distinguish between these two mechanisms.

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Registry No. 1, 82764-27-0; 2, 82764-30-5; 3, 116840-62-1; 4, 82764-28-1; 5, 82764-29-2; $AgBF_4$, 14104-20-2; cyclopropane, 75-19-4; methylcyclopropane, 594-11-6; cyclopentane, 287-92-3.

Synthesis and Molecular Structure of Lithium Tri-*tert*-butylberyllate, $Li[Be(t\text{-}C_4H_9)_3]$

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Summary: Di-*tert*-butylberyllium, $(t\text{-}C_4H_9)_2Be$, and *tert*-butyllithium, $(t\text{-}C_4H_9)Li$, react in pentane to produce clear, colorless needlelike crystals of $Li[Be(t\text{-}C_4H_9)_3]$ in high yield. A single-crystal X-ray diffraction study at −149 °C has established the trigonal-planar arrangement of the *tert*-butyl groups around beryllium.

We have recently initiated a survey of the organometallic chemistry of beryllium and report herein the synthesis and structural characterization of a new crystalline organoberyllium compound, lithium tri-*tert*-butylberyllate, $Li[Be(t\text{-}C_4H_9)_3]$. Structures for the related compounds $LiBeH_3$[1] and $Li_2[Be(CH_3)_4]$[2] have previously been deduced from X-ray powder diffraction data. The dynamics of the $Be(CH_3)_2/LiCH_3$ system in diethyl ether has been studied by IR and variable-temperature ^1H NMR spectroscopy and was shown to be very fluxional at ambient temperature.[3] The structure of $[NaBe(C_2H_5)_2{\cdot}O(C_2H_5)_2]_2$ has also been determined by single-crystal X-ray diffraction.[4,5] This structure has a nominally trigonal-planar arrangement around beryllium with two Be–C bonds and a hydrogen-bridged Be–Be bond.

In a typical synthesis utilizing a glass high vacuum system, 550 mg (4.47 mmol) of di-*tert*-butylberyllium, $(t\text{-}C_4H_9)_2Be$, prepared by the method of Head, Holley, and Rabideau[6] was condensed onto a frozen (−196 °C) solution of 286 mg (4.47 mmol) of freshly sublimed *tert*-butyllithium, $(t\text{-}C_4H_9)Li$, in 5 mL of dry pentane. The reaction vessel was sealed and allowed to warm to ambient temperature. The two reactants mixed by diffusion only. Colorless needle-shaped crystals of the title compound began to form after a few minutes. After 5 h the product was collected by filtration, washed with pentane, and dried under vacuum. Yield: 669 mg (3.60 mmol, 80.5% of theory). NMR spectra in C_6D_6: ^1H, $\delta = 1.01$ ppm; ^9Be, $\delta = 19.5$ ppm; ^7Li, $\delta = -2.30$ ppm; ^{13}C, $\delta = 32.6$ ppm (q, $J = 15$ Hz, 9 C), $\delta = 17.3$ ppm (s, 3 C).

Solid $Li[Be(t\text{-}C_4H_9)_3]$ fumes in air but appears to be very stable under vacuum or in an inert atmosphere. It exhibits good solubility in benzene, toluene, tetrahydrofuran, glyme, and diethyl ether and is slightly soluble in pentane. When heated at 70 °C under high vacuum, it sublimes with little decomposition. A low-temperature ^1H NMR study in a toluene-d_8/CF_3Br mixed solvent (ca. 50/50) system showed only a single resonance down to −140 °C. The room-temperature ^{13}C NMR spectrum (C_6D_6) shows resonances characteristic of *tert*-butyl groups. In ethereal solvents such as THF, glyme, or ethyl ether, di-*tert*-butylberyllium etherate, $(t\text{-}C_4H_9)_2Be{\cdot}O(C_2H_5)_2$, and *tert*-butyllithium react readily to produce a clear, colorless solution. The ^9Be NMR spectra of these solutions exhibit signals which are shifted about 2 ppm upfield from the resonances for the title compound in ether-free solvents.

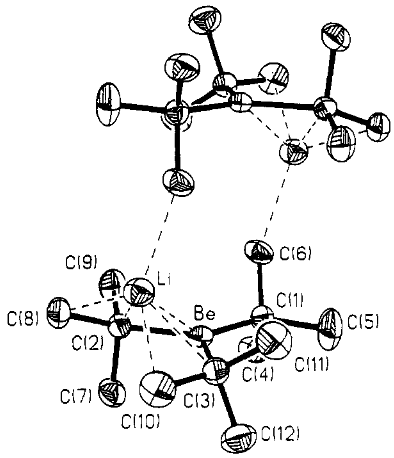

Figure 1. ORTEP plot (50% probability thermal ellipsoids) of $Li[Be(t\text{-}C_4H_9)_3]$ showing the trigonal-planar arrangement of the three *tert*-butyl groups around beryllium and the dimeric orientation of the molecules in the unit cell.

