

Structural Characterization and Dynamic Solution Behavior of the Disodio and Lithio–Sodio Geminal Organodimetallics $[\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CNa}_2\}_2]$ and $[\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CLiNa}\}_2]$

Katherine L. Hull, Bruce C. Noll, and Kenneth W. Henderson*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670

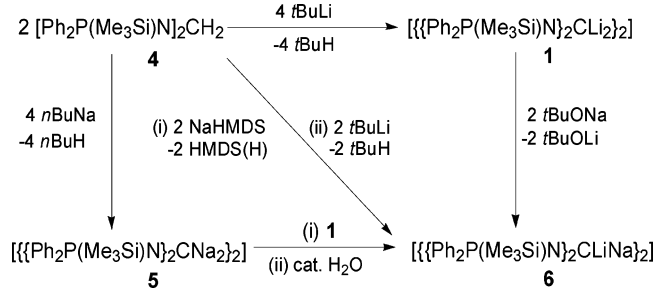
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Summary: The title disodio complex may be prepared by the double deprotonation of a neutral bis(phosphinimine) ligand using 2 equiv of the strong base *n*-BuNa, whereas the mixed Li/Na derivative can be prepared by controlled sequential deprotonation, by transmetalation, or by mixing the homometallic analogues. The compounds form dimers with the ligands capping an Na_4 square or a Li_2Na_2 rhomboid, and these are the first examples of R_2C^{2-} dianions containing a heavy alkali metal to be structurally characterized.

Geminal organodimetallics, R_2CM_2 , are well-established as an important class of in situ prepared intermediates in organic synthesis.¹ Attempts at characterizing these complexes to gain an understanding of their bonding and reactivity has met with limited success, due to a combination of their metastability and poor solubility in many instances. A good deal of attention has been focused on the dilithio derivatives;² however, only three crystal structures of unadulterated dilithiated geminal carbanions have been reported, namely $[\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CLi}_2\}_2]$ ³ (**1**), $[\{\{\text{Me}_3\text{Si}(\text{NC})\text{CLi}_2\}_2 \cdot 6\text{Et}_2\text{O}\}]$ ⁴ (**2**), and the polymer 9,9-dilithiofluorene⁵ (**3**). A handful of mixed-anion complexes containing both a dilithio geminal dianion and either a monometalated ligand fragment or an Li_2O unit are also known.⁶ The characterization of heavier alkali-metal derivatives remains even more inadequate, with their existence generally only inferred by indirect quenching studies or through the use of theoretical calculations.^{7–9} Nevertheless, the generation of such complexes is useful to access dianions of weakly acidic substrates.¹⁰

Over the past few years our group has investigated the preparation of geminal di-alkali-metal complexes of α, α' -stabilized carbanions substituted by electron-withdrawing groups, including cyanides, sulfonyls, phosphonates, and phosphine oxides.¹¹ Although several dimetalated complexes have been prepared, their structural characterization has remained frustratingly

Scheme 1. Synthetic Routes to Geminal Organodimetallics **1**, **5**, and **6**



elusive. We turned our attention to the phosphinimine ligand bis(*N*-diphenyl(trimethylsilyl)phosphinimino)methane (**4**), which was used independently by Cavell and Stephan to prepare the dilithio complex **1**. From our previous experience, the sterics and electronics of this ligand appeared ideally suited to supporting dimetallic complexes of the heavier alkali metals. We now report the culmination of this work through the synthesis of $[\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CNa}_2\}_2]$ (**5**) and $[\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CLiNa}\}_2]$ (**6**), the first examples of disodio and mixed-alkali-metal geminal organodimetallic compounds to be structurally characterized. Scheme 1 summarizes the successful synthetic strategies applied.

Various attempts to prepare **5** through the deprotonation of **4** using ≥ 2 equiv of sodium hexamethyldisilazide (NaHMDS) or NaH resulted only in monosodiation.¹² A transmetalation strategy was then investigated by reacting preformed **1** with excess *t*-BuONa in toluene-*d*₈. ¹H NMR spectroscopic monitoring (see below) indicated the immediate formation of a major new species, and subsequently, high-quality crystals were obtained from a reaction conducted in benzene. Single-crystal X-ray analysis revealed the formation of the unexpected heterodimetallic complex $\text{6} \cdot 2\text{C}_6\text{H}_6$ (Figure 1).¹³

* To whom correspondence should be addressed. E-mail: khenders@nd.edu. Fax: +1 574 631 6652. Tel: +1 574 631 8025.

