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A Novel Synthetic Approach to Diaminoacetylenes: Structural Characterization and Reactivity of Aromatic and Aliphatic Ynediamines

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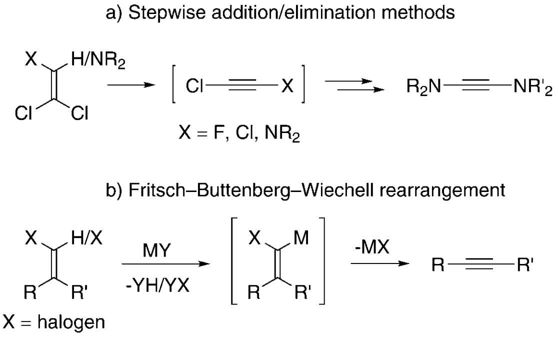
Acetylenes represent an important class of compounds with a broad range of applications as versatile reagents, linkers, or ligands,[1] and numerous novel reactions involving, for instance, cycloadditions,[2] cross-couplings,[3] and alkyne metathesis[4] have been developed during the last few decades. The reactivity and electronic properties of alkynes are largely dictated by the nature of their substituents and the degree of conjugation. Accordingly, heteroatom-functionalized acetylenes have been shown to display a large variety of different reactivity patterns,[5] with nitrogen-functionalized systems such as electron-rich ynamines (1-aminoalkynes) and ynamides (1-amidoalkynes) having found particularly widespread use in organic synthesis.[6,7] In contrast, only a small number of bis(nitrogen-functionalized) acetylenes of the type $R_2NC{\equiv}CNR_2$ have been described in the literature, although the preparation of the first ynediamine, 1,2-bis(diethylamino)acetylene, from 1,1-dichloro-2-fluoroethylene was reported in 1964 by Viehe and Reinstein.[8] These highly reactive compounds were prepared by stepwise addition of amines/amides to in situ prepared dihaloacetylenes or chloroaminoacetylenes, followed by elimination (Scheme 1 a).[9] However, these synthetic protocols are rather tedious and involve the use of several equivalents of lithium amides; these obstacles, together with the high reactivity of diaminoalkynes, have hampered the widespread use of these compounds in organic synthesis, although a number of applications in organometallic chemistry have been reported during the last two decades.[10]



Scheme 1. Preparative routes to alkynes.

In searching for a new access to diaminocyclopropenylidenes[11,12] and their heavier analogues,[13] we became interested in developing a general synthetic approach that can be adapted to the preparation of diaminoalkynes with a variable substitution pattern. This approach is based on the Fritsch–Buttenberg–Wiechell (FBW) rearrangement, which was originally developed for the preparation of diarylacetylenes (tolanes) from 2,2-diaryl-1-chloroalkenes[14,15] and involves the generation of halogen–metal–vinylidene species followed by 1,2-migration and concomitant metal halide elimination (Scheme 1b).[16] Notably, the FBW rearrangement has recently evolved into a valuable synthetic methodology for the preparation of polyyne structures, which can be accessed by treatment of 1,1-dibromo-2,2-dialkynylethenes with *n*-butyllithium (*n*BuLi).[17] Developing a similar protocol for the synthesis of diaminoalkynes required the preparation of the corresponding 2,2-dibromo-1,1-ethenediamines of type **2** (Scheme 2), which, to the best of our knowledge, have not been described in the literature to date, although a limited number of dichloro derivatives have been reported that were obtained unexpectedly[18] or as by-products.[19] α,α-Dibromoolefins are generally prepared from aldehydes or ketones by a dibromoolefination protocol by using Ph_3P/CBr_4;[20] however, the low reactivity of the corresponding *N,N,N′,N′*-tetrasubstituted ureas precludes the application of this method for the preparation of compounds **2**.

