Communications

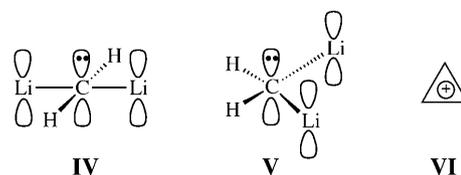# A Monomeric Dilithio Methandiide with a Distorted *trans*-Planar Four-Coordinate Carbon**

*Oliver J. Cooper, Ashley J. Wooles, Jonathan McMaster, William Lewis, Alexander J. Blake, and Stephen T. Liddle**

The proposal of tetrahedral geometry for four-coordinate carbon (**I**) by van't Hoff in 1874 was a seminal advance in the understanding of the structural properties of molecules, and this theory subsequently became a cornerstone of organic chemistry.[1]

I   **II**   **III**
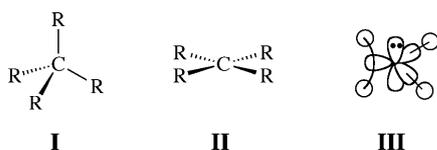
This paradigm of tetrahedral four-coordinate carbon appeared absolute for many years. Nevertheless, chemists have long been fascinated with the concept that compounds exhibiting a planar four-coordinate carbon geometry might be found (**II**).[2] Nearly a hundred years after van't Hoff's proposal, planar four-coordinate carbon became more seriously considered after Hoffmann described a theoretical model for this geometry in which an sp^2-hybridized carbon forms two two-electron-two-center (2e,2c) bonds and a two-electron-three-center (2e,3c) bond to the four substituents (**III**).[3] For the simplest example, methane, the tetrahedral geometry is more stable relative to the planar form by about 530 kJ mol^{-1}.[3,4] Therefore, to experimentally realize planar four-coordinate carbon, various strategies to impose a planar four-coordinate geometry have been pursued, and of these, organometallic derivatives have delivered the most significant advances.[5]

For genuine methanes, von Schleyer showed theoretically[6] and experimentally[7] that the sequential replacement of hydrogen atoms with alkali metals results in an increase in the stabilization of planar four-coordinate methanes. Furthermore, for disubstituted methane derivatives, such as H_2CLi_2, the *trans*-planar form (**IV**) was found to be destabilized by about 125 kJ mol^{-1} relative to the *cis*-planar form (**V**).[6] Although the linear 2e,3c π orbital in the *trans*

[*] O. J. Cooper, A. J. Wooles, Dr. J. McMaster, Dr. W. Lewis, Prof. A. J. Blake, Dr. S. T. Liddle
School of Chemistry, University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
Fax: (+44) 115-951-3563
E-mail: stephen.liddle@nottingham.ac.uk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002483.

IV   **V**   **VI**

geometry is reminiscent of the allyl cation, the *cis* form is more stable because the 2e,3c π orbital can be considered homoaromatic and *iso*-conjugate to the cyclopropenium cation (**VI**).

