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Lithiations of Bis-diphenyl-*N*-trimethylsilylphosphiniminomethane: An X-ray Structure of a 1,1-Dilithiomethane Derivative

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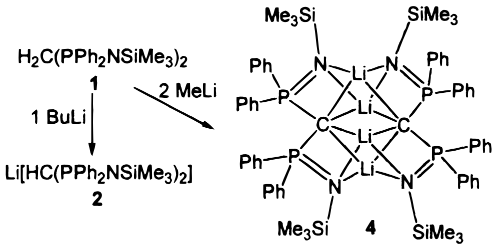
Lithium reagents are extremely important in organic and organometallic synthetic chemistry. The nature and structure of such reagents has been the subject of extensive investigation for more than two decades.[1,2] Despite this lengthy period of study such reagents continue to be of interest from several perspectives including synthetic methodology, structure, and theoretical implications.[3−11] Although recent reports have addressed the nature of a variety of poly-lithiated species[3−7] the nature of the simplest multiple-lithiated compound dilithiomethane, first prepared in 1955,[12] remains a fundamental question. Initial computational studies[13] predicted a small energy difference between planar and tetrahedral structures of dilithiomethane, whereas subsequent ab initio computations[14] considered dimeric and trimeric structures. Experimental data regarding the structure of $(CH_2Li_2)_n$ are limited. Flash vaporization mass spectroscopy[15] have shown monomeric and dimeric units to be present in the gas phase, while solid-state NMR studies[16] have inferred a single C environment in the solid aggregate and thus a high-symmetry structure. The computational predictions of a planar tetracoordinate $RR'CLi_2$ carbon geometry about carbon were realized experimentally for cyclopropenyllithium dimers[5] via the incorporation of pendant chelating ligands. We adopted a similar approach, in addressing the question of the structure of dilithiomethane. Herein, we report the mono- and dilithium derivatives of bis-diphenyl-*N*-trimethylsilylphosphiniminomethane. Structural data are reported for the latter 1,1-dilithiomethane derivative.

In the course of our studies of the chemistry of phosphinimines, our attention was drawn to the compound $CH_2(PPh_2NSiMe_3)_2$, **1**, as a potential precursor to stable lithiated derivatives. The protons on the central carbons of **1** are expected to be acidic by analogy to the P(III) species $CH_2(PPh_2)_2$.[17−19] Perhaps more importantly however, the presence of the phosphinimine nitrogen atoms offers donor atoms capable of coordinating to Li, thus stabilizing lithiated species. Compound **1**[20] is readily prepared via the literature method of oxidation of the diphosphine with Me_3SiN_3.[21] Treatment of **1** with 1 equiv of *n*-butyllithium in THF over a 12-h period followed by workup afforded the yellow-green compound $Li[CH(PPh_2NSiMe_3)_2]$, **2**,[20] in 78% yield (Scheme 1). The formulation of **2** as the monolithium salt of **1** was consistent with the observation of a triplet at 3.62 ppm in the ^1H NMR spectrum, integrating to one proton. The downfield shift of the ^{31}P chemical shift of **2** to 17.5 ppm suggested the coordination of the phosphinimine nitrogen to lithium. Despite repeated efforts to structurally characterize **2**, X-ray quality crystals were not obtained. The formulation of **2** was further supported by the formation of the derivative $[CH(PPh_2NSiMe_3)_2]GaCl_2$ **3**[20] from the stoichiometric reaction of **2** with $GaCl_3$.[22]

Scheme 1



Dilithiation of the central carbon of **1** was also possible. Reaction of **1** with excess methyllithium in benzene and subsequent workup resulted in the isolation of colorless crystals of the new species **4**[20] in 68% yield (Scheme 1). This product gives rise to a single resonance in the ^{31}P NMR spectrum at 14.4 ppm. Resonances attributable to aryl and $SiMe_3$ groups were observed in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra.[23] The formulation of **4** was subsequently unambiguously determined via X-ray crystallography to be $[Li_2C(PPh_2NSiMe_3)_2]_2$ (Figure 1).[24]

The molecular structure of **4** reveals the dimeric nature, in which two $[Li_2C(PPh_2NSiMe_3)_2]$ units are oriented "head to head" such that the four lithium and two carbon atoms form a distorted octahedral arrangement (Figure 1). Each of the four nitrogen atoms bridge two lithium atoms. The dissymmetry of these bridges is

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[1] Streitwieser, A.; Bachrach, S. M.; Dorigo, A.; Schleyer, P. v. R.; Sapse, A. M.; Schleyer, P. V. R., Ed.; Wiley: New York, 1995; p 1.