Alternatively, we studied the bromination of 1,1-ethenediamines (or ketene aminals) **1** and started our investigation

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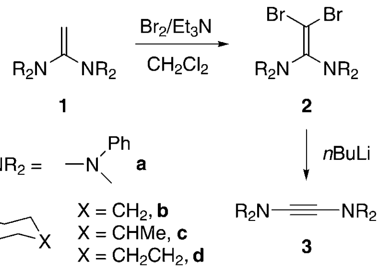


Scheme 2. Synthesis of α,α-dibromoketene aminals **2** and diaminoalkynes **3**.

with the diamine $(PhMeN)_2C{=}CH_2$ (**1a**), which can be prepared on a large scale by a two-step procedure starting from *N*-methylaniline.[21] Addition of two equivalents of bromine to a solution of **1a** in CH_2Cl_2 at 0 °C in the presence of an excess of Et_3N cleanly afforded the dibromide **2a** as a pale yellow crystalline solid in 73 % yield (Scheme 2). The molecular structure of **2a** was determined by X-ray diffraction analysis (Figure 1);[22] the asymmetric unit contains one half of the molecule, which displays crystallographic C_2 symmetry about an axis passing through the C1–C2 double bond. At 1.338(6) Å, this bond length is virtually identical to those determined for the dichloroketene aminals 2-(dichloromethylene)-1,3-dimesitylimidazoline (1.337(6) Å) and 2-(dichloromethylene)-4,5-dichloro-1,3-dimesitylimidazole (1.353(4) Å).[19] The C–C double bond in **2a** is significantly twisted and exhibits an interplanar angle of 17.6° between the CN_2 and CBr_2 planes. The nitrogen atoms are in a slightly distorted trigonal-planar environment (sum of angels at N = 359.3°); the two NC_3 planes deviate strongly from a coplanar arrangement, either with each other or with the C–C double bond, as, for instance, indicated by the torsion angles C3-N-C2-N′ = 47.3° and C4-N-C2-N′ = 57.0°.

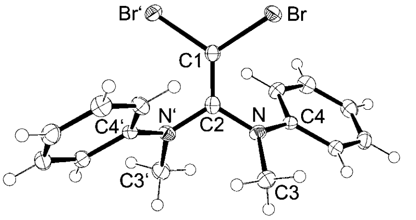


Figure 1. ORTEP diagram of **2a** with thermal displacement parameters drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.338(6), C1–Br 1.887(2), C2–N 1.394(3); C2-C1-Br 123.12(11), C1-C2-N 121.8(2), N-C2-N’ 116.4(4), Br-C1-Br’ 113.8(2).

Fortunately, this route could also be applied to the bromination of the aliphatic ketene aminals **1b**–**1d**, which can be obtained in high yield from the reaction of *N*,*N*-dimethylacetamide dimethylacetal, $MeC(OMe)_2NMe_2$ with the appropriate amines piperidine (**1b**), 4-methylpiperidine (**1c**), and homopiperidine (**1d**). This method was recently described for the preparation of a morpholine derivative and is driven by the volatility of methanol and dimethylamine.[23] The bromination of **1b**–**1d** proceeded cleanly under the same conditions as described for **1a** (vide supra), and the dibromoketene aminals **2b**–**2d** were isolated as yellow solids in satisfactory yield (67–85 %). Upon treatment with one equivalent of *n*BuLi at 0 °C in toluene (**2a**) or hexane (**2b**–**2d**), all dibromides **2** underwent the FBW rearrangement to form the diaminoalkynes **3a**–**3d** in 77–90 % yield as colorless oils (**3b**, **3d**) or crystalline solids (**3a**, **3c**), respectively (Scheme 2). All ynediamines were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. In the $^{13}C\{^1H\}$ NMR spectra, the resonances for the acetylenic carbon resonances are found between $\delta = 72$ and 78 ppm, which falls in the normal range expected for alkynes.

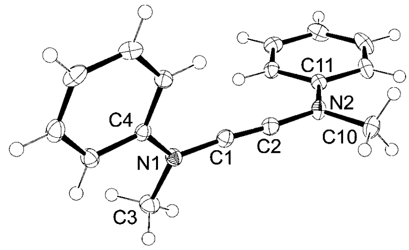


Figure 2. ORTEP diagram of **3a** with thermal displacement parameters drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.1992(12), C1–N1 1.3461(11), C2–N2 1.3442(10); C1-C2-N2 174.10(9), C2-C1-N1 176.28(9).