The greater stabilization of a *cis*- relative to *trans*-planar four-coordinate carbon suggests that *cis*-planar methanes should be more prevalent than their *trans* isomers. Gas-phase theoretical models of H_2CMM' (M = Li; M' = Li–Cs) show dimers of typically D_{2d} symmetry that can be considered to be derived from *cis*-planar H_2CMM' units containing a formal four-coordinate carbon center.[8,9] As the simplest prototype H_2CLi_2 adopts a polymeric salt-like structure,[10] investigations have targeted methandiides with bulky solubilizing groups.[11] The groups of Cavell and of Stephan simultaneously reported the dimeric complex [{Li$_2$(bipm$^{N\text{-TMS}}$)}$_2$] (bipm$^{N\text{-TMS}}$ = C(PPh$_2$NSiMe$_3$)$_2$).[12,13] The groups of Henderson and of Harder have subsequently reported the dimeric homo- and heterometallic heavier alkali metal congeners [{MM'(bipm$^{N\text{-TMS}}$)}$_2$] (M = Li; M' = Li, Na, K)[14] and [{M$_2$(bipm$^{N\text{-Ph}}$)}$_2$] (M = K, Rb).[9] We have reported the dimeric dilithio complex [{Li$_2$(bipm$^{N\text{-Mes}}$)}$_2$] (Mes = 2,4,6-Me$_3$C$_6$H$_2$),[15] and Le Floch and Mézailles have reported dimeric [{Li$_2$(bipm$^{N\text{-R}}$)}$_2$] (R = (S)-MeCHiPr) and [{Li$_2$(C[PPh$_2$S]$_2$)}$_2$·n(OEt$_2$)] (n = 2, 3).[16] In all cases, these dilithio methandiides can be considered to formally derive from the orthogonal dimerization of two planar [R$_2$CMM'] units that contain a *cis*-planar four-coordinate carbon atom. Notable by their absence are the corresponding monomeric and *trans*-planar congeners.
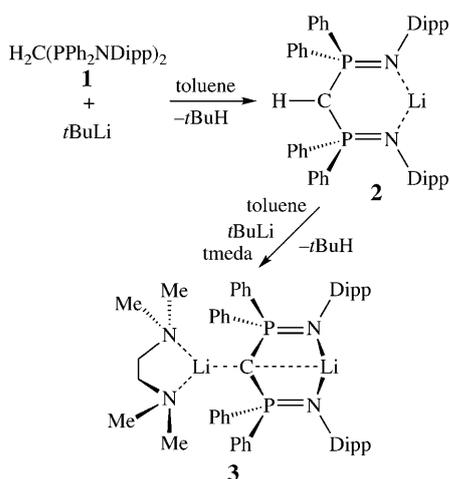
Herein, we describe the synthesis of a monomeric dilithio methandiide complex **3** that is notable for the fact it exhibits a distorted *trans*-planar four-coordinate carbon atom; this compound was obtained by the simple addition of the chelating diamine tetramethylethylenediamine (tmeda) to aid deprotonation (Scheme 1).

As part of our investigations of f-block methandiides,[15,17] we have utilized dilithio methandiides such as [{Li$_2$(bipm$^{N\text{-TMS}}$)}$_2$] and [{Li$_2$(bipm$^{N\text{-Mes}}$)}$_2$] as ligand-transfer agents. However, to tune ligand substitution patterns, we investigated the use of the sterically demanding methane derivative H_2(bipm$^{N\text{-Dipp}}$) (**1**; Dipp = 2,6-diisopropylphenyl)[18]

Scheme 1. Synthesis of **3** from **2** and **2** from **1** by deprotonation. Dipp = 2,6-diisopropylphenyl.

to prepare lithium ligand-transfer reagents. Accordingly, treatment of **1** with one equivalent of *t*BuLi in toluene afforded [Li{H(bipm$^{N\text{-Dipp}}$)}] (**2**) as colorless crystals in 71% yield after work-up and recrystallization. This formulation is supported by the CHN elemental analysis and NMR and FTIR spectroscopic data.

The molecular structure of **2** is illustrated in Figure 1.[19] Complex **2** is monomeric and solvent-free in the solid state. The lithium atom is not coordinated to the methanide center (Li1···C1 3.196(8) Å), but is bound by the two imino nitrogen atoms, with a bite angle of 117.7(4)°. The absence of a Li···C contact[20] is underscored by the fact the CP$_2$N$_2$Li ring is essentially planar (root-mean-square deviation 0.07 Å). The electron-deficient nature of the lithium atom is suggested by a weak interaction with a Dipp-C$_{ipso}$ center (Li1···C26 = 2.765(8) Å). The Li1–N1 and Li1–N2 bonds (1.881(8) and 1.880(8) Å) are short compared to typical Li–N distances of

about 2.0 Å in related bipm complexes,[20] and are short even in comparison to lithium amides.[21] The C1–P1 and C1–P2 bonds (1.700(4) and 1.698(4) Å) are shorter than those observed in **1**,[22] but the P1–N1 and P2–N2 bonds (1.600(3) and 1.607(3) Å) are essentially unchanged.

