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Biradicaloids

Stable Heterocyclopentane-1,3-diyls**

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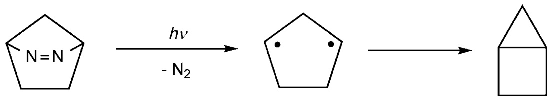
Abstract: *Diphosphadiazanediyl, $[(\mu\text{-}NR)P]_2$ (R = Ter = 2,6-dimesitylphenyl), is known to readily activate small molecules with multiple bonds. CO is an especially intriguing species for activation, because either 1,1- or 1,2-bridging mode would lead to a [1.1.1]bicycle or a carbene, respectively. The activation of CO with diphosphadiazanediyl already occurs at ambient temperatures (1 bar, 25 °C). However, CO is involved in an unprecedented ring expansion reaction under preservation of the biradical character, which leads to the formation of the first stable cyclopentane-1,3-diyl analogue displaying photochromic molecular switch characteristics.*

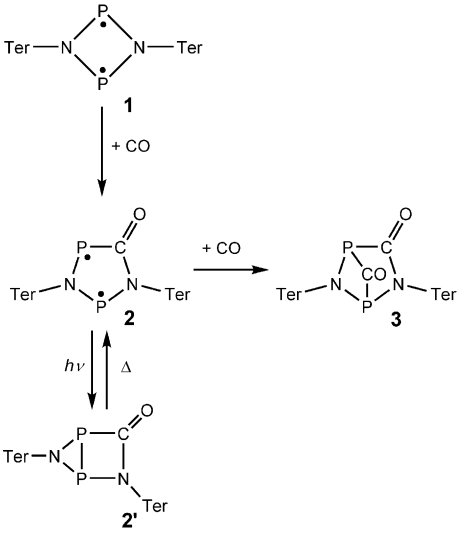
Singlet biradicaloids have been studied intensively as they are putative intermediates in the processes of bond formation and bond breaking.[1] Owing to the existence of two unpaired electrons in these molecules, their isolation is generally difficult and only possible if steric congestion is utilized to diminish their reactivity. This is especially true for five-membered biradicaloid ring molecules. Although the parent compound, cyclopentane-1,3-diyl, was already observed in 1990 by Adams et al.,[2] cyclopentane-1,3-diyls were frequently targeted in recent research by means of in situ spectroscopy and computations[3–6] and were reviewed by M. Abe lately.[7,8] The common way of generating such 1,3-biradicals is the photolytic denitrogenation of bicyclic azoalkanes (Scheme 1). Until now, these species are not isolable, because observed cyclopentanediyls have lifetimes of only below one second. However, trapping products,[9–12] ring-closed species (housanes),[4,5,10,13–16] or cyclopentenes after group migration[11,17] were obtained.



Scheme 1. Generation of cyclopentane-1,3-diyl and its ring closure to housane ([2.1.0]bicyclopentane).

Small Group 15 molecules have been in the focus of our research for several years, which led to the isolation of the first cyclo-1,3-diphospha-2,4-diazane-1,3-diyl in 2011 and the heavier homologue, diarsadiazanediyl in 2013.[18–20] Recent advances in carbonylation reactions utilizing the reactivity of frustrated Lewis pairs[21,22] stimulated our interest to explore the activation of CO by main-group singlet biradicaloids. For CO, neither the 1,1-bridging mode is anticipated to be favored, because of the high ring strain of a [1.1.1]bicycle, nor the 1,2-bridging mode, which then would be a carbene. Herein, we report on the carbonylation of diphosphadiazanediyl, which enabled the synthesis of the first stable cyclopentane-1,3-diyls by an unprecedented ring expansion of diphosphadiazanediyl.

The conversion of $[(\mu\text{-}NTer)P]_2$ (**1**, Ter = 2,6-dimesitylphenyl) with CO occurred at ambient temperature and 1 bar of CO pressure, forming biradical **2** (Scheme 2).[23] However, unlike other activations of small molecules (such as S_8, CS_2, $H_2C{=}CH_2$, $HC{\equiv}CH$) with **1**, the reaction proceeded very slowly. After 24 h, the initially orange solution had turned red, but there were still 75 % of the starting material present in the mixture according to ^{31}P NMR spectroscopy. Therefore, a steel reactor was used and the CO pressure increased to 60 bar. After 48 h full conversion was observed and **2** was obtained in 80 % yield of isolated product. The reaction can easily be followed by ^{31}P NMR spectroscopy, as **2** can be identified by a characteristic AB pattern in the ^{31}P NMR spectrum (254.1, 197.4 ppm, $^2J_{PP} = 94.2$ Hz; cf. singlet at 276.4 ppm for **1**). In addition, small amounts (< 5 %, $\delta[^{31}P] = 169.9$ and 246.3 ppm, $^2J_{PP} = 45$ Hz) of double CO addition product **3** were observed after addition of another equivalent of CO to **2**. However, sufficient amounts of **3** to



Scheme 2. Preparation of biradical **2** and housane **2′** under UV light.