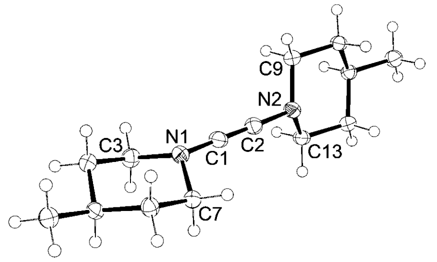
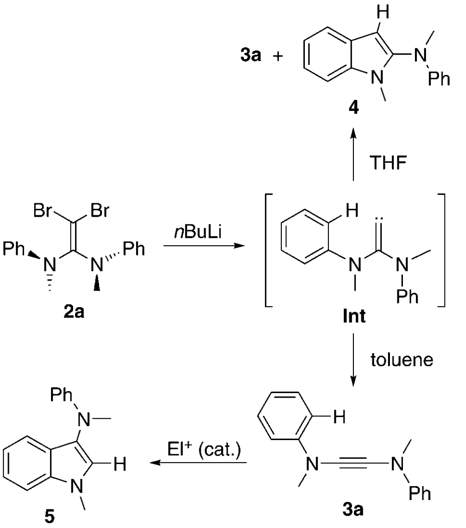


Figure 3. ORTEP diagram of **3c** with thermal displacement parameters drawn at 50 % probability. Selected bond lengths [Å] and angles [°] for C1–C2 1.206(2), C1–N1 1.357(2), C2–N2 1.359(2); C1-C2-N2 177.87(14), C2-C1-N1 173.92(14).

Surprisingly, there are no reports available on X-ray crystal structure determinations of diaminoalkynes, although a perpendicular conformation was theoretically predicted for diaminoacetylene, $H_2NC{\equiv}CNH_2$.[24,25] Single crystals of **3a** and **3c** were obtained from a hexane (**3a**) or tetramethylsilane solution (**3c**) at −30 °C, and the resulting molecular structures are shown in Figure 2 and Figure 3, respectively.[22] In agreement with the theoretical prediction,[24] the amino substituents in **3a** and **3c** exhibit strongly twisted orientations, affording approximately C_2-symmetric molecules with axial chirality. The nitrogen atoms in **3a** are in a trigonal-planar environment (sum of angles at N1/N2 = 359.8°/360.0°), and the angle between these two NC_3 planes is 77.1°, indicating a pronounced deviation from a perfectly perpendicular orientation, which might be ascribed to crystal packing effects. In contrast, the nitrogen atoms in **3c** reside in a distinctly trigonal-pyramidal coordination sphere as indicated by the angle sums of 341.6° (N1) and 344.6° (N2). The dihedral angle between the two NC$_3$ planes is 78.5°, revealing a similar twist as observed for **3a**. In both molecules, the N-C-C-N axes are close to linearity with C-C-N angles of 174.10(9)°/176.28(9)° in **3a** and 177.87(14)°/173.92(14) in **3c**. The C1−C2 bond lengths are 1.1992(12) Å in **3a** and 1.206(2) Å in **3c**, in agreement with the presence of C−C triple bonds; a similar, albeit slightly shorter C−C bond length of 1.189(5) Å was recently reported for an *ortho*-anisyl-substituted ynamide, which also displays an orthogonal conformation in the solid state.[26]

During the formation of **3a** from the reaction **2a** with *n*BuLi in toluene, we were able to isolate a minor byproduct in approximately 3% yield, which was identified as 2-(*N*′-methyl-*N*′-phenylamino)-*N*-methylindole (**4**) by comparison of its NMR spectroscopic data with those reported in the literature (Scheme 3).[27] The yield of **4** increased to 54% if the lithiation reaction was performed in tetrahydrofuran (THF) or if coordinating additives such as *N,N,N*′,*N*′-tetramethylethylenediamine (tmeda) were added to the toluene solution prior to the addition of *n*BuLi. Compound **4** could be isolated in pure form by fractional crystallization at +3°C from a **3a**/**4** mixture dissolved in hexane. Single-crystal X-ray diffraction analysis confirmed the molecular structure of **4** (Figure 4).[22] Mechanistically, the formation of **4** can be rationalized by an intramolecular insertion of the intermediate vinylidene species **Int** into an *ortho*-C−H bond of one of the phenyl rings (Scheme 3), which resembles the formation of cyclopentene derivatives from thermally generated alkenylidenes by 1,5-CH insertion.[16,28] It should be noted, however, that insertion into alkyl C−H bonds is common, whereas examples of solution-state insertion into significantly less reactive aromatic C−H bonds are rare and were only relatively recently reported.[29] Similar reactivity was also observed for *N*-arylaminovinylidene species that were generated by addition of anilides to alkynyliodonium triflates.[30]



Scheme 3. Formation of indole derivatives by intramolecular CH insertions.