[2] Sorger, K.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Mol. Struct. THEOCHEM* **1995**, *338*, 317.

[3] Jemmis, E. D.; Subramanian, G.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 9504.

[4] Davies, R. P.; Raithby, P. R.; Snaith, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1215.

[5] Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 6924.

[6] Sygula, A.; Fronczek, F. R.; Rabideau, P. W. *J. Organomet. Chem.* **1996**, *526*, 389.

[7] Harder, S.; Lutz, M.; Streitwieser, A. *J. Am. Chem. Soc.* **1995**, *117*, 2361.

[8] Ashe, A. J., III; Kampf, J. W.; Savla, P. M. *Organometallics* **1993**, *12*, 3350.

[9] Ludvig, M.; Lagow, R. J. *J. Org. Chem.* **1990**, *55*, 4880.

[10] Kawa, H.; Manley, B. C.; Lagow, R. J. *Polyhedron* **1988**, *7*, 2023.

[11] Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A. *J. Organomet. Chem.* **1988**, *339*, 7.

[12] Ziegler, K.; Nagel, K.; Patheiger, M. *Z. Anorg. Allg. Chem.* **1955**, *282*, 345.

[13] Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apoloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.

[14] Jemmis, E. D.; Schleyer, P. v. R.; Pople, J. A. *J. Organomet. Chem.* **1978**, *154*, 327.

[15] Kawa, H.; Manley, B. C.; Lagow, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5313.

[16] Gurak, J. a.; Chinn, J. W.; Lagow, R. J.; Steinfink, H.; Yannoni, C. S. *Inorg. Chem.* **1984**, *23*, 3717.

[17] Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Muller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

[18] Karsch, H. H.; Grauvogl, G.; Duebelly, B.; Muller, G. *Organometallics* **1992**, *11*, 4238.

[19] Karsch, H. H.; Duebelly, B.; Grauvogl, G.; Lachmann, J.; Muller, G. *Organometallics* **1992**, *11*, 4245.

[20] **1**: ^1H NMR (C_6D_6, 25 °C) δ 7.77 (8H, m), 7.15 (12H, m), 3.39 (2H, t, $|J_{P-H}| = 13.9$ Hz), 0.35 (18H, s); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 137.84 (d, $|J_{P-C}| = 101$ Hz), 131.90 (t, $|J_{P-C}| = 4$ Hz), 130.81, 128.39, 37.91 (t, $|J_{P-C}| = 68$ Hz), 4.51; ^{31}P NMR (C_6D_6, 25 °C) δ −4.67. **2**: ^1H NMR (C_6D_6, 25 °C) δ 7.68 (8H, m), 7.05 (12H, m), 3.62 (1H, br t), 0.14 (18H, s); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 142.27 (d, $|J_{P-C}| = 95.8$ Hz), 131.56 (t, $|J_{P-C}| =3.8$ Hz), 129.41, 127.80, 23.76 (t, $|J_{P-C}| =129$ Hz), 4.53; ^{31}P NMR (C_6D_6, 25 °C) δ 17.54. **3**: ^1H NMR (C_6D_6, 25 °C) δ 7.76 (8H, m), 6.95 (12H, m), 4.03 (1H, t, $|J_{P-H}| = 12.82$), 0.35 (18H, s); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 134.67 (d, $|J_{P-C}| = 86$ Hz), 132.64 (t, $|J_{P-C}| =4.4$ Hz), 131.31, 128.42, 29.47 (t, $|J_{P-C}| =117.4$ Hz), 4.33; ^{31}P NMR (C_6D_6, 25 °C) δ 32.33. **4**: ^1H NMR (C_6D_6, 25 °C) δ 7.51 (16H, m), 7.00 (24H, m), 0.05 (36H, s); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 139.21 (d, $|J_{P-C}| = 77$ Hz), 131.18 (t, $|J_{P-C}| =6$ Hz), 129.14, 128.72, 4.58; ^{31}P NMR (C_6D_6, 25 °C) δ 14.43.

