uranium atom positions were obtained from three-dimensional Patterson maps, and subsequent least-squares refinements and difference electron density maps were used to determine the positions of the remaining atoms. It was evident from the early

least-squares refinements that the structure suffered from severe thermal motion and disorder which caused distortions in the C-C distances and large anisotropies in the thermal parameters. An attempt at obtaining a low-temperature set of data was unsuccessful as the crystal underwent an unresolved transformation and diffracted X-rays poorly. To manage these problems, distance restraints[6d] were applied and isotropic thermal parameters were assigned to the two lithium atoms and to all but one of the carbon atoms. In the difference maps, several peaks were observed about the cp rings that were suitable sites for the methyl carbon atom, and this indicated disorder. These methyl peaks were included in the refinements as half atoms, and were retained if their adjusted thermal parameter was less than 30 $Å^2$. One methyl group on each cyclopentadienyl group bonded to the uranium atoms survived this procedure. On the cp ring that lies on a 2-fold axis between lithium atoms, two methyl carbon atoms remained which was interpreted as a static disorder of two carbon positions, although the treatment of the methyl group positions does not fully treat the disorder, it at least indicates the predominant positions of the ring methyl groups. The bridging carbon atom C(53) between the two uranium atoms was well-behaved and was refined with no restraints and with anisotropic thermal parameters. The other atoms refined with anisotropic thermal parameters were the two uranium and four nitrogen atoms. The x and y coordinates of C48 prevented the least-squares refinements from converging and had to be fixed. Estimated hydrogen atom parameters with the exception of those of the methyl groups on the cp rings were included but not refined. The structure was refined by full-matrix least-squares to a conventional R factor of 0.053, [2165 data, $F^2 > 3\sigma(F^2)$ against 276 parameters]. Details of the refinements and other crystallographic data is given in Table I of Supplementary Material. (c) Templeton, L.K.; Templeton, D.H. Abstracts, American Crystallographic Association: Storrs, CT, Series 2, Vol. 1, p. 143. (d) Waser, J. Acta Cryst. **1963**, 16, 1091.

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Figure Captions

Figure Ia. ORTEP drawing of $[Li_2Me_2NCH_2CH_2NMe_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}MeC_5H_4)]$ fragment. Li-C(ave.) = 2.31(3) Å, Li-N(ave.) = 2.09(1) Å, N(3)-Li-N(4) = 86.7(22)°, N-Li-ring centroid(ave.) = 136°.

Figure Ib. ORTEP drawing of $[(\eta^5\text{-}MeC_5H_4)_6U_2(\mu\text{-}Me)]$ fragment. U-C(CP)(ave.) = 2.82(4) Å, U-ring centroid(ave.) = 2.57 Å, U-C(53)(ave.) = 2.72(1) Å, U-C(53)-U = 176.9(11)°, ring centroid-U-C(53)(ave.) = 100°, ring centroid-U-ring centroid(ave.) = 117°.