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enable its isolation, even by long-term exposure of **2** to 60 bar of CO, could not be generated owing to fast CO release upon removal of CO pressure. Optimized reaction conditions of the large scale synthesis of **2** resulted in 95 % conversion of **1** into **2** after 9 h at 60 bar CO pressure. These findings were corroborated by computations of the model system $[(\mu\text{-NR})\text{P}]_2$ (**1**Ph) and two CO molecules with R = phenyl regarding the reaction mechanism and thermodynamics (Supporting Information, Figure S1).[23]

Repeated attempts to elucidate the structure of **2** by single-crystal X-ray diffraction resulted in poor data sets owing to crystal decomposition at various temperatures (−40, −100, −170 °C) but allowed the unequivocal identification of **2** (Figure 1), because the data at least confirmed the connectivity. To preclude phase transition as a possible reason for crystal decomposition, different solvates were crystallized (solvent-free and bis-thf solvate). Unfortunately, this approach was futile. As the sample was cooled with nitrogen, another sample was exposed to 100 bar of N_2 pressure at ambient temperature, but no reaction with N_2 was observed, which left the X-ray irradiation itself as a plausible cause for crystal decomposition. Thus we studied the influence of irradiation; as for the 1,3-diphospha-cyclobutane-2,4-diyl, the formation of a transannular bond could be induced by irradiation.[24] UV irradiation of deep red **2** resulted in the formation of a colorless product **2′** (Scheme 2, $\delta[^{31}\text{P}] = -105.7$, -99.4 ppm, $|J_{\text{PP}}| = 52.0$ Hz) in accord with theoretically obtained data (Supporting Information).[23] The ^{31}P shifts and relatively small $^{1}J_{\text{PP}}$ coupling constants were characteristic for $\lambda^3\lambda^3$-azadiphosphiridines, clearly indicating the formation of a housane-type product.[25,26] Isolation of the colorless product failed owing to intrinsic transformation of housane **2′** into biradical **2** (Scheme 2) within an hour at ambient temperature in benzene solution (**2**Ph→**2′**Ph, $\Delta G^{298} = 7.0$ kcal mol^{-1}; Scheme 2). The intense red color of **2** is caused by a π–π* transition in the five-membered ring ($\lambda_{\text{max}} = 531$ nm), which is supported by TD-DFT computations ($\lambda_{\text{max,theo}} = 591$ nm). Therefore, it can be assumed that upon UV irradiation the LUMO (π*) is populated, which in turn features a large coefficient for a transannular P–P bond (Figures 2 and 3). Such behavior can be referred to as a photochromic molecular switch.[27,28] In contrast to the parent species cyclopentanediyl (or housane; Scheme 1), biradical **2** (cyclopentanediyl analogue) is stabilized by intramolecular π electron delocalization (see below; Figure 2) thus the housane is less stable (7.0 kcal mol^{-1}), while for parent cyclopentanediyl there is no such stabilization possible. However, the housane **2′** also represents a stable minimum species on the potential energy surface. It should be noted that the irradiation–equilibration cycle is not fully reversible and quickly shows decomposition products.

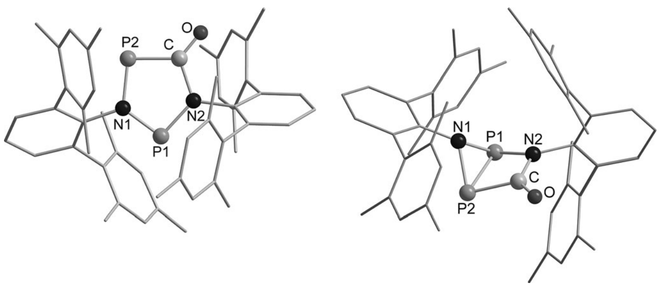


Figure 1. Calculated structures of cyclopentanediyl **2** (left) and housane **2′** (right). Selected computed bond lengths [Å] and angles [°]: **2**: P1⋯P2 2.961, N1–P1 1.687, N2–P1 1.669, N1–P2 1.741, P2–C 1.793, C–N2 1.434, C–O 1.223; P1-N1-P2 120.5, Σ_{pentagon} angles: 539.7. **2′**: P1–P2 2.167, N1–P1 1.757, N2–P1 1.797, N1–P2 1.792, P2–C 1.917, C–N2 1.382, C–O 1.208; P1-N1-P2 75.3, Σ_{pentagon} angles 462.3.