With the discovery of **2** in hand, we attempted a second deprotonation. The addition of one equivalent of *t*BuLi to **2** in toluene (or addition of two equivalents of *t*BuLi to **1**) did not remove the methanide hydrogen, and only **2** was rerecovered. This is surprising, as *t*BuLi effects double-deprotonation of H$_2$(bipm$^{N\text{-R}}$) to give [{Li$_2$(bipm$^{N\text{-R}}$)}$_2$] (R = SiMe$_3$, Mes).[14,15] However, addition of one equivalent of tmeda to the reaction mixture smoothly afforded deprotonation of **2** at room temperature.[23] Following work-up and recrystallization, [Li$_2$(bipm$^{N\text{-Dipp}}$)·tmeda] (**3**) was isolated as colorless crystals in 61% yield, and the characterization data support this formulation. In particular, following the second deprotonation, the ^{31}P NMR spectrum exhibits a singlet at $\delta = 7.16$ ppm ($\delta = 17.8$ ppm for **2**), and the ^{7}Li NMR spectrum exhibits two broad signals at $\delta = 1.95$ and 2.37 ppm (singlet at $\delta = 2.00$ ppm for **2**). In common with other dilithio methandiides,[9,12–16] the methandiide signal in the ^{13}C NMR spectrum was not observed. These observations suggested the formation of an unusual methandiide with two distinct lithium environments. Therefore, we determined the structure of **3** by X-ray crystallography.

The molecular structure of **3** is shown in Figure 2.[19] In contrast to previously reported dialkali metal methandiides, **3** crystallizes as a monomer, where the methandiide center adopts a distorted *trans*-planar geometry. The root-mean-square deviation from the mean plane of C1, P1, P2, Li1, and Li2 is only 0.34 Å, and C1 deviates from this plane by 0.007(2) Å. The Li1-C1-Li2 angle is 161.41(12)°, and this distortion from linearity is attributed to the close fit of the

Figure 2. Molecular structure of **3**. Ellipsoids set at 30% probability, and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1–N1 1.929(3), Li1–N2 1.885(3), Li1–C1 2.531(3), Li1···C36 2.659(3), Li2–N3 2.153(3), Li2–N4 2.113(3), Li2–C1 2.124(3), P1–C1 1.6816(14), P2–C1 1.6782(14), P1–N1 1.6266(12), P2–N2 1.6226(12); N1-Li1-N2 131.64(16), P1-C1-P2 132.05(9), Li1-C1-Li2 161.41(12), Li1-C1-P1 73.13(8), Li1-C1-P2 73.22(8), Li2-C1-P1 114.79(11), Li2-C1-P2 107.94(10).
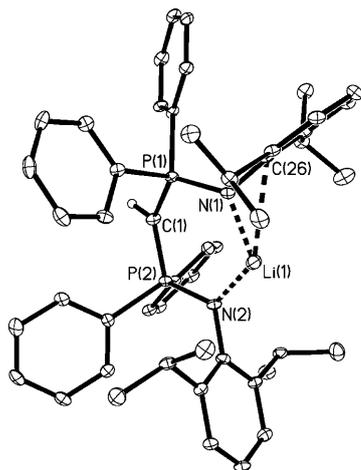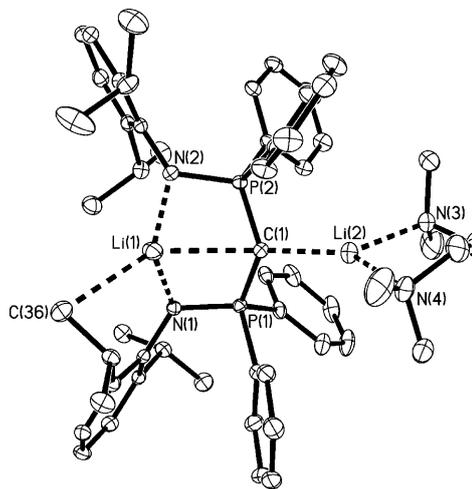

Figure 1. Molecular structure of **2**. Ellipsoids set at 30% probability, and hydrogen atoms except at C1 omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1–N1 1.881(8), Li1–N2 1.880(8), Li1···C26 2.765(8), P1–C1 1.700(4), P2–C1 1.698(4), P1–N1 1.600(3), P2–N2 1.607(3); N1-Li1-N2 117.7(4), P1-C1-P2 134.7(3).