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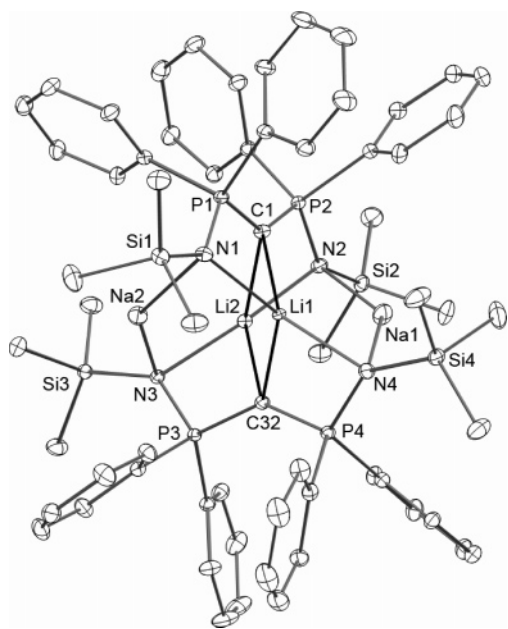


Figure 1. ORTEP view (50% probability) of the geminal lithio-sodio complex **6**·2C₆H₆ with lattice benzenes and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Li(1) = 2.229(2), C(1)–Li(2) = 2.278(2), C(32)–Li(1) = 2.259(2), C(32)–Li(2) = 2.295(2), C(1)–Na(1) = 3.1152(12), C(1)–Na(2) = 3.1530(11), C(32)–Na(1) = 3.0214(11), C(32)–Na(2) = 3.1575(12), N(1)–Li(1) = 2.116(2), N(4)–Li(1) = 2.135(2), N(2)–Li(2) = 2.134(2), N(3)–Li(2) = 2.123(2), N(1)–Na(2) = 2.4403(10), N(3)–Na(2) = 2.4207(10), N(2)–Na(1) = 2.3925(12), N(4)–Na(1) = 2.4078(11), P(1)–N(1) = 1.6168(9), P(2)–N(2) = 1.6127(9), P(3)–N(3) = 1.6159(10), P(4)–N(4) = 1.6109(9), P(1)–C(1) = 1.6752(10), P(2)–C(1) = 1.6772(10), P(3)–C(32) = 1.6773(11), P(4)–C(32) = 1.6778(12); P(1)–C(1)–P(2) = 134.79(6), P(3)–C(32)–P(4) = 134.33(6), C(1)–P(1)–N(1) = 106.95(5), C(1)–P(2)–N(2) = 106.54(5), C(32)–P(3)–N(3) = 107.25(5), C(32)–P(4)–N(4) = 106.45(5).

Complex **6** may also be prepared by the sequential addition of NaHMDS followed by *t*-BuLi. However, reversing this order yields only the monolithiated product. This observation led us to investigate the use of the substantially stronger base *n*-BuNa to mediate the disodiation reaction.¹⁴ ¹H NMR spectroscopic monitoring of the reaction between 2 equiv of *n*BuNa and **4** in benzene-*d*₆ indicated complete deprotonation of the methylene

(13) **Synthesis of 6:** the phosphinimine **4** (0.559 g, 1.00 mmol) was dissolved in 10 mL of dry benzene, and *t*-BuLi (1.70 M, 1.24 mL, 2.10 mmol) was then added slowly to the solution at ambient temperature. The resulting yellow mixture was stirred for 1.5 h (the formation of dilithio **1** was confirmed by in situ NMR studies). *t*-BuONa (0.211 g, 2.20 mmol) was then added slowly to the mixture via a solids addition tube. The volume of the solution was reduced in vacuo until precipitation ensued. The mixture was then heated to afford a clear yellow solution. Cooling to ambient temperature resulted in the formation of pale yellow crystals (isolated yield: 0.303 g, 52%). The resulting compound was highly air-sensitive and required manipulation inside an argon-filled glovebox. The crystals decomposed without melting above 200 °C. The complex crystallizes with two benzene molecules per dimer, as determined by X-ray crystallography, but is partially removed on evacuation. ¹H NMR (500 MHz, toluene-*d*₈, 25 °C): δ 7.51 (m, 16H, *o*-H, Ph), 6.96 (m, 24H, *m*-, *p*-H, Ph), 0.09 (s, 36H, CH₃Si). ¹³C{¹H} NMR: not assigned due to multiple broad overlapping signals. ³¹P{¹H} NMR (121 MHz, toluene-*d*₈, 25 °C): δ 14.60. ²⁹Si NMR (99 MHz, toluene-*d*₈, 25 °C): δ -12.86 (t, ²J_{P-Si} = 7.73 Hz). ⁷Li NMR (194 MHz, toluene-*d*₈, 25 °C): δ 0.58. Crystallographic data for **6**: C₇₄H₈₈Li₂Na₄Na₂P₄Si₄; triclinic, *P*1, *a* = 14.5700(6) Å, *b* = 14.5952(6) Å, *c* = 18.6933(8) Å, α = 91.530(3)°, β = 105.048(2)°, γ = 104.295(2)°, *V* = 3702.4(3) Å³, *Z* = 2. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 4.04 and 8.78% (wR2 = 9.29 and 11.95%) for 24 855 reflections with *F*_o² > 2σ(*F*_o²) and all data, respectively.

