ChemPubSoc Europe
DOI: 10.1002/chem.201504724
CHEMISTRY
A European Journal
Communication

Carbene Complexes

Preparation and Isolation of a Chiral Methandiide and Its Application as Cooperative Ligand in Bond Activation

Kai-Stephan Feichtner, Simon Englert, and Viktoria H. Gessner*[a]

Abstract: The activation of element–hydrogen bonds by means of metal–ligand cooperation has received increasing attention as alternative to classical activation processes, which exclusively occur at the metal center. Carbene complexes derived from methandiide precursors have been applied in this chemistry enabling the activation of a series of E–H bonds by addition reactions across the M=C bond. However, no chiral carbene complexes have been applied to realize stereoselective transformations to date. Herein, we report the isolation and structure elucidation of an enantiomerically pure dilithiomethane, which could be prepared by direct double deprotonation. The obtained dilithium salt was used for the preparation of the first chiral methandiide-derived carbene complex, which was applied in stereoselective cooperative S–H bond activation.

The selective formation of chiral compounds by asymmetric catalysis fascinates chemists since many years. This field of chemistry has grown rapidly due to its importance in a variety of synthetic routes in the chemical and pharmaceutical industry, as well as for the preparation of agrochemicals, fragrances, or flavors.[1] The transfer of stereoinformation in stereoselective processes normally relies on the use of chiral ligands. Thus, the development of new asymmetric transformations often depends on the design of new ligand systems. Most of the metal complexes employed make use of chiral phosphine ligands as source of stereoinformation.[2] However, in the past years, phosphines have often been replaced by carbene ligands. Because of their strong donor ability, carbenes were found to be excellent ligands to support robust metal complexes active in a variety of different reactions,[3] including asymmetric transformations.[4]

Typically, carbene ligands act as so-called spectator ligands, solely controlling transformations at the metal center by manipulating its electronic and steric properties. However, in the last years, a number of reports have appeared, in which carbene ligands actively participate in bond activation reactions by means of metal–ligand cooperation involving a transition from a M=C double to a M–C single bond.[5] Particularly, nucleophilic carbene complexes with late transition metals have proven to be applicable in this chemistry.[6] One way to access these unusual carbene species is the use of methandiide precursors, such as **A**–**C** (Figure 1 a).[7] These ligands allowed the isolation of a series of unique complexes with metal–carbon bonds varying between predominantly electrostatic interactions and "real" metal–carbon double bonds.[8–10] This flexibility facilitated bond-activation reactions by active participation of the M=C linkage.[11] For example, carbene complexes derived from methandiide **C** could also be applied in reversible bond-activation (e.g., **D** to **E**; Figure 1 b) and transfer hydrogenation reactions.[12,13] Because of this application of methandiides as cooperating ligands, the preparation of chiral derivatives and metal complexes thereof would be desirable. Until today, no chiral carbene complex based on a methandiide ligand has been reported, which is mainly due to synthetic difficulties involved in the preparation and isolation of such dianionic compounds. Given the stability and accessibility of the sulfonyl substituted system **C**, we assumed that the analogous sulfoximine **1** might be a suitable precursor to selectively access chiral carbene complexes.[14] Herein, we report the preparation and isolation of the enantiomerically pure dilithiomethane **1**, as well as its use as carbene ligand and in the cooperative, stereoselective activation of S–H bonds.

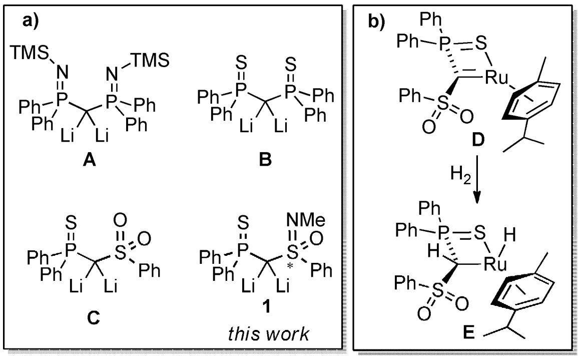


Figure 1. a) Methandiides used in the synthesis of carbene complexes and b) H_2 activation by a carbene complex by metal–ligand cooperation.