[21] Appel, V. R.; Ruppert, I. *Z. Anorg. Allg. Chem.* **1974**, *406*, 131.

[22] X-ray data confirm the formulation of **3**, Ong, C. M.; Stephan, D. W. unpublished results.

[23] A resonance attributable to the central carbon of **4** was not observed despite modifications to the acquisition parameters. This is attributed to the excessive relaxation time and the absence of NOE enhancement for this carbon, resulting from dilithiation.

[24] **4**: space group: *P*-1, $a = 12.5550(2)$ Å, $b = 17.2620(3)$ Å, $c = 19.3446(2)$ Å, $\alpha = 98.4190(10)°$, $\beta = 103.0770(10)°$, $\gamma = 105.3830(10)°$, $V = 3841.13(10)$ Å^3, $Z = 2$, $R = 0.0546$, $R_w = 0.1341$, GOF = 0.950.

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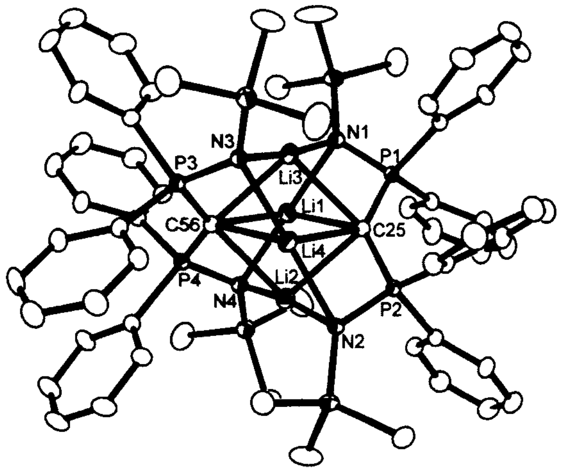

Figure 1. ORTEP drawing of **4**; 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. P−N$_{avg}$ 1.630(3) Å, P(1)−C(25) 1.687(3) Å, P(2)−C(25) 1.694(3) Å, P(3)−C(56) 1.696(3) Å, P(4)−C(56) 1.700(3) Å, N(1)−Li(1) 2.073(7) Å, N(1)−Li(3) 2.143(6) Å, N(2)−Li(4) 2.100(6) Å, N(2)−Li(2) 2.145(6) Å, N(3)−Li(4) 2.086(6) Å, N(3)−Li(3) 2.143(6) Å, N(4)−Li(1) 2.068(7) Å, N(4)−Li(2) 2.132(6) Å, C(25)−Li(2) 2.348(7) Å, C(25)−Li(3) 2.357(6) Å, C(25)−Li(4) 2.417(7) Å, C(25)−Li(1) 2.451(7) Å, C(56)−Li(3) 2.348(7) Å, C(56)−Li(2) 2.356(6) Å, C(56)−Li(4) 2.438(7) Å, C(56)−Li(1) 2.441(7) Å; P−N−Li$_{range}$ 88.7(2)−92.5(2)°, Li−N−Li$_{avg}$ 69.5(3)°, N−Li−N$_{avg}$ 174.3(5)°, P(1)−C(25)−P(2) 132.3(2)°, P(3)−C(56)−P(4) 132.7(2)°, Li(2)−C(25)−Li(3) 88.6(2)°, Li(2)−C(25)−Li(4) 60.6(2)°, Li(3)−C(25)−Li(4) 60.7(2)°, Li(2)−C(25)−Li(1) 60.1(2)°, Li(3)−C(25)−Li(1) 60.2(2), Li(4)−C(25)−Li(1) 92.7(2), Li(3)−C(56)−Li(2) 88.6(2), Li(3)−C(56)−Li(4) 60.6(2)°, Li(2)−C(56)−Li(4) 60.2(2)°, Li(3)−C(56)−Li(1) 60.5(2)°, Li(2)−C(56)−Li(1) 60.1(2)°, Li(4)−C(56)−Li(1) 92.5(2)°.