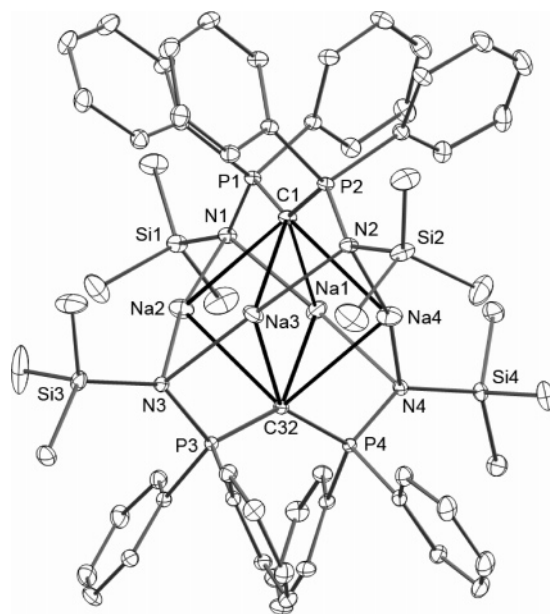


Figure 2. ORTEP view (50% probability) of the geminal disodio complex **5**·2C₆H₆ with lattice benzenes and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Na(1) = 2.7559(10), C(1)–Na(2) = 2.8578(10), C(1)–Na(3) = 2.7230(10), C(1)–Na(4) = 2.8210(10), C(32)–Na(1) = 2.7420(10), C(32)–Na(2) = 2.8503(11), C(32)–Na(3) = 2.7346(10), C(32)–Na(4) = 2.8422(11), N(1)–Na(1) = 2.3234(9), N(1)–Na(2) = 2.3941(9), N(2)–Na(3) = 2.3889(9), N(2)–Na(4) = 2.3775(9), N(3)–Na(2) = 2.3849(9), N(3)–Na(3) = 2.3653(9), N(4)–Na(1) = 2.3255(10), N(4)–Na(4) = 2.3793(10), P(1)–N(1) = 1.6167(8), P(2)–N(2) = 1.6137(8), P(3)–N(3) = 1.6177(8), P(4)–N(4) = 1.6100(8), P(1)–C(1) = 1.6881(9), P(2)–C(1) = 1.6901(9), P(3)–C(32) = 1.6891(9), P(4)–C(32) = 1.6937(9); P(1)–C(1)–P(2) = 128.36(5), P(3)–C(32)–P(4) = 129.76(6), C(1)–P(1)–N(1) = 108.69(4), C(1)–P(2)–N(2) = 108.42(4), C(32)–P(3)–N(3) = 108.39(4), C(32)–P(4)–N(4) = 108.10(4).

unit within a few minutes. Crystallization followed by X-ray analysis confirmed the successful formation of the geminal disodio complex **5**·2C₆H₆ (Figure 2).¹⁵

Although the crystal structures of **1**, **5**, and **6** form related dimeric structures, there are significant differences within their

(14) *n*-BuNa was prepared by the transmetalation reaction between *n*-BuLi and *t*-BuONa in hexane solution under a nitrogen atmosphere according to the literature procedure: Lochmann, L.; Pospíšil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 7, 257.