Li(tmeda) unit into the pocket formed by the four *P*-phenyl rings, which is confirmed by inspection of a space.filling plot;[22] this deviation also accounts for the small displacement of C1 from the P_2Li_2 plane. The P1-C1-P2 angle (132.05(9)°) is distorted from the ideal angle expected for a *trans*-planar geometry owing to its incorporation into the CP_2N_2Li ring.[24] Li2 is coordinated to the methandiide center and the two tmeda nitrogen atoms with bond lengths of 2.124(3), 2.153(3), and 2.113(3) Å, respectively. Li1 is coordinated to the two imino nitrogen atoms with bond lengths of 1.929(3) and 1.885(3) Å and to the methandiide with a Li1−C1 distance of 2.531(3) Å. The weak binding of Li1 to C1 is supported by the deviation of Li1 from the P_2N_2 plane by 0.78 Å towards C1 with a P_2N_2Li fold angle of 119.2(9)°. Furthermore, the Li1−N1 bond is somewhat longer than the corresponding bond in **2**. Both Li−C bonds in **3** exceed the sum of the covalent radii of lithium and carbon (2.08 Å),[25] but are well within the corresponding sum of the van der Waals radii (3.90 Å),[26] reflecting the ionic nature of the lithium–ligand interactions. A Li1···C36 distance of 2.659(3) Å suggests an additional weak contact. The endocyclic C−P bonds are shortened by about 0.03 Å and the P−N bonds elongated by about 0.03 Å compared to those in **2**.

We carried out a single-point-energy DFT calculation on **3** using the ADF2009.01 code to gain insight into the electronic structure of **3**.[27] Calculated NPA charges from an NBO analysis[28] yielded values of −1.60 for C1, −1.14 (av.) for N1 and N2, +1.56 (av.) for P1 and P2, +0.89 for Li1, and +0.88 for Li2. Calculated NAO Wiberg bond indexes gave values of +1.24 (av., P−C), +1.01 (av., P−N), +0.01 (av., Li−N_{tmeda}), +0.03 (av., Li−N_{imino}), +0.03 (Li1−C1), and +0.02 (Li2−C1), which, together with the NPA charges, underscores the ionic nature of the lithium bonding. Inspection of the HOMO (Figure 3a) reveals an essentially non-bonding lone pair, which is approximately orthogonal to the Li-C-Li vector; this orbital is of 23.7% 2s and 76.2% 2p character. The lone pair principally described by HOMO−5 (Figure 3b) resides along the Li-C-Li vector and is comprised of an admixture of carbon 2p (98.5%) and 2s (1.4%). The orbital models **III–V**, which are important for the development of the field of planar four-coordinate carbon, have largely been superseded by ionic interpretations where lithium bonding is involved.[29] Therefore, as the Li−C bonds in **3** are predominantly electrostatic, 2e,2c and 2e,3c descriptions, which imply covalency, are not appropriate; however, these descriptions are useful in a formal sense to classify the electronic structure of the methandiide center in **3**. Thus, and in contrast to **III–V**,[3,6]

we conclude that an appropriate orbital representation of **3** is **VII**, in which an approximate pseudo sp^2-hybridized carbon is bound to the four substituents through two 2e,2c bonds and one asymmetric 2e,3c bond.[30]
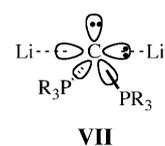
To summarize, we have prepared a dilithio methandiide that contains an unusual monomeric distorted *trans*-planar four-coordinate carbon. This result provides an experimentally determined complement to theoretical models, and we propose that this unusual geometry is due to the steric demands of the $bipm^{N\text{-}Dipp}$ dianion combined with the presence of tmeda.
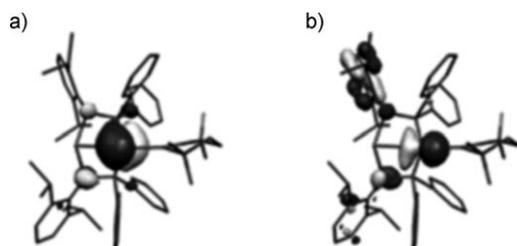
VII

Experimental Section

Figure 3. Khon–Sham orbital representations of **3** at the 0.05 e Å^3 level: a) HOMO (161 A, −3.799 eV); b) HOMO−5 (156 A, −4.782 eV).

[1] Although le Bel is often jointly credited with van't Hoff for the proposal of tetrahedral four-coordinate carbon, it has been pointed out that the credit should go to van't Hoff alone; see: a) N. N. Greenwood, *J. Chem. Soc. Dalton Trans.* **2001**, 2055; b) J. H. van't Hoff, *Arch. Neerl. Sci. Exactes Nat.* **1874**, 445; c) J. A. le Bel, *Bull. Soc. Chim. Fr.* **1874**, *22*, 337.

