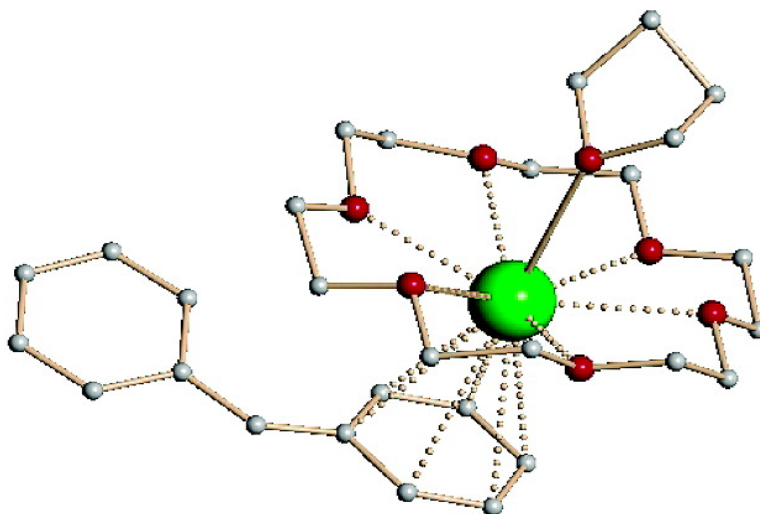


An Examination of Metal–Ligand Binding Modes in Rubidium Diphenylmethanide

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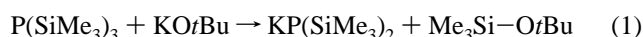
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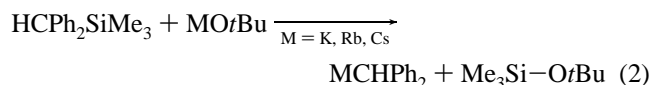
Alkali organometallics have been utilized for some time in a variety of applications, as summarized in several excellent reviews on the subject.^{1–4} In addition to their value in organic synthesis, these compounds (particularly the potassium salts) have shown enormous utility in the preparation of organometallic compounds of heavier group II and III metals and are discussed as reactive intermediates in superbases chemistry.⁵ An understanding of the structure–function relations of the reagents requires detailed insights into the metal–ligand binding, and extensive investigations have resulted in theory rationalizing metal–ligand binding trends.⁶ The essence of this theory is that smaller cations, due to their higher charge density, are more capable of inducing charge localization in the anion. Structural information on heavy alkali metal benzyl and triphenyl derivatives includes several examples,^{6–9} although information on the related diphenyls remains scant.^{1,10,11}

In our pursuit of heavy alkaline earth organometallics, we identified a recently reported class of silyl-substituted diphenylmethanes as ideal starting materials.¹² While preparation of organometallic lithium compounds is typically facile,¹³ difficulties in preparing the heavier alkali metal congeners necessitate alternate access routes. Most commonly, “superbase” chemistry, utilizing *n*BuLi/MO*t*Bu mixtures (M = Na, K, Rb, Cs),⁵ is employed, although this method can suffer from lack of selectivity and difficulties in separating the lithium side product. Previous work has shown that the alkali metal assisted scission of element–silicon bonds can lead to metalated products through extrusion of silyl ether (eq 1).^{14,15}



It was expected that the additional drive to form a resonance stabilized anion, as seen here, would make this reaction extremely facile and provide for a powerful new route to these compounds.

The reaction of the silylated ligand with heavy alkali metal *tert*-butoxides (K, Rb, Cs) cleanly affords the diphenylmethanide derivatives under subsequent formation of silyl ether,¹⁶ demonstrating the strong thermodynamic drive toward Si–O bond formation.



We here present crown ether encapsulated rubidium diphenylmethanide, where two different solid-state modifications with different metal coordination modes are observed. Crystallization at –23 °C led to the η^3 contact rubidium diphenylmethanide **1** (Figure 1) in which the metal assumes a geometry with one face capped by the crown ether and the other occupied by the ligand, resulting in a metal coordination number of nine.

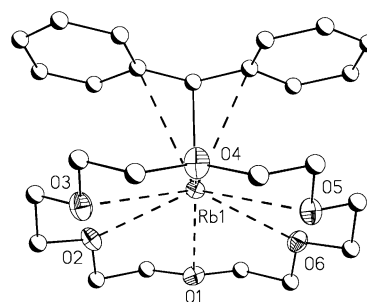


Figure 1. Crystal structure of **1**. Non-carbon atoms are displayed as thermal ellipsoids with 30% probability. Hydrogen atoms have been removed for clarity.

The rubidium is directly bonded to the deprotonated methylene carbon of the ligand at a distance of 3.063(3) Å with two longer interactions to the phenyl rings at 3.311(3) and 3.393(3) Å. The methine hydrogen position was calculated, and the geometry around the ipso carbon displays a C2–C1–C8 angle of 132.6(3)°. These compare favorably with those in the separated lithium and contact sodium structures.^{10,11} The phenyl rings are slightly twisted (4.4° and 7.6°) relative to the plane of the methine, methine hydrogen, and ipso carbons. This is in contrast to the alkali metal triphenylmethanides, in which these angles regularly exceed 25°.⁶

Crystallization of the reaction mixture at 4 °C leads to the formation of the η^6 coordinated rubidium diphenylmethanide **2** where the metal is again encapsulated by crown ether (Figure 2).