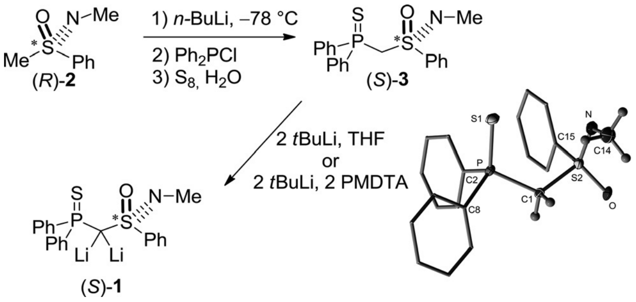
For the preparation of the optically pure methandiide **1**, the sulfoximines (*S*)-**2** and (*R*)-**2** were synthesized by a multistep procedure from thioanisole following literature procedures

---

[a] *K.-S. Feichtner, S. Englert, Dr. V. H. Gessner*
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: vgessner@uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/forschungsgruppen/dr_v_gessner/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504724.

(see the Supporting Information for experimental details).[15] Racemic resolution with camphor sulfonic acid selectively gave way to both enantiomers in pure form. The sulfoximine was then converted to **3** by deprotonation at the sulfur bound methyl group, treatment with Ph_2PCl and oxidation with elemental sulfur (Scheme 1). Work-up gave **3** as colorless solid in 57% yield. Compound **3** was characterized by multinuclear NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis. The phosphorus signal appears at $\delta_P = 33.1$ ppm in the $^{31}P\{^1H\}$ NMR spectrum, the PCH_2S protons as characteristic AB system at $\delta_H = 4.38$ and 4.71 ppm ($J_{AB} = 15.2$ Hz, $^2J_{PH} = 10.3$ Hz) in the ^1H NMR spectrum. The molecular structures of both enantiomers (Scheme 1 and the Supporting Information) confirmed the configuration at the stereogenic sulfur atom with bond lengths being in the expected regions. Measurements of the specific rotation gave a value of $[\alpha]_D^{20} = 63.3 \pm 1.5^\circ$ for the *R*-enantiomer, and a value of $[\alpha]_D^{20} = 59.6 \pm 1.6^\circ$ for the *S*-enantiomer.



Scheme 1. Preparation of the chiral dilithiomethane (*S*)-**1**. Molecular structure of (*S*)-**3**. Selected bond lengths [Å] and angles [°]: C–S 1.824(2), C–P 1.836(2), P–S 1.946(1), S–O 1.457(1), S–N 1.507(2), S–C_{Ph} 1.762(2), P–C_{Ph} 1.815(2); P-C-S 118.6(1); see the Supporting Information for data of the *R*-enantiomer.