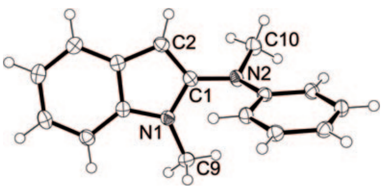


Figure 4. ORTEP diagram of **4** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: C1−N1 1.3878(16), C1−N2 1.4047(16), C1−C2 1.3661(18); N1-C1-C2 110.17(11), N1-C1-N2 119.53(11), C2-C1-N2 130.23(12).

The observed dependence of the **3a**/**4** ratio on the solvent polarity can be satisfactorily explained by postulating that lithiation of the dibromide **2a** does not generate the free vinylidene **Int**, but rather affords a LiBr–carbenoid adduct (see Scheme 1) of the type [Li(Br)C=C{N(Me)Ph}$_2$] (**Int**·LiBr), the aggregation and reactivity of which is strongly affected by the coordinating ability of the solvent, as generally observed for α-halogenoorganolithium compounds.[16,31] Apparently, polar solvents such as THF disfavor the FBW rearrangement by providing a long-lived vinylidene intermediate that undergoes intramolecular 1,5-CH-insertion, whereas the observed predominant formation of the diaminoalkyne **3a** in a nonpolar solvent such as toluene by 1,2-migration is in full agreement with recent high-level DFT calculations, showing "that the most facile FBW pathways occur in aggregated species."[32]

Another interesting reactivity pattern associated with the presence of *N*-phenyl substituents in the diaminoacetylene **3a** was discovered upon studying its coordination chemistry towards transition metals. Whereas a rich organometallic chemistry can be established based on the aliphatic diaminoacetylenes **3b**–**3d**,[10,33] the addition of electrophilic metal ions, such as Au$^+$, Pd^{2+}, exclusively afforded 3-(*N*′-methyl-*N*′-phenylamino)-*N*-methylindole (**5**), which represents a structural isomer of **4**. Apparently, these electrophiles catalyze the 1,2-addition of an *ortho*-C−H bond of one of the phenyl rings across the C−C triple bond (Scheme 3). The same reaction can be achieved by acid catalysis, and treatment of a solution of **3a** in acetone with *p*-toluenesulfonic acid resulted in a markedly exothermic reaction and cleanly afforded the indole **5**, the molecular structure of which was additionally established by X-ray diffraction analysis (Figure 5).[22] In analogy to the reactivity of ynamines and ynamides,[7] the formation of **5** can be rationalized by formation of an intermediate keteniminium ion, which triggers the observed intramolecular hydroarylation reaction. A closely related mechanism was recently proposed for the formation of related indoles from aminochlorocarbenes under comparatively harsh conditions (DMSO, 110–150°C, 7–18 h).[34] Fi-

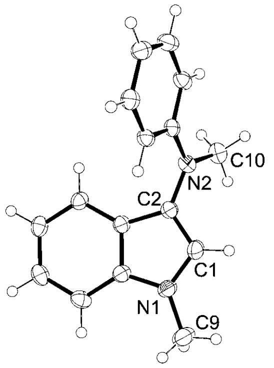


Figure 5. ORTEP diagram of one of the two independent molecules **5** with thermal displacement parameters drawn at 50 % probability. Selected bond lengths [Å] and angles in molecule 1 [°]: C1–N1 1.374(2), C1–C2 1.367(2) C2–N2 1.414(2); N1-C1-C2 110.26(11), N2-C2-C1 125.67(12), C1-N1-C9 125.20(11). In molecule 2, the indole ring is disordered over two positions (minor component 7 % occupied).

nally, exclusive formation of **5** is also observed in the presence of water, indicating that intramolecular cyclization is much faster than intermolecular nucleophilic addition. In contrast, aliphatic ynediamines are extremely moisture-sensitive and readily add water to form the corresponding aminoacid amides $R_2NCH_2–C(O)NR_2$.[7]