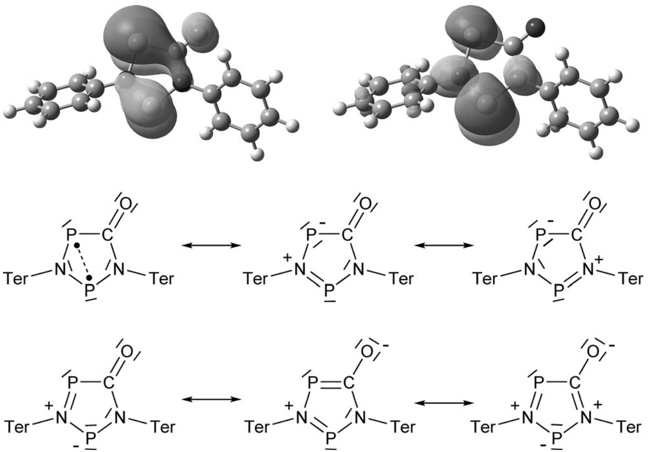


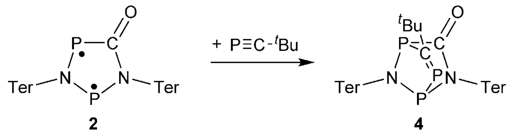
Figure 2. Top: HOMO (left) and LUMO (right) for model compound **1 Ph**; bottom: important resonance structures of **2**.[23]

More spectroscopic evidence could be derived from ^{1}H and ^{13}C NMR data revealing two magnetically inequivalent terphenyl substituents (Supporting Information).[23] The structural model of **2** was further supported by elemental analysis and mass spectrometry (CI), as there were fragments corresponding to TerNCO and TerNC, indicating a direct N–C bonding motif. Additionally, the peak with highest intensity is $\mathbf{1}^{+}$ and $[M]^{+}$ is less than 2 %, showing that CO is easily expelled upon ionization. Biradical **2** can be prepared in bulk and is extremely moisture- and air-sensitive. In the solid state as well as in solution, **2** is stable for at least six months when stored at −40 °C. The decomposition temperature of solid **2** was found to be as high as 148 °C.

Both our (poor) X-ray (of pure **2** and **2**·thf solvate) and computed structural data (pbe1pbe/6-31G(d,p))[23] are in good agreement, featuring an almost planar five-membered ring (computed deviation from planarity less than 6.2°) and also the C=O unit is embedded in the plane formed by the five-membered ring (< OCPN 178.7°). The central phenyl rings of the terphenyl groups on the nitrogen atoms are twisted to each other, forming a pocket with four mesityl groups in which the five-membered ring is very well sterically protected (Figure 1). As indicated by the P–N distances as well as NBO analysis, the N1-P1-N2 unit carries significantly more double bond character than the N1-P2-C moiety (N1–P1 1.687, N2–P1 1.669 vs. N1–P2 1.741, P2–C 1.793 Å). The transannular P⋯P distance amounts to 2.961 Å, which is rather long compared to that in biradicaloid **1** (2.612 Å; cf. $\Sigma r_{\text{cov}}(\text{P–P}) = 2.22$ Å, $\Sigma r_{\text{vdW}}(\text{P}\cdots\text{P}) = 3.35$ Å).[29] In contrast, housane **2′** exhibits a three-membered ring annulated to an almost perpendicular lying four-membered heterocycle with a P–P banana single bond (P1–P2 2.167 Å), P–N single bonds (N1–P1 1.757, N2–P1 1.797, N1–P2 1.792 Å) and a localized