The direct double deprotonation of **3** was first studied by using the *S*-enantiomer. Lithiation experiments were conducted with different organolithium bases in combination with nitrogen ligands for their activation. The conversions were followed by $^{31}P\{^1H\}$ NMR spectroscopy. First attempts with two equivalents of methyllithium or *n*-butyllithium in THF (both combinations have successfully been used for the synthesis of methandiide **C**) showed only incomplete conversion to the desired methandiide **1** ($\delta_P = 19.1$ ppm). Removal of the solvent and dissolving in C_6D_6 or [D$_8$]THF always led to product mixtures of **1** and considerable amounts of the monolithiated species ($\delta_P = 29.7$ ppm). This was also the case when using an excess of organolithium reagent. Nevertheless, single crystals of (*S*)-**1** could be obtained by slow diffusion of pentane into a THF/Et_2O solution of (*S*)-**1** with three equivalents of methyllithium. Under these conditions, the excessive base resulted in the decomposition of silicone grease and the incorporation of one equivalent of Me_3SiOLi into the crystalline product (see below).[16] However, for a more convenient preparation of (*S*)-**1** and its further application, either a 1:1 mixture of *t*BuLi and *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDTA) or two equivalents of *t*BuLi in THF were applied. Although the later combination could only be used in situ,[17] the PMDTA adduct could be isolated as highly air- and moisture-sensitive, pale yellow solid in 52% yield. Unfortunately, all attempts to grow single crystals of the PMDTA adduct failed, yet NMR data suggest the formation of a 2:1 adduct [(*S*)-**1**·(PMDTA)$_2$], which DFT studies indicated to be monomeric (see the Supporting Information for computational details). [D$_8$]Toluene solution of [(*S*)-**1**·(PMDTA)$_2$] exhibited only broadened signals in the ^1H, ^7Li, and $^{31}P\{^1H\}$ NMR spectra at ambient temperature. Variable-temperature (VT) NMR studies showed a sharpening of these signals upon cooling to −40 °C, thus indicating exchange processes or fluxional behavior at ambient temperature. At −40 °C, [(*S*)-**1**·(PMDTA)$_2$] is characterized by the absence of any methylene proton and a singlet at $\delta_P = 22.4$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. The ^7Li NMR spectrum exhibited two singlets at $\delta_{Li} = 0.60$ and 1.28 ppm, which is consistent with the NMR data reported for a monomeric bis(iminophosphinoyl)methandiide.[7d] Compound [(*S*)-**1**·(PMDTA)$_2$] is stable as a solid and can be stored at ambient temperature for weeks.

The molecular structure of dilithiomethane (*S*)-**1** is depicted in Figure 2 (triclinic space group $P\bar{1}$). The asymmetric unit contains four dimers and additional THF and diethyl ether solvent molecules. The two subunits of the pseudo-C_2 symmetric dimers consist of one molecule of (*S*)-**1**, Me_3SiOLi, and two coordinating THF molecules. In the structure, the three lithium atoms form a Li_3 triangle, on top of which the silanolate is coordinating. The metalated carbon atoms exhibit two contacts to the lithium atoms with bond lengths between 2.153(6) and 2.311(5) Å.[18] The P–C and S–C bond lengths within the P-C-S backbone are considerably contracted compared to the diprotonated precursor **3**, the P–C by 11% and S–C bond 7%. This is well in line with other dilithiomethanes[7] and can be attributed to strong electrostatic interactions involved with the negative charge on the central carbon atom. Negative hyperconjugation effects additionally lead to an elongation of the P–S, S–O, S–N, and P/S–C_{Ph} bonds. All lithium atoms are four coordinate with Li–N, Li–O, and Li–S distances in the range of those reported for related compounds.[19]

With successful isolation of the chiral dilithiomethane, we next addressed its application as ligand in carbene complexes to probe its use in stereoselective bond-activation reactions by means of metal–ligand cooperation. Hence, a THF solution of (*R*)-**1** was treated with [(*p*-cymene)$RuCl_2$]$_2$ at −78 °C, which upon warming to room temperature resulted in a color change to blue and the formation of a single new product, as was evidenced by a new signal at $\delta_P = 41.3$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Work-up to remove the formed LiCl afforded the desired carbene complex (*R*)-**4** as blue solid in 64% yield (Scheme 2). Most characteristic for the formation of (*R*)-**4** is the low-field shifted signal of the carbene carbon atom, which appears as doublet at $\delta_C = 129.8$ ppm with a coupling constant of $^1J_{PC} = 59.3$ Hz in the $^{13}C\{^1H\}$ NMR spectrum. This signal is thus in the range of other nucleophilic carbene complexes.[9] The proton and carbon atoms of the phosphorus-bound phenyl groups and the cymene ligand are diastereotopic and thus give rise to two sets of signals in the ^1H and