We envisage that the new general approach for the preparation of diaminoacetylenes of type **3** provided herein will advance the application of these electron-rich compounds in organometallic chemistry and material science. In addition, the facile FBW rearrangement upon lithiation of the fairly stable 2,2-dibromo-1,1-ethenediamines **2** also allows the generation of these species on demand and the development of novel organic transformations without the prerequisite of isolating larger quantities of these highly reactive alkyne derivatives. In addition, we have shown that arylamino-substituted systems such as the dibromide **2a** and the diaminoalkyne **3a** can be used for the preparation of indole derivatives, which might also develop into a useful and important synthetic method in view of the ubiquity of indole heterocycles in the structures of many biologically active natural products.[35]

Keywords: alkynes · carbenoids · diaminoacetylenes · Fritsch–Buttenberg–Wiechell rearrangement · indoles · vinylidenes

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[1] a) *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Dietrich), VCH, Weinheim, **1995**; b) *Acetylene Chemistry—Chemistry, Biology and Material Science* (Eds.: F. Dietrich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**.

[2] See, for instance: special issue on "Applications of Click Chemistry": a) *Chem. Soc. Rev.* **2010**, *39*(4), pp. 1221–1408, edited by M. G. Finn, V. Fokin; b) C. Spiteri, J. E. Moses, *Angew. Chem.* **2010**, *122*, 33–36; *Angew. Chem. Int. Ed.* **2010**, *49*, 31–33.

[3] See, for instance: a) J. A. Marsden, M. M. Haley in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 317–394; b) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017.

[4] See, for instance: a) M. Tamm, X. Wu, *Chem. Today* **2010**, *28*, 60–63; b) W. Zhang, J. S. Moore, *Adv. Synth. Catal.* **2007**, *349*, 93–120.

[5] a) B. Witulski, C. Alayrac in *Science of Synthesis, Vol. 24* (Ed.: A. de Meijere), Thieme, **2005**, p. 781; b) B. Witulski, C. Alayrac, in *Science of Synthesis, Vol. 24* (Ed.: A. de Meijere), Thieme, **2005**, p. 905.

[6] a) H. G. Viehe, *Angew. Chem.* **1967**, *79*, 744–755; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 767–778; b) H. G. Viehe in *Chemistry of Acetylenes* (Ed.: H. G. Viehe), Marcel Dekker, New York, **1969**, pp. 861–912.

[7] K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2010**, *110*, 5064–5106.

[8] H. G. Viehe, M. Reinstein, *Angew. Chem.* **1964**, *76*, 537; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 582.

[9] a) S. Y. Delavarenne, H. G. Viehe, *Chem. Ber.* **1970**, *103*, 1198–1208; b) L. Réne, Z. Janousek, H. G. Viehe, *Synthesis* **1982**, 645; c) L. Brandsma, H. D. Verkruijsse, *Synth. Commun.* **1991**, *21*, 811–813; d) G. Himbert, H. Naßhan, S. Kosack, *Synlett* **1991**, 117–118.

[10] See, for instance: a) H. Fischer, K. Treier, J. Hofmann, *J. Organomet. Chem.* **1990**, *384*, 305–314; b) H. Fischer, T. Meisner, J. Hofmann, *J. Organomet. Chem.* **1990**, *397*, 41–49; c) H. Fischer, O. Podschadly, A. Früh, C. Troll, R. Stumpf, A. Schlageter, *Chem. Ber.* **1992**, *125*, 2667–2673; d) H. Fischer, C. Troll, *J. Chem. Soc. Chem. Commun.* **1994**, 457; e) J. Heck, K.-A. Kriebisch, W. Massa, S. Wocadlo, *J. Organomet. Chem.* **1994**, *482*, 81–84; f) H. Fischer, O. Podschadly, G. Roth, S. Herminghaus, S. Klewitz, J. Heck, S. Houbrechts, T. Meyer, *J. Organomet. Chem.* **1997**, *541*, 321–332; g) C. Hartbaum, E. Mauz, G. Roth, K. Weissenbach, H. Fischer, *Organometallics* **1999**, *18*, 2619–2627; h) A. C. Filippou, T. Rosenauer, *Angew. Chem.* **2002**, *114*, 2499–2502; *Angew. Chem. Int. Ed.* **2002**, *41*, 2393–2396; i) A. Goswami, C.-J. Maier, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2004**, 2635–2645; j) A. Goswami, C.-J. Maier, H. Pritzkow, W. Siebert, *J. Organomet. Chem.* **2005**, *690*, 3251–3259.