[2] Selected references: a) M. Wu, Y. Pei, X. C. Zeng, *J. Am. Chem. Soc.* **2010**, *132*, 5554; b) G. Merino, M. A. Méndez-Rojas, A. Vela, T. Heine, *J. Comput. Chem.* **2007**, *28*, 362; c) P. D. Pancharatna, M. A. Méndez-Rojas, G. Merino, A. Vela, R. Hoffmann, *J. Am. Chem. Soc.* **2004**, *126*, 15309; d) Z. X. Wang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2002**, *124*, 11979; e) R. Choukroun, P. Cassoux, *Acc. Chem. Res.* **1999**, *32*, 494; f) W. Siebert, A. Gunale, *Chem. Rev.* **1999**, *99*, 367; g) D. R. Rasmussen, L. Radom, *Angew. Chem.* **1999**, *111*, 3051; *Angew. Chem. Int. Ed.* **1999**, *38*, 2875; h) L. Radom, D. R. Rasmussen, *Pure Appl. Chem.* **1998**, *70*, 1977; i) K. Sorger, P. von R. Schleyer, *J. Mol. Struct.* **1995**, *338*, 317.

[3] R. Hoffmann, R. W. Alder, C. F. Wilcox, *J. Am. Chem. Soc.* **1970**, *92*, 4992.

[4] More recent calculations give a value of about 546 kJ mol^{-1}; see: M. J. M. Pepper, I. Shavitt, P. von R. Schleyer, M. N. Glukhovtsev, R. Janoschek, M. Quack, *J. Comput. Chem.* **1995**, *16*, 207.

[5] a) G. Erker, *Chem. Soc. Rev.* **1999**, *28*, 307; b) D. Röttger, G. Erker, *Angew. Chem.* **1997**, *109*, 840; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 812, and references therein.

[6] J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. von R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419.

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

[8] A. Streitwieser, S. M. Bachrach, A. Dorigo, P. von R. Schleyer in *Lithium Chemistry* (Eds.: A. M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, p. 19.

[9] L. Orzechowski, G. Jansen, S. Harder, *Angew. Chem.* **2009**, *121*, 3883; *Angew. Chem. Int. Ed.* **2009**, *48*, 3825.

[10] G. D. Stucky, M. M. Eddy, W. H. Harrison, R. Lagow, H. Kawa, D. E. Cox, *J. Am. Chem. Soc.* **1990**, *112*, 2425.

[11] a) J. H. Chen, J. Guo, Y. Li, C. W. So, *Organometallics* **2009**, *28*, 4617; b) G. Linti, A. Rodig, H. Pritzkow, *Angew. Chem.* **2002**, *114*, 4685; *Angew. Chem. Int. Ed.* **2002**, *41*, 4503; c) J. F. K. Müller, M. Neuburger, B. Spingler, *Angew. Chem.* **1999**, *111*, 97; *Angew. Chem. Int. Ed.* **1999**, *38*, 92; d) W. Zarges, M. Marsch, K. Harms, G. Boche, *Chem. Ber.* **1989**, *122*, 1307.

[12] A. Kasani, R. P. Kamalesh Babu, R. McDonald, R. G. Cavell, *Angew. Chem.* **1999**, *111*, 1580; *Angew. Chem. Int. Ed.* **1999**, *38*, 1483.

[13] C. M. Ong, D. W. Stephan, *J. Am. Chem. Soc.* **1999**, *121*, 2939.

[14] a) K. L. Hull, I. Carmichael, B. C. Noll, K. W. Henderson, *Chem. Eur. J.* **2008**, *14*, 3939; b) K. L. Hull, B. C. Noll, K. W. Henderson, *Organometallics* **2006**, *25*, 4072.

[15] O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, *39*, 5074.

[16] a) M. Demange, L. Boubekeur, A. Auffrant, N. Mézailles, L. Ricard, X. Le Goff, P. Le Floch, *New J. Chem.* **2006**, *30*, 1745; b) T. Cantat, L. Ricard, P. Le Floch, N. Mézailles, *Organometallics* **2006**, *25*, 4965.