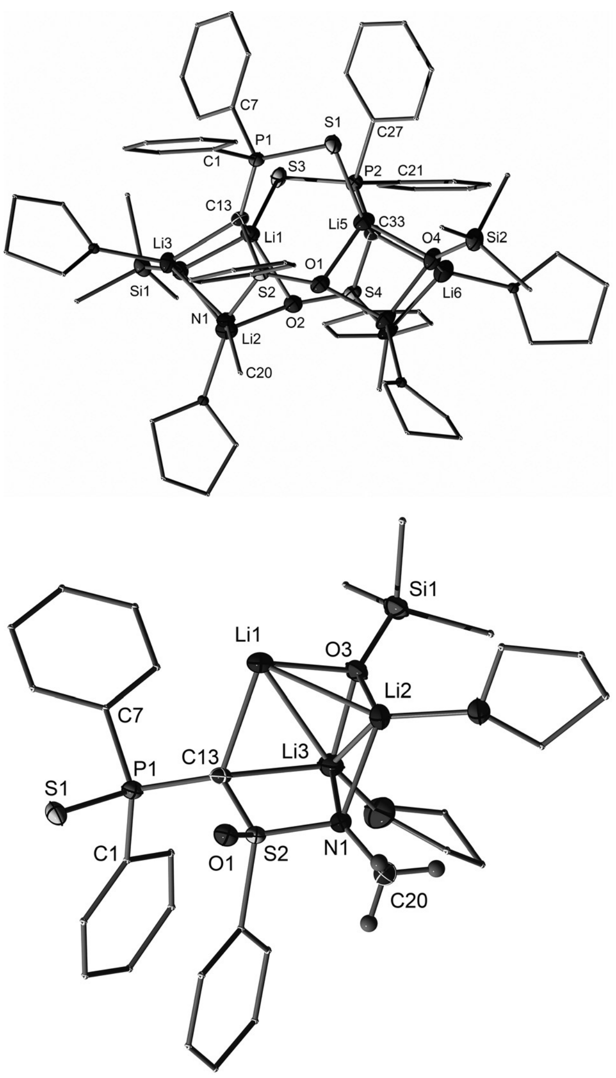
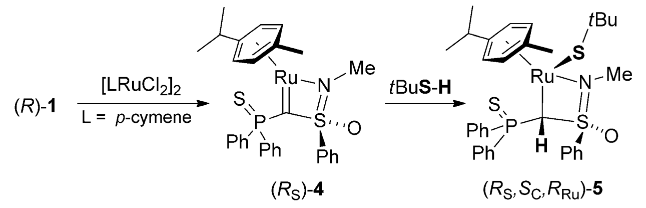


Figure 2. Top: molecular structure of the chiral dilithiomethane (*S*)-**1** crystallized with Me$_3$SiOLi [((*S*)-**1**·Me$_3$SiOLi·THF)$_2$]. Bottom: its monomeric subunit. Further molecules of **1** and additional solvent molecules are omitted for clarity; displacement ellipsoids are drawn at the 50% probability. Selected bond lengths [Å] and angles [°] (′ corresponds to further dimers in the asymmetric unit): P1–C1 1.719(3), P2–C21 1.721(3), P1′–C1′ 1.722(3), P2′–C21′ 1.715(3), P1′′–C1′′ 1.705(3), P2′′–C21′′ 1.710(3), S2–C1 1.622(3), S4–C21 1.620(3), S2′–C1′ 1.619(3), S4′–C21′ 1.627(3), S1–P1 2.0030(11), S3–P2 2.010(1), S1′–P1′ 2.0040(10), S3′–P2′ 2.0070(10), S2–O1 1.492(2), S2–N1 1.589(2), S4–O2 1.495(2), S4–N2 1.586(2), S2′–O1′ 1.494(2), S2′–N1′ 1.583(2), S4′–O2′ 1.500(2), S4′–N2′ 1.580(2), C1–Li3 2.180(6), C1–Li1 2.315(6), C21–Li6 2.179(6), C21–Li5 2.311(5), C1′–Li3′ 2.190(5), C1′–Li1′ 2.295(5), C21′–Li6′ 2.202(6), C21′–Li5′ 2.289(5); S2-C1-P1 117.86(16), S4-C21-P2 117.35(16), S2′-C1′-P1′ 116.1(2), S4′-C21′-P2′ 116.8(2).