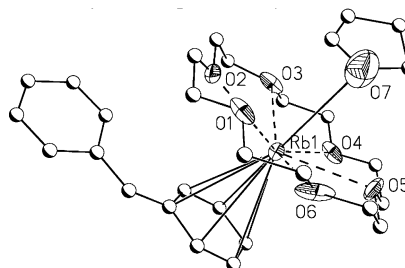


Figure 2. Crystal structure of **2**. Non-carbon atoms are displayed as thermal ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

The metal sits slightly below the center of the crown ether with average Rb–O distances of 2.85(5) Å. THF is located at an axial position, while one η^6 coordinated ligand phenyl group occupies the other with a metal–ring (centroid) distance of 3.076(9) Å, resulting in a formal coordination number of 13. On average, the phenyl bond lengths in the bound ring do not deviate significantly from those in the unbound ring with values of 1.382–1.412(15) Å. With the methine hydrogen atom in a calculated position, the geometry of the central carbon compares well with **1**, displaying a C2–C1–C8 angle of 133.0(9)°.

The curious ability of rubidium diphenylmethanide to afford two binding modes, apparently dependent on crystallization temperature, suggested that the rapidly crystallized η^3 product **1** (crystallized at $-23\text{ }^\circ\text{C}$) was the kinetic product and the slower forming η^6 compound **2** (crystallized at $4\text{ }^\circ\text{C}$) is a more stable thermodynamic modification. Variable-temperature NMR and calculational studies were conducted to explore this supposition.

Previous theoretical work focused on the degree of charge localization induced by the cation in the ligand.^{3,6} The prevailing theory suggests that the larger, more diffuse cations flatten the potential energy surface and allow for larger flexibility in π -type coordination, as observed in **2**.⁶

Single-point energies were calculated for **1** and **2** from crystallographic coordinates to obtain their relative energies. The η^6 modification energy was determined with and without the coordinated THF (**2a**, **2b**) to calculate both the THF binding energy to the cation and an absolute energy difference between the anion positions in the η^3 and η^6 modifications. The energies reported here for modifications **2a** and **2b** represent the energy of the complete η^6 complex **2a** and the sum of the component energies of the THF and remaining η^6 complex ([crown ether-rubidium-diphenylmethanide] + THF), respectively. Energy differences between **2a** and **2b** are taken as representative of the binding interaction (energy) between the THF and remaining η^6 complex.

Restricted Hartree–Fock (RHF) and DFT/B3LYP (DFT) energy calculations were performed using the GAMESS-US quantum chemistry package¹⁷ with the Hay–Wadt VDZ ECP for Rb and the 6-31g** basis set for O, C, and H. The DFT program DMol³ was also used in its nonperiodic mode with the BLYP energy functional and the complete set of available numerical basis functions for each atom for the calculation of single-point energies.¹⁸ The standard complement of these numerical basis functions in DMol³ compares favorably with the 6-31g** basis set.¹⁹ These basis functions are described in detail elsewhere.¹⁹

The DMol³ and GAMESS DFT energy calculations find that the η^6 modification **2a** is more stable than η^3 by 16.35 (**2a**) and 31.05 (**2b**) kJ/mol, respectively. The RHF/6-31g** energies reverse the DFT results, with the η^3 modification lying 16.98 kJ/mol below η^6 . While the DMol³ and GAMESS DFT calculations agree on the greater stability of the η^6 modification, the two disagree as to whether the THF–Rb interaction is favored or disfavored. The GAMESS DFT calculations of **2a** and (**2b** + THF) find that the THF– η^6 binding interaction is net-stabilizing by 9.85 kJ/mol, while the DMol³ calculations find that the interaction is net-destabilizing by 12.48 kJ/mol. This local destabilization in the DMol³ calculations is less than the energy difference between η^3 and η^6 , and the η^6 form is still taken to be of lower energy. The same RHF component analysis finds that the THF coordination to the remaining η^6 modification is destabilizing by 2.66 kJ/mol.

The GAMESS DFT energy calculations are favored over the RHF results on the basis of extensive precedent, and the determination of the η^6 as the lower-energy form in both DFT methods is taken as consistent with this modification being, to within the ability of the single-point energy calculations to accurately reproduce the interactions between anion and cation in these systems, the thermodynamic product.

To glean further information on the binding modes of these two modifications, we undertook variable-temperature NMR studies. It was believed that if both compounds maintained structural integrity in solution it would be possible to observe a transition from one structure to the other.

The spectra of both compounds at ambient temperature suggested that each structure dissociates into charge-separated ions in solution, with values for both the ¹³C and ¹H spectra agreeing well with reported data for diphenylmethyl anions with no cationic interaction.^{20–22} While peak splitting was observed at descending temperature, this compared favorably with an expected slowing of phenyl rotation, as seen before.²³ The dissociation into separated ions is quite common for crown-encapsulated alkali metals, because of the high stability of the stabilized cation.^{12,24}

In summary, the isolation of two different solid-state modifications of rubidium diphenylmethanides may be understood on the basis of their small, but significant, energetic difference, pointing toward difficulties in predicting solid-state modifications in compounds of this type. The advent of a powerful method of preparation and extensive solid-state computational methods should further aid in the exploration of these interesting compounds.

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Supporting Information Available: Crystal structure data and experimental preparations for **1** and **2** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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