[11] V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722–724.

[12] a) D. Holschumacher, C. G. Hrib, P. G. Jones, M. Tamm, *Chem. Commun.* **2007**, 3661–3663; b) H. Schumann, M. Glanz, F. Girgsdies, F. E. Hahn, M. Tamm, A. Grzegorzewski, *Angew. Chem.* **1997**, *109*, 2328–2330; *Angew. Chem. Int. Ed.* **1997**, *36*, 2232–2234.

[13] B. Pintér, T. Veszprémi, *Organometallics* **2008**, *27*, 5571–5576.

[14] a) P. Fritsch, *Justus Liebigs Ann. Chem.* **1894**, *279*, 319–323; b) W. P. Buttenberg, *Justus Liebigs Ann. Chem.* **1894**, *279*, 324–337; c) H. Wiechell, *Justus Liebigs Ann. Chem.* **1894**, *279*, 337–344.

[15] G. Körbich, P. Buck in *Chemistry of Acetylenes* (Ed.: H. G. Viehe), Marcel Dekker, New York, **1969**, pp. 99–168.

[16] R. Knorr, *Chem. Rev.* **2004**, *104*, 3795–3849.

[17] a) E. Jahnke, R. R. Tykwinski, *Chem. Commun.* **2010**, *46*, 3235–3249; b) W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski, *Angew. Chem.* **2009**, *121*, 8056–8060; *Angew. Chem. Int. Ed.* **2009**, *48*, 7915–7919.

[18] a) W. E. Parham, J. R. Potoski, *Tetrahedron Lett.* **1966**, *7*, 2311–2314; b) W. Kantlehner, U. Dinkeldein, H. Bredereck, *Justus Liebigs Ann. Chem.* **1979**, 1354–1361.

[19] A. J. Arduengo III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakash, *J. Am. Chem. Soc.* **1997**, *119*, 12742–12749.

[20] E. J. Corey, P. L. Fuchs, *Tetrahedron Lett.* **1972**, *13*, 3769–3772.

[21] C. Jutz, H. Amschler, *Chem. Ber.* **1963**, *96*, 2100–2108.

[22] Crystal data for **2a**: $C_{16}H_{16}N_2Br_2$, $M_r = 396.13$, hexagonal, $P6_122$, $a = b = 6.9995(2)$, $c = 54.0623(13)$ Å, $V = 2293.82(11)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.721$ Mg m^{-3}, $\mu = 6.6$ mm^{-1}, $T = 100(2)$ K, $Cu_{K\alpha}$ radiation ($\lambda = 1.54184$ Å). The structure was refined by using the program SHELXL-97 to $wR2 = 0.0545$ for 94 parameters and all 1574 unique reflections, with $R_1 = 0.0265$, GOF = 1.1. Crystal data for **3a**: $C_{16}H_{16}N_2$, $M_r = 236.31$, $0.26 \times 0.18 \times 0.18$ mm, monoclinic, $P2_1/c$, $a = 10.4497(2)$, $b = 14.8574(2)$, $c = 8.3947(2)$ Å, $\beta = 95.922(2)°$, $V = 1296.37(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.211$ Mg m^{-3}, $\mu = 0.07$ mm^{-1}, $T = 100(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $wR2 = 0.1079$ for 165 pa-