Scheme 2. Preparation of carbene complex (R_S)-**4** and its use in stereoselective cooperative S–H activation.

^{13}C{^{1}H} NMR spectrum. Single crystals of (*R*)-**4** were grown by cooling of a saturated toluene solution to −30 °C. The molecular structure confirms the three-coordinate, planar carbon atom (sum of angles: 356.9(3)°) with a short Ru–C distance of 1.962(6) Å (Figure 3). This bond length is in the range of other known Ru=C double bonds.[13a, 20] The P–C and S–C distances are longer than in dilithiomethane **1** and thus reflect an efficient charge transfer from carbon to the metal when going from the methandiide to the carbene complex. The M=C double bond character in (*R*)-**4** was also confirmed by natural bond orbital (NBO) analysis showing σ and π interactions, which are almost equally distributed between both atoms (61.1 and 63.8% at C) yet with a slight polarization towards the carbon atom (qC$_{\text{NBO}} = -0.95$). The Wiberg bond index of WBI$_{\text{Ru–C}} = 1.04$ is in the range of other nucleophilic carbene complexes with late transition metals (see the Supporting Information for details).[9] Contrary to **D** (Figure 1), the ligand in (*R*)-**4** selectively coordinates to the metal through the sulfoximine nitrogen and not through the thiophosphinoyl moiety due to stronger coordination ability of nitrogen. It is interesting to note, that the *p*-cymene ligand coordinates to the metal in that way, that its *i*Pr moiety arranges *trans* to the phenyl group of the sulfoximine and thus minimizes repulsion between the two groups. The diastereotopic splitting of the signals of the cymene ligand in the NMR spectra suggests that this arrangement is also present in solution with no fluxional behavior at ambient temperature.

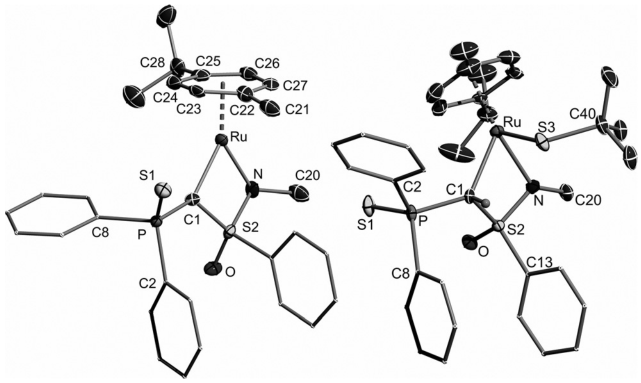


Figure 3. Molecular structures of the chiral carbene complex (R_S)-**4** (left) and the activation product (R_S,S_C,R_{Ru})-**5** (right). Hydrogen atoms (except for H1 at C1 in **5**) and benzene solvent are omitted for clarity; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: (R_S)-**4**. Ru–C1 1.962(6), Ru–N 2.065(6), Ru–S2 2.7067(17), S2–O 1.445(4), S1–P 1.977(2), S2–N 1.583(5), P–C1 1.757(7), P–C2 1.801(7); S2-C1-P 123.5(4), S2-C1-Ru 95.5(3), P-C1-Ru 137.9(3); **5**: Ru–N 2.144(2), Ru–C1 2.160(3), Ru–S3, S1–P 1.9520(10), S2–N 1.553(2), 2.4291(8), S2–C1 1.756(2), P–C1 1.812(3); S2-C1-P 114.38(13).