[17] a) A. J. Wooles, O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2010**, *29*, 2315; b) A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Dalton Trans.* **2010**, *39*, 500; c) D. P. Mills, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2009**, *28*, 6771; d) D. P. Mills, O. J. Cooper, J. McMaster, W. Lewis, S. T. Liddle, *Dalton Trans.* **2009**, 4547; e) S. T. Liddle, D. P. Mills, B. M. Gardner, J. McMaster, C. Jones, W. Woodul, *Inorg. Chem.* **2009**, *48*, 3520; f) S. T. Liddle, J. McMaster, J. Green, P. L. Arnold, *Chem. Commun.* **2008**, 1747.

[18] S. Al-Benna, M. J. Sarsfield, M. Thornton-Pett, D. L. Ormsby, P. J. Maddox, P. Brès, M. Bochmann, *J. Chem. Soc. Dalton Trans.* **2000**, 4247.

[19] Crystal data for **2**: $C_{49}H_{55}LiN_2P_2$, $M_r = 740.83$, space group $P\bar{1}$, $a = 8.7295(18)$, $b = 10.760(2)$, $c = 22.535(5)$, $\alpha = 91.698(4)$, $\beta = 98.613(4)$, $\gamma = 101.745(4)$, $V = 2045.0(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.203$ g cm^{-3}; Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.143$ mm^{-1}, $T = 90$ K. 15074 data (7159 unique, $R_{int} = 0.062$, $\theta < 25°$). Data were collected on a Bruker SMART APEX CCD diffractometer and were corrected for absorption (transmission 0.56–0.75). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values to give w$R2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2} = 0.1827$, conventional $R = 0.0807$ for F values of 4762 with $F_0^2 > 2\sigma(F_0^2)$, $S = 1.057$ for 495 parameters. Residual electron density extrema were 0.90 and -0.46 e Å^{-3}. Crystal data for **3**: $C_{55}H_{70}Li_2N_4P_2$, $M_r = 862.97$, space group $P2_1/n$, $a = 13.54592(13)$, $b = 21.64626(20)$, $c = 17.42775(15)$, $\beta = 98.9911(9)$, $V = 5047.35(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.136$ g cm^{-3}; Cu$_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\mu = 1.066$ mm^{-1}, $T = 90$ K. 27441 data (9031 unique, $R_{int} = 0.024$, $\theta < 67.5°$). Data were collected on a Oxford Diffraction SuperNova Atlas CCD diffractometer and were corrected for absorption (transmission 0.88–0.97). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values to give w$R2 = 0.0914$, conventional $R = 0.0355$ for F values of 7685 with $F_0^2 > 2\sigma(F_0^2)$, $S = 1.043$ for 580 parameters. Residual electron density extrema were 0.34 and -0.31 e Å^{-3}. CCDC 774584 (**2**) and 774585 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] The absence of Li−C contacts in substituted methanides is not uncommon; see: S. T. Liddle, D. P. Mills, A. J. Wooles, *Organomet. Chem.* **2010**, *36*, 29, and references therein.

[21] a) K. Gregory, P. von R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47; b) R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167.

[22] See the Supporting Information for full details.

[23] Tmeda has long been known to activate organolithium reagents; see: B. J. Wakefield in *The Chemistry of Organolithium Compounds*, Pergamon, Elmsford, New York, **1974**.

[24] Closely related carbodiphosphoranes exhibit a range of P-C-P angles, indicating a shallow potential energy surface with respect to bending; see: a) G. E. Hardy, W. C. Kaska, B. P. Chandra, J. I. Zink, *J. Am. Chem. Soc.* **1981**, *103*, 1074; b) G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin, *J. Am. Chem. Soc.* **1978**, *100*, 8001; c) A. T. Vincent, P. J. Wheatley, *J. Chem. Soc. Dalton Trans.* **1972**, 617.

[25] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.

[26] S. S. Batsanov, *Inorg. Mater.* **2001**, *37*, 871.

[27] a) C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391; b) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[28] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, Weinhold, F. NBO 5.0., Theoretical Chemistry Institute, University of Wisconsin: Madison, **2001**.

[29] C. Lambert, P. von R. Schleyer, *Angew. Chem.* **1994**, *106*, 1187; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129.

[30] As discussed in Ref. [17c], a 'captodative' description of the bonding in **3** is also worthy of consideration; see: M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295.