reflected in the short and long Li−N distances averaging 2.082(8) and 2.141(8) Å. The proximity of trimethylsilyl substituents on the nitrogen atoms associated with Li(2) and Li(3) accounts for the longer Li−N distances. These distances compare to the Li−N distance in $Li[CH_2PPh_2(NPh)]$ of 2.00(1) Å.[25] The C_2N_2 coordination sphere about each lithium atom is quite distorted from a tetrahedral geometry, with average N−Li−N angle of 174.3(5)° and average C−Li−N angles of 70.9(5) and 113.4(5)°. The phenyl substituents on neighboring phosphorus atoms are oriented in pairwise parallel fashion. The interplanar distances of approximately 3.3−3.5 Å are consistent with a series of π-stacking interactions on the periphery of the molecule.

The most interesting feature of the structure of **4** is the geometry about the carbon centers (Figure 2). The P−C distances average 1.694(5) Å; slightly shorter than those seen in **3**. As well, the P−C−P angles which average 132.5(3)° in **4** is increased over the P−C−P angle of 123.2(2)° seen in **3**. The two P−C−P planes are essentially perpendicular to each other as the angle between the P−C−P planes is 89.5(2)°. The Li−C distances for Li(2) and Li(3) (2.352(8) Å) are slightly shorter than those for Li(1) and Li(4) (2.437(8) Å). Distances across the C_2Li_4 pseudo-octahedron are slightly dissymmetric with the Li(1)−Li(4) distance of 3.524(9) Å being slightly greater than the Li(2)−Li(3) 3.286(9) Å. This distortion is thought to be a result of the steric demands of trimethylsilyl groups.

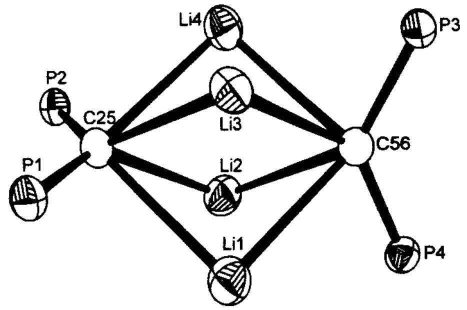

Figure 2. $Li_4[CP_2]_2$ core of **4**.

Theoretical computations by Schleyer et al.[14] considered a variety of possible structures for CH_2Li_2. Ab initio computations predicted that the most stable dimer would involve a head-to-head dimeric formulation of $(CH_2Li_2)_2$ in which four lithium atoms bridge two perpendicular CH_2 units. Although described as the approach of planar monomers, the distinction between planar and tetrahedral units essentially vanishes as the differences in the predicted Li−C distances (2.166, 2.041 Å) is small. While the structural data for **4** are remarkably similar in gross features to that of the predicted model, the Li−C distances in **4** are significantly longer than those in the calculated structure. Moreover, distortions of the C_2Li_4 core geometry in **4** are not consistent with the approach of two planar dilithiomethane units. However, Schleyer et al. also noted that although a symmetric dimer was not a local minimum, the geometry in which all four Li atoms are coplanar and the C−Li were equivalent was only 1.9 kcal/mol above the minimum described above. In this regard, it is noteworthy that the four lithium atoms in **4** are coplanar with the largest deviation from the mean plane being 0.002 Å. It is clear that the minor discrepancies between the theoretical prediction and the experimental data are attributable to the presence of donor ligands on Li in **4** and their absence from the computational models.

In summary, we have prepared and characterized mono- and dilithio derivatives of 1,1-bis-diphenylphosphino-*N*-trimethylsilylmethane. Despite continuing interest in dilithio compounds over the past 30 years, this report represents the first to provide structural data for a 1,1-dilithiomethane derivative. Reactivity and utility of these and related anions in main group and transition metal chemistry are the subjects of continuing efforts.

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Supporting Information Available: Spectroscopic and crystallographic information tables (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Lopez-Ortiz, F.; Pelaez-Arrango, E.; Tejerina, B.; Perez-Carreno, E.; Garcia-Granda, S. *J. Am. Chem. Soc.* **1995**, *117*, 9972.