With successful isolation of the first chiral methandiide derived carbene complex, its application in stereoselective bond-activation chemistry by means of metal–ligand cooperation was probed. Treatment of a solution of (R_S)-**4** in toluene at −78 °C with *tert*-butylthiol resulted in an immediate color change from blue to red and the selective formation of a single new product ($\delta_{\text{P}} = 42.4$ ppm). Isolation gave the S–H activation product (R_S,S_C,R_{Ru})-**5**, which was isolated as red solid in 95 % yield. The NMR spectra of **5** (as well as of the crude reaction product) showed only one set of signals, thus being in line with the stereoselective bond activation and the formation of a single diastereoisomer via addition of the S–H bond from only one side of the former Ru=C double bond. X-ray crystallography revealed the formation of the (R_S,S_C,R_{Ru})-isomer of the thiolato complex (Figure 3, right). Thereby, this isomer is formed by the selective attack of the thiol from the side of the Ru=C bond *trans* to the *i*Pr group of the *p*-cymene ligand. In the molecular structure (orthorhombic space group $P2_12_12_1$), the Ru–C1 bond is elongated (2.160(3) Å) compared to the carbene complex, thus being in line with a transition from a Ru=C double bond to a single bond. Overall, the activation occurred through a metal–ligand cooperation with the carbene ligand serving as proton acceptor. To the best of our knowledge, such a stereoselective cooperative bond-activation reaction by a carbene ligand has never been reported before.

In conclusion, we have reported the preparation and isolation of an enantiomerically pure dilithiomethane and its use as ligand for the preparation of the first chiral carbene complex of its kind. The complex allowed the activation of the S–H bond in *t*BuSH by metal–ligand cooperation, which resulted in the stereoselective formation of the thiolato complex. This has been the first example of the use of a methandiide-derived carbene complex in stereoselective transformations. Future studies are focusing on the application in further activation reactions, as well as stoichiometric and catalytic asymmetric transformations.

Acknowledgements

We thank the DFG (Emmy Noether grant), the Dr.-Otto-Röhm-Gedächtnisstiftung, and the Fonds der Chemischen Industrie for financial support. We also thank Rockwood Lithium GmbH for the supply of chemicals.

Keywords: alkali metals · bond activation · carbenes · lithium · structure elucidation

[1] For reviews, see: a) M. Breuer, K. Ditrich, T. Habicher, B. Hauer, M. Kesseler, R. Stuermer, T. Zelinski, *Angew. Chem. Int. Ed.* **2004**, *43*, 788; *Angew. Chem.* **2004**, *116*, 806; b) N. B. Johnson, I. C. Lennon, P. H. Moran, J. A. Ramsden, *Acc. Chem. Res.* **2007**, *40*, 1291; c) J. M. Hawkins, T. J. N. Watson, *Angew. Chem. Int. Ed.* **2004**, *43*, 3224; *Angew. Chem.* **2004**, *116*, 3286.

[2] a) A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932; b) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946; c) M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518; d) M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125; e) M. D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc.* **1977**, *99*, 6262.

[3] For recent reviews, see: a) K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Hermann, F. E. Kühn, *Chem. Rev.* **2014**, *114*, 5215; b) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2009**, *109*, 3445; c) L.-A. Schaper, S. J. Hock, W. A. Hermann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2013**, *52*, 270; *Angew. Chem.* **2013**, *125*, 284; d) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122; *Angew. Chem.* **2008**, *120*, 3166; e) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940; *Angew. Chem.* **2010**, *122*, 7094; f) L. Mercs, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903.

[4] For reviews on asymmetric catalysis, see: a) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; b) F. Wang, L.-J. Liu, W. Wang, S. Li, M. Shi, *Coord. Chem. Rev.* **2012**, *256*, 804; c) D. Enders, T. Balensiefer, *Acc. Chem. Res. Acc. Chem. Rev.* **2004**, *37*, 534; d) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; *Angew. Chem.* **2002**, *114*, 1342; e) L. H. Gade, S. Bellemin-Laponnaz, *Coord. Chem. Rev.* **2007**, *251*, 718.

[5] For reviews on metal ligand cooperation, see: a) V. K. K. Praneeth, M. R. Ringenberg, T. R. Ward, *Angew. Chem.* **2012**, *124*, 2; b) O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440; c) H. Grützmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 1814; *Angew. Chem.* **2008**, *120*, 1838; d) J. I. van der Vlug, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2009**, *48*, 8832; *Angew. Chem.* **2009**, *121*, 8990; e) S. Schneider, J. Meiners, B. Askevold, *Chem. Eur. J.* **2012**, *18*, 412; f) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270; g) J. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236; *Angew. Chem. Int. Ed.* **2015**, *127*, 12406.