A single-crystal X-ray diffraction study of lithium tri-*tert*-butylberyllate at −149 °C revealed that the molecule crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.515$ (2) Å, $b = 8.546$ (2) Å, $c = 11.293$ (3) Å, $\alpha = 72.90$ (2)°, $\beta = 70.49$ (2)°, $\gamma = 62.08$ (2)°, $V = 675.2$ (3) Å^3, and $Z = 2$. Diffraction data was collected on a Nicolet diffractometer using Mo Kα radiation. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, and positional parameters of the hydrogen atoms were refined with fixed isotropic thermal parameters. Final least-squares refinement gave $R = 4.1\%$ and $R_w = 5.0\%$ using 1380 reflections having $F > 5.0\sigma(F)$. Lithium tri-*tert*-butylberyllium crystallizes solvent-free from pentane solutions as a dimeric unit having C_i symmetry as shown in Figure 1. The geometry around the beryllium atom is trigonal planar with the beryllium atom and the three tertiary carbon atoms (from the *tert*-butyl groups) lying in one plane. The planarity of this unit is clearly indicated by the fact that the sum of the three C–Be–C angles is 359.9°. The lithium atom resides above this plane in a cavity having close contacts with Be, C(2), C(3), C(8), C(10), H(8B), H(8C), and H(10B) and with C(6A), H(6A) and H(6B) of the second molecule. The Be–C(1) distance is 1.812 (4) Å, which is similar to Be–C distances in $[NaBe(C_2H_5)_2{\cdot}O(C_2H_5)_2]_2$[4,5] and $Li_2[Be(CH_3)_4]$.[2] The distances Be–C(2) and Be–C(3) are longer at 1.854 (4) Å and 1.864 (3) Å, respectively, apparently due to interaction with the Li atom. The Be–Li distance is 2.227 (6) Å and the four C–Li distances within the molecular unit average 2.228 Å. This value is similar to LiC distances in methyllithium (2.30 Å)[7,8] and ethyllithium (2.18 Å).[9] The Li–C(6A)

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distance to the second molecular unit of the dimer is slightly longer at 2.407 (4) Å. Additionally, the C(2)–Be–C(3) angle is distorted from the expected trigonal planar 120° to 117.1 (2)°, apparently due to the interaction with the lithium atom. The exact nature of this interaction is not understood. While the trigonal-planar arrangement of the alkyl groups around beryllium suggests that lithium has an electrostatic interaction with the organoberyllium anion, the fact that the compound sublimes and dissolves in hydrocarbon solvents suggests a more covalent interaction.

We are currently investigating the reaction chemistry of $Li[Be(t\text{-}C_4H_9)_3]$ and related organometallic compounds of beryllium and lithium and will report on these at a later date.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, and bond distances and angles (8 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Thermodynamic Control of Stereochemistry in Alkylation of Chiral Transition-Metal β-Oxoacyl Compounds: Enolization without Epimerization

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Summary: Deprotonation of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)Re}(CO)_4$ (**1**) in THF solution and addition of CH_3I lead to the C-alkylation product $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH(CH_3)CO)Re}(CO)_4$ (**2-D**), isolated as a single diastereomer (91% yield). In THF-d_8 solution, **2-D** exists in equilibrium with its enol form $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COC(CH_3)C(OH))Re}(CO)_4$ (**4**); K_{eq} = 0.10 at 23 °C. Deprotonation of **2-D** and alkylation with CD_3I generate $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COC(CH_3)(CD_3)CO)Re}(CO)_4$ (**5-D-d_3**), with >97% diastereoselectivity.

The alkylation chemistry of chiral β-oxoacyl transition metal complexes offers intriguing possibilities for asymmetric bond formation. This is particularly true in light of the role that the 1,3-dicarbonyl functionality plays in organic chemistry. However, application of metallaenolate methodology to the β-oxoacyl system raises interesting and important questions concerning enolization phenomena as well as alkylation regiochemistry.[1] Specifically, the formation of new chiral centers which bear an acidic hydrogen will be significant only if thermodynamic control of stereochemistry is operative or if the rate of enolization is sufficiently slow on the laboratory time scale.

We report herein that stereoselective methylation of the metallaenolate derived from chiral β-oxoacyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)Re}(CO)_4$ (1) is indeed under thermodynamic control. In addition, the newly formed tertiary carbon center is readily deprotonated and C-alkylated a second time to generate a new quaternary carbon center with excellent diastereoselectivity.[2]

We recently reported the synthesis of the first stable β-oxoacyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)Re}(CO)_4$ (1) from reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_2Li)$ and $Re(CO)_5(OSO_2CF_3)$.[3] Deprotonation of 1 (310 mg, 0.32 mmol, ~0.01 M) in THF with *t*-BuOK (0.44 mmol) and quenching the resultant enolate anion with excess CH_3I (~32 mmol) led to isolation of the C-alkylated product $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH(CH_3)CO)Re}(CO)_4$ (**2-D**) as a single diastereomer in 91% yield. In addition to **2-D**, the O-alkylation product $(\eta^5\text{-}C_5Me_2)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCHC(OCH_3))Re}(CO)_4$ (**3**) is formed in ~4% yield as determined by ^1H NMR spectroscopy on the crude reaction mixture.[4] Complex **3** was synthesized in 18% isolated yield from similar reaction of the enolate from 1 with $(CH_3)_3O^+BF_4^-$.

We were unable to assign the stereochemistry for **2-D** on the basis of spectroscopic data; however, by single-

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