(15) **Synthesis of 5:** the phosphinimine **4** (0.559 g, 1.00 mmol) was placed inside a nitrogen-filled Schlenk tube and dissolved on the addition of 10 mL of dry benzene. The solid base *n*-BuNa¹³ (0.168 g, 2.10 mmol) was added slowly to the solution via a solids addition tube at ambient temperature. The mixture was stirred for 30 min until complete dissolution occurred. The volume of the solution was reduced in vacuo until precipitation ensued. The mixture was then heated to afford a clear yellow solution. Cooling to ambient temperature resulted in the formation of yellow crystals (isolated yield: 0.414 g, 69%). The resulting compound was highly air-sensitive and required manipulation inside an argon-filled glovebox. The crystals decomposed without melting above 200 °C. The complex crystallizes with two benzene molecules per dimer, as determined by X-ray crystallography, but is partially removed on evacuation. ¹H NMR (500 MHz, toluene-*d*₈, 25 °C): δ 7.44 (m, 16H, *o*-H), 6.90 (m, 24H, *m*-, *p*-H), -0.04 (s, 36H, CH₃Si). ¹³C{¹H} NMR (200 MHz, toluene-*d*₈, 25 °C): δ 142.42 (m, *i*-C), 130.05 (t, *o*-C), 128.49 (s, *p*-C), 127.70 (s, *m*-C), 40.99 (t, ¹J_{PC} = 89.9 Hz, CNa₂P₂), 4.32 (s, CH₃Si). ³¹P{¹H} NMR (121 MHz, toluene-*d*₈, 25 °C): δ 7.56. ²⁹Si NMR (99 MHz, toluene-*d*₈, 25 °C): δ -15.35 (t, ²J_{P-Si} = 8.5 Hz). Crystallographic data for **5**: C₇₄H₈₈Na₄Na₄P₄Si₄; triclinic, *P*1, *a* = 12.3275(2) Å, *b* = 17.0832(3) Å, *c* = 19.6578(4) Å, α = 101.4513(10)°, β = 103.1949(10)°, γ = 103.7451(10)°, *V* = 3772.64(12) Å³, *Z* = 2, *T* = 100 K. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 3.24 and 4.08% (wR2 = 8.48 and 9.21%) for 21 266 reflections with *F*_o² > 2σ(*F*_o²) and all data, respectively.

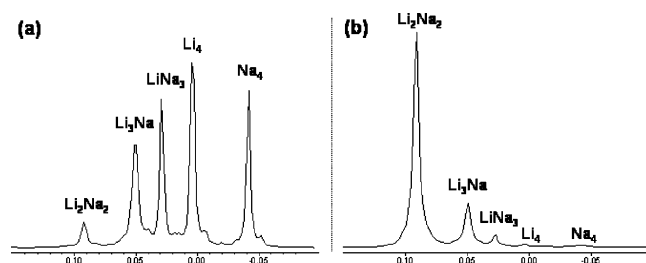


Figure 3. ^1H NMR spectra obtained on mixing **1** and **5** in toluene- d_8 at 25 °C: (a) after several minutes; (b) upon equilibration.

cage cores. All three compounds possess four coplanar metal centers, but whereas the Li_4 and Na_4 atoms in **1** and **5** define approximately square rings, the Li_2Na_2 atoms in **6** are arranged in a distinctly rhombohedral manner (mean $\text{Li}\cdots\text{Na}\cdots\text{Li}$ and $\text{Na}\cdots\text{Li}\cdots\text{Na}$ angles are 58.2 and 121.7°). This distortion in **6** is further exemplified by the long sodium to carbanion distances, ranging from 3.0214(11) to 3.1575(12) Å, and these interactions can be considered as very weak at best. In comparison, the mean $\text{Li}-\text{C}$ distances in **6** are shorter by 0.13 Å (mean) than those in **1**, ranging from 2.226(3) to 2.292(3) Å.^{3,16} The strong core $\text{Li}-\text{C}$ bonding may explain why the transmetalation reaction ceased after formation of **6**. Overall, complex **6** can be described as a contact ion pair composed of a central [$\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{-CLi}\}_2\text{]}^{2-}$ dianionic core with a pair of outer two-coordinate Na^+ ions connected to a nitrogen center from each of the ligands. In contrast, all four sodium centers in **5** form reasonably strong interactions to the carbanions, with the $\text{Na}-\text{C}$ distances ranging from 2.7230(10) to 2.8578(10) Å.¹⁷ The $\mu_4\text{-CNa}_4$ motif in **5** is a unique arrangement for a molecular structure, and its identification unambiguously establishes the ability of R_2C^{2-} units to bind directly to heavy-alkali-metal counteranions.