[6] a) D. V. Gutsulyak, W. E. Piers, J. Borau-Garcia, M. Parvez, *J. Am. Chem. Soc.* **2013**, *135*, 11776; b) L. E. Doyle, W. E. Piers, J. Borau-Garcia, *J. Am. Chem. Soc.* **2015**, *137*, 2187; c) R. J. Burford, W. E. Piers, M. Parvez, *Organometallics* **2012**, *31*, 2949; d) C. C. Comanescu, V. M. Iluc, *Organometallics* **2014**, *33*, 6059; e) C. C. Comanescu, V. M. Iluc, *Organometallics* **2015**, *34*, 4684.

[7] For examples: a) A. Kasani, R. P. K. Babu, R. McDonald, R. G. Cavell, *Angew. Chem. Int. Ed.* **1999**, *38*, 1483; *Angew. Chem.* **1999**, *111*, 1580; b) C. M. Ong, D. W. Stephan, *J. Am. Chem. Soc.* **1999**, *121*, 2939; c) T. Cantat, L. Ricard, P. Le Floch, N. Mézailles, *Organometallics* **2006**, *25*, 4965; d) M. Demange, L. Boubekeur, A. Auffrant, N. Mézailles, L. Ricard, X. Le Goff, P. Le Floch, *New J. Chem.* **2006**, *30*, 1745; e) O. J. Cooper, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2010**, *49*, 5570; *Angew. Chem.* **2010**, *122*, 5702; f) P. Schröter, V. H. Gessner, *Chem. Eur. J.* **2012**, *18*, 11223; g) L. Orzechowski, G. Jansen, S. Harder, *Angew. Chem. Int. Ed.* **2009**, *48*, 3825; *Angew. Chem.* **2009**, *121*, 3883.

[8] For examples, see: a) O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 2383; *Angew. Chem.* **2011**, *123*, 2431; b) R. G. Cavell, R. P. K. Babu, A. Kasani, R. McDonald, *J. Am. Chem. Soc.* **1999**, *121*, 5805; c) G. Lin, N. D. Jones, R. A. Gossage, R. McDonald, R. G. Cavell, *Angew. Chem. Int. Ed.* **2003**, *42*, 4054; *Angew. Chem.* **2003**, *115*, 4188; d) T. Cantat, T. Arliguie, A. Noel, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, *J. Am. Chem. Soc.* **2009**, *131*, 963; e) D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2012**, *134*, 10047; f) T. Cantat, N. Mézailles, L. Ricard, Y. Jean, P. Le Floch, *Angew. Chem. Int. Ed.* **2004**, *43*, 6382; g) L. Orzechowski, G. Jansen, S. Harder, *J. Am. Chem. Soc.* **2006**, *128*, 14676; h) V. Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, M. J. Calhorda, L. F. Veiros, *Organometallics* **2004**, *23*, 2412.

[9] For a recent review on methandiide derived carbene complexes, see: V. H. Gessner, J. Becker, K.-S. Feichtner, *Eur. J. Inorg. Chem.* **2015**, 1841.

[10] V. H. Gessner, F. Meier, D. Uhrich, M. Kaupp, *Chem. Eur. J.* **2013**, *19*, 16729.

[11] a) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2010**, *132*, 14379; b) J.-Y. Guo, Y.-C. Chan, Y. Li, R. Ganguly, C.-W. So, *Organometallics* **2015**, *34*, 1238; c) E. Nicolas, B. Martin-Vaca, N. Mézailles, D. Bourissou, L. Maron, *Eur. J. Inorg. Chem.* **2013**, 4068; d) R. G. Cavell, R. P. K. Babu, K. Aparna, *J. Organomet. Chem.* **2001**, *617–618*, 158; e) V. Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, *Organometallics* **2008**, *27*, 1809.