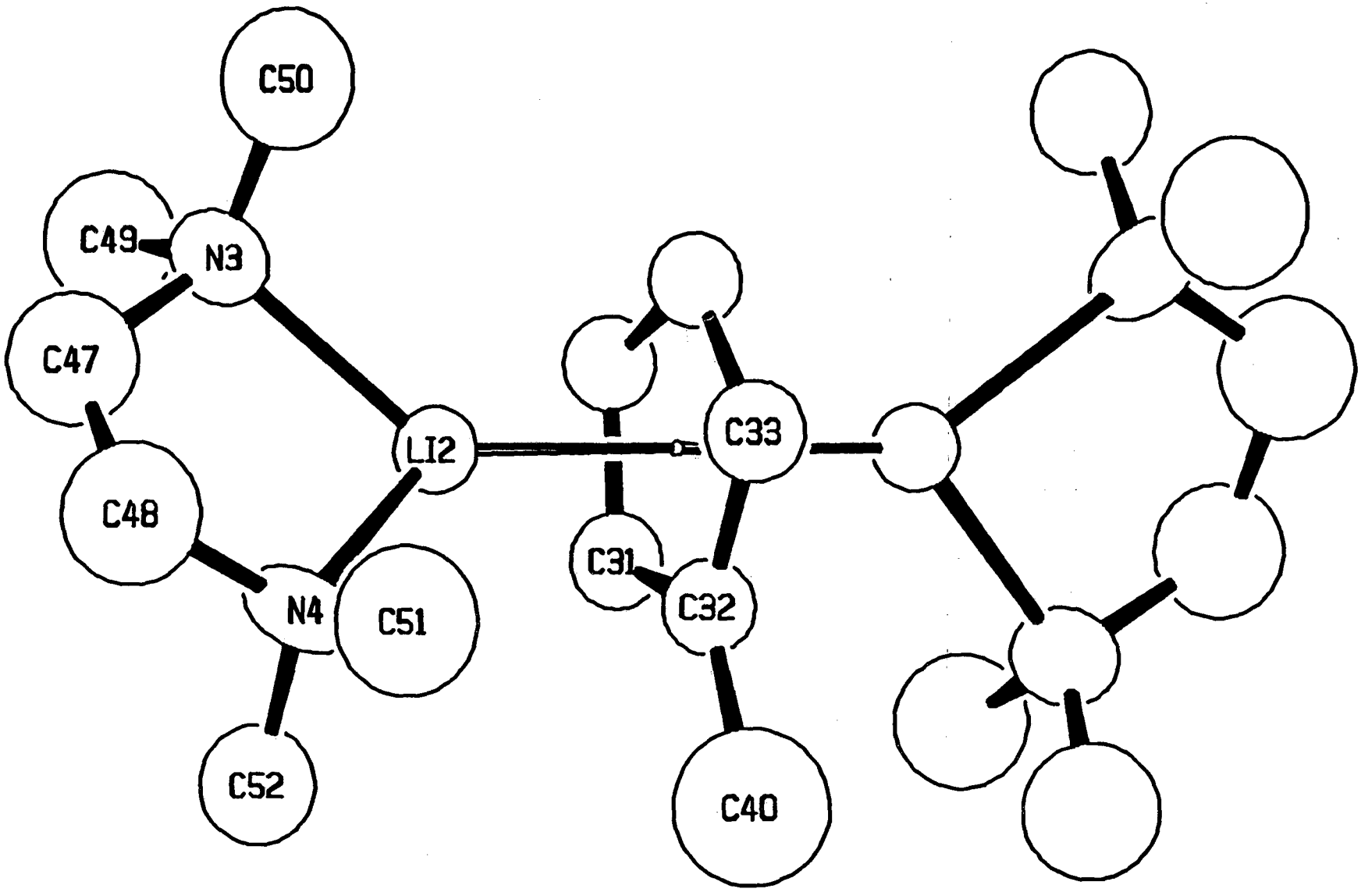

Figure 1a

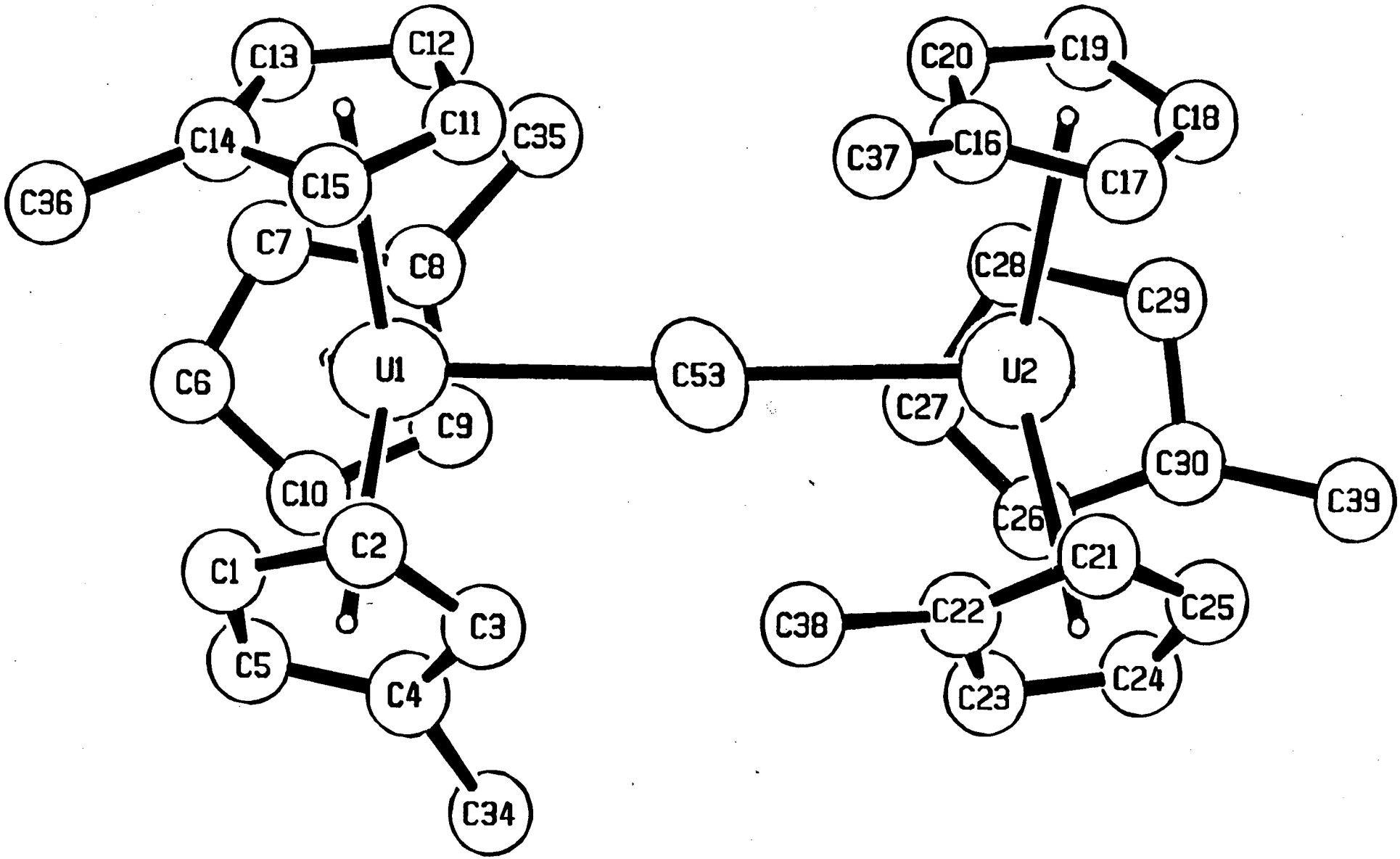
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Figure 1b

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