rameters and 3628 unique reflections, with $R_1=0.0365$, GOF = 1.1. Crystal data for **3c**: $C_{14}H_{24}N_2$, $M_r=220.35$, triclinic, $P\bar{1}$, $a=5.5739(10)$, $b=9.9713(14)$, $c=12.4075(18)$ Å, $\alpha=102.813(12)°$, $\beta=98.707(14)°$, $\gamma=94.473(12)°$, $V=660.21(18)$ Å^3, $Z=2$, $\rho_{calcd}=1.108$ Mg m^{-3}, $\mu=0.5$ mm^{-1}, $T=100(2)$ K, $Cu_{K\alpha}$ radiation ($\lambda=1.54184$ Å). $wR2=0.1134$ for 147 parameters and 2702 unique reflections, with $R_1=0.0412$, GOF = 0.98. Crystal data for **4**: $C_{16}H_{16}N_2$, $M_r=236.31$, monoclinic, $P2_1/c$, $a=7.1049(2)$, $b=16.0471(6)$, $c=11.3223(4)$ Å, $\beta=104.878(4)°$, $V=1247.61(7)$ Å^3, $Z=4$, $\rho_{calcd}=1.258$ Mg m^{-3}, $\mu=0.6$ mm^{-1}, $T=100(2)$ K, $Cu_{K\alpha}$ radiation ($\lambda=1.54184$ Å). $wR2=0.1143$ for 165 parameters and 2578 unique reflections, with $R_1=0.0437$, GOF = 1.07. a significant difference peak of 0.8 e Å^{-3} could not be satisfactorily explained. Crystal data for **5**: $C_{16}H_{16}N_2$, $M_r=236.31$, triclinic, $P\bar{1}$, $a=10.1550(6)$, $b=11.9707(6)$, $c=12.2685(8)$ Å, $\alpha=112.448(6)°$, $\beta=106.138(6)°$, $\gamma=96.567(5)°$, $V=1282.56(13)$ Å^3, $Z=4$, $\rho_{calcd}=1.224$ Mg m^{-3}, $\mu=0.6$ mm^{-1}, $T=100(2)$ K, $Cu_{K\alpha}$ radiation ($\lambda=1.54184$ Å). $wR2=0.1063$ for 370 parameters and 5295 unique reflections, with $R_1=0.0396$, GOF = 1.09. Details of the X-ray crystal structure determinations can be found in the Supporting Information. CCDC-784154 (**2a**), 784155 (**3a**), 784156 (**3c**), 784157 (**4**) and 784158 (**5**) 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.

[23] S. N. Gradl, J. J. Kennedy-Smith, J. Kim, D. Trauner, *Synlett* **2002**, 0411–0414.

[24] DFT calculations at the B3LYP/6-31+G* level predict the orthogonal conformer of $H_2NC{\equiv}CNH_2$ to be more stable by 5.2 kcal mol^{-1} than the planar conformer, see: S. Ohashi, S. Inagaki, *Tetrahedron* **2001**, *57*, 5361–5367.

[25] S. Toyota, *Chem. Rev.* **2010**, *110*, 5398–5424.

[26] M. R. Tracey, Y. Zhang, M. O. Frederick, J. A. Mulder, R. P. Hsung, *Org. Lett.* **2004**, *6*, 2209–2212.

[27] This compound has been described previously and was obtained by a palladium-catalyzed amination of 2-bromo-*N*-methylindole: M. W. Hooper, M. Utsunomiya, J. F. Hartwig, *J. Org. Chem.* **2003**, *68*, 2861–2873.

[28] W. Kirmse, *Angew. Chem.* **1997**, *109*, 1212–1218; *Angew. Chem. Int. Ed.* **1997**, *36*, 1164–1170.

[29] a) T. Kitamura, L. Zheng, H. Taniguchi, M. Sakurai, R. Tanaka, *Tetrahedron Lett.* **1993**, *34*, 4055–4058; b) R. R. Tykwinski, J. A. Whiteford, P. J. Stang, *J. Chem. Soc. Chem. Commun.* **1993**, 1800–1801.

[30] a) K. S. Feldman, M. M. Bruendl, K. Schildknegt, *J. Org. Chem.* **1995**, *60*, 7722–7723; K. S. Feldman, M. M. Bruendl, K. Schildknegt, A. C. Bohnstedt, *J. Org. Chem.* **1996**, *61*, 5440–5452.

[31] Solvent effects are generally very important for the reactivity of α-halogenoorganolithium compounds, see for instance: G. Köbrich, *Angew. Chem.* **1967**, *79*, 15–27; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 41–52.

[32] L. M. Pratt, N. V. Nguyen, O. Kwon, *Chem. Lett.* **2009**, *38*, 574–575.

[33] A. R. Petrov, M. Tamm, unpublished results.

[34] Y. Cheng, Y.-H. Zhan, H.-X. Guan, H. Yang, O. Meth-Cohn, *Synthesis* **2002**, 2426–2430.

[35] See, for instance: a) G. R. Humphrey, J. T. Kuethe, *Chem. Rev.* **2006**, *106*, 2875–2911; b) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2005**, *105*, 2873–2920.

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