[12] a) J. Becker, V. H. Gessner, *Organometallics* **2014**, *33*, 1310; b) J. Becker, V. H. Gessner, *Dalton Trans.* **2014**, *43*, 4320.

[13] a) J. Becker, T. Modl, V. H. Gessner, *Chem. Eur. J.* **2014**, *20*, 11295; b) J. Weismann, V. H. Gessner, *Eur. J. Inorg. Chem.* **2015**, 4192; c) J. Weismann, V. H. Gessner, *Chem. Eur. J.* **2015**, 21, 16103; d) J. Weismann, V. H. Gessner, *Chem. Commun.* **2015**, *51*, 14909.

[14] To date, two sulfoximines have been used to access chiral dilithium methandiides. However, either competing intramolecular deprotonation reactions or only low yields were observed: a) J. F. K. Müller, M. Neuburger, B. Spingler, *Angew. Chem. Int. Ed.* **1999**, *38*, 3549; *Angew. Chem.*

1999, *111*, 3766; b) J. F. K. Müller, M. Neuburger, M. Zehnder, *Helv. Chim. Acta* **1997**, *80*, 2182.

[15] a) C. S. Shiner, A. H. Berks, *J. Org. Chem.* **1988**, *53*, 5542; b) J. Brandt, H.-J. Gais, *Tetrahedron: Asymmetry* **1997**, *8*, 909.

[16] Decomposition of silicone grease is common in lithium chemistry. The formation of crystals of **2-Li$_2$** with incorporated Me_3SiOLi is reproducible when using the same crystallization conditions (see the Supporting Information). For other examples, see: a) P. C. Andrews, S. D. Bull, M. Koutsaplis, *New J. Chem.* **2010**, *34*, 1678–1691; b) I. Haiduc, *Organometallics* **2004**, *23*, 3.

[17] Isolation as a solid always resulted in partial protonation to the monolithiated compound.

[18] For reviews on structures of organolithium compounds, see: a) V. H. Gessner, C. Däschlein, C. Strohmann, *Chem. Eur. J.* **2009**, *15*, 3320; b) T. Stey, D. Stalke in *The Chemistry of Organolithium Compounds*, (Eds.: Z. Rappoport, I. Marek), Wiley, Chichester, **2004**, pp. 47–120.

[19] For examples, see: a) C. Kupper, S. Molitor, V. H. Gessner, *Organometallics* **2014**, *33*, 347; b) W.-P. Leung, Y.-C. Chan, T. C. W. Mak, *Organometallics* **2013**, *32*, 2584; c) E. Carl, D. Stalke, *Chem. Eur. J.* **2014**, *20*, 15849; d) R. Fleischer, A. Rothenberger, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1105; *Angew. Chem.* **1997**, *109*, 1140; e) M. G. Davidson, P. R. Raithby, A. L. Johnson, P. D. Bolton, *Eur. J. Inorg. Chem.* **2003**, 3445; f) D. Olbert, H. Görls, D. Conrad, M. Westerhausen, *Eur. J. Inorg. Chem.* **2010**, 1791; g) A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, G. M. Robertson, S. D. Robertson, *Angew. Chem. Int. Ed.* **2011**, *50*, 8375; *Angew. Chem.* **2011**, *123*, 8525; h) W. Clegg, B. Conway, E. Hevia, M. D. McCall, L. Russo, R. E. Mulvey, *J. Am. Chem. Soc.* **2009**, *131*, 2375.

[20] For examples, see: a) M. Leutzsch, L. M. Wolf, P. Gupta, M. Fuchs, W. Thiel, C. Farès, A. Fürstner, *Angew. Chem.Int. Ed.* DOI: 10.1002/anie.201506075; b) P. González-Herrero, B. Weberndörfer, K. Ilg, J. Wolf, H. Werner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3266; *Angew. Chem.* **2000**, *112*, 3392; c) S. Manzini, C. A. U. Blanco, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 6514; d) E. J. Smith, N. E. Pridmore, A. C. Whitwood, J. M. Lynam, *Organometallics* **2014**, *33*, 7260.

Received: November 24, 2015