Solution studies of the dimetallics provided valuable insights into their dynamic behavior. The ^1H , ^{13}C , ^7Li , and ^{29}Si NMR spectra of **5** in toluene- d_8 display a single set of resonances in each instance. Moreover, variable-temperature ^1H NMR experiments between 25 and -80 °C showed <0.1 ppm variations in the chemical shift positions, indicating no discernible aggregation phenomena. Cryoscopic studies on **5** confirmed that the dimer found in the solid state is retained in benzene solution (0.05 M), with a measured molecular weight of 1268.7 (± 16.3) g/mol (theoretical 1205.5 g/mol).

Complex **6** again displayed a set of major NMR resonances, but these were accompanied by multiple smaller signals ($\sim 20\%$ in total by integration). The identities of the solution species were elucidated on monitoring the mixing of the homometallic compounds **1** and **5** by ^1H NMR spectroscopy. Five distinct Me_3Si signals were found immediately upon mixing **1** and **5** (Figure 3a). Three of these signals were readily assigned to **1**, **5**, and **6** by comparison with the authentic samples. Interestingly, the relative ratios of the signals changed with time, such that as **1** and **5** were depleted, the unassigned signals at 0.05 and 0.03 ppm grew. In turn, these signals then decreased to produce predominantly **6** (Figure 3b). The final spectrum is identical with that obtained on dissolution of crystals of **6**. The new

signals were identified by NMR as the 3:1 heterodimetallic complexes [$\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CLi}_3\text{Na}\}_2$] (**7**) and [$\{\{\text{Ph}_2\text{P}(\text{Me}_3\text{Si})\text{N}\}_2\text{CLiNa}_3\}_2$] (**8**) by preparing 3:1 and 1:3 stoichiometric mixtures of **1** and **5**. X-ray analyses of crystals deposited from these solutions also supported the formation of the 3:1 complexes; however, cocrystallization prevented their independent characterization.

The intermediate appearance of the 3:1 complexes **7** and **8** excludes the formation of **6** occurring via the most expected mechanism: dissociation of dimeric **1** and **5** to monomers followed by heterometallic recombination.¹⁶ During an attempted kinetic investigation of this rearrangement process, we discovered that the rate of formation of **6** was dramatically accelerated in the presence of water. Under strictly anhydrous conditions the equilibration of **1** and **5** to **6** took several days, whereas addition of substoichiometric amounts of water to this mixture resulted in equilibration within a few hours.

Therefore, exchange of the metals appears to occur by partial protonation of the otherwise stable dimetallics **1** and **5** to yield labile intermediates that then form the 3:1 complexes **7** and **8**. In turn, these complexes rearrange to form the thermodynamically favored complex **6**. Indeed, geometry optimization calculations at the B3LYP/6-31G* level of theory were completed on the full molecules **1**, **5**, and **6** and indicate that the mixed-metal aggregate is energetically preferred over its homometallic counterparts by 7.61 kcal/mol. The observation of the additive-catalyzed formation of heterodimetallic **6** may also have important repercussions in considering aggregate assembly mechanisms and rate studies in other s-block systems.

Finally, an added attraction of studying disodio geminal diorganometallics is the ability to observe the ^{13}C NMR signal of the carbanion. No signal could be located for this key center in **1** or **6**, due to broadening associated with attachment to lithium.³ In **5** the chemical shift position of δ 40.99 (triplet, $^1J_{\text{PC}} = 89.9$ Hz) is similar to that of δ 37.84 in the free ligand **4** and is downfield compared with the value of δ 27.41 found for the monosodiated carbanion, which does not contain an $\text{Na}-\text{C}$ bond.^{12a} This supports the assertion that the $\text{Na}-\text{C}$ interactions in **5** are retained in solution, as found in the solid state.

In summary, this study provides structural authentication for the formation of heavy group 1 and mixed-alkali-metal geminal bimetallic compounds. We envision that bis(phosphinimines) will prove to be excellent ligands for further investigations into the preparation of novel geminal dimetallics incorporating the highly reactive s-block metals.¹⁸

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Supporting Information Available: Crystallographic data for **5** and **6** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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