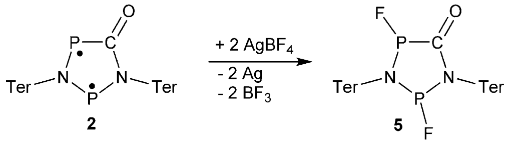
C=O double bond. These structural peculiarities of biradical **2** are also reflected by NBO/NRT analysis exhibiting resonance between biradicaloid and zwitterionic structures of the six π electrons containing five-membered heterocycle (Figure 2). NBO occupation of p atomic orbitals perpendicular to the five-membered ring amounts to 5.7 *e* (C 0.84, N1 1.70, P1 0.66, N2 1.60, P2 0.90). Furthermore, the NBO analysis revealed a 3-center–4-electron bond along the P-N-P moiety (NBO hyperbond), which is supported by the Wiberg bond indices, that total 2.42 and 2.43, respectively, for both P atoms, involving a transannular P···P contribution of 0.39. Aromaticity was also deduced from NICS calculations.[30] For **2**, NICS(0) equals −7.5 ppm and the NICS(1) values are −5.7 and −5.3 ppm, respectively. The frontier orbitals display the characteristic features of biradicals with the LUMO strongly localized on both P atoms in a bonding fashion but antibonding around the NPNP moiety and the HOMO antibonding between both P atoms but bonding along PCN and PN. Therefore, increasing the population of the LUMO results in a transannular P···P bonding situation, finally in the formation of a housane, in accord with experiment (see above). Delocalization into the CO π bond is less pronounced. CASSCF(2,2) computations confirmed the biradicaloid nature of **2**. The dominant contributions to the CI wave function for the ^{1}A state are $\Phi(^1\text{A}) = 0.94\,|\pi_1{}^2\pi_2{}^2\pi_3{}^2> -0.33\,|\pi_1{}^2\pi_2{}^2\pi_4{}^2>$.[23] A good measure for the biradical character is $\beta = 2c_2{}^2/(c_1{}^2 + c_2{}^2)$, which amounts to 0.22 (22 %) for **2** (cf. [(μ-NTer)P]$_2$ (**1**) 25 %).[18,19,31–34] Also the natural orbital occupation numbers (HOMO: 1.44 and LUMO: 0.56*e*) clearly indicate open shell singlet biradical character.[35]

As an example for the reactivity of the new cyclopentanediyl, a reaction with a phosphaalkyne was carried out (Scheme 3). Indeed, *t*Bu−C≡P readily added selectively transannular in almost quantitative yield as shown by ^{31}P NMR studies, elemental analysis, Raman spectroscopy, and X-ray structure elucidation. Full selectivity is achieved by steric congestion, which clearly favors addition of the terminal P atom of *t*Bu−C≡P to P1 in **2** and the C atom bearing the sterically demanding *t*Bu group to P2 of **2**. The pocket formed by both terphenyl substituents in **1** becomes distorted upon CO insertion leading to a better protection of the P1 atom (Figures 1 and 3). In agreement with experiment, the other isomer is computed to be 18.9 kcal mol^{-1} less favorable in energy. Upon addition of *t*Bu-C≡P the CO stretch is bathochromically shifted from 1705 cm^{-1} to 1663 cm^{-1}, which indicates stronger conjugation effects in **4** than in **2** with respect to the C=O bond. **4** exhibits an AMX pattern in the ^{31}P NMR spectrum: P2 (61.6 ppm) couples only weakly with the two other P atoms ($|^2J_{\text{PP}}| = 17.0$, 14.3 Hz), while the latter (346.3 for P3 and 145.2 ppm for P1) possess a typically large coupling of $|^1J_{\text{PP}}| = 224$ Hz. Single-crystal X-ray diffraction confirmed the molecular structure of **4** exhibiting now a puckered five-membered P$_2$N$_2$C heterocycle bridged by a P−C unit. In contrast to **2**, the [2.2.1]bicyclic central structural motif of **4** displays N−P bonds ranging from 1.733(2) to 1.749(2) Å, which clearly correspond to polarized single bonds, while the former phosphaalkyne triple C2−P3 bond is elongated to 1.6804(1) Å (cf. Σr_{cov}(P=C) = 1.69 Å).[29] Compared to **2**, the transannular P···P distance is slightly shortened and amounts to 2.8109(7) Å, but there is no bonding interaction as shown by NBO and MO analysis.



Scheme 3. Synthesis of **4**.

Furthermore, halogenation is possible, for example, by treatment with AgBF$_4$ leading to the fluorinated compound **5** (Scheme 4). Owing to the two prochiral P atoms of **2** several isomers can be formed in this reaction. Three of such isomers could be observed by ^{31}P and ^{19}F NMR spectroscopy (Supporting Information, Tables S1,S2). Some crystals suitable for X-ray structure elucidation were obtained in low yield (Figure 3), that confirmed the structure of **5** featuring a slightly puckered five-membered P$_2$N$_2$C ring (P2-N1-P1-N2 14.8(1)°) and fluorine atoms attached to the two P atoms in a trans fashion (*R*,*R* isomer). The NMR data display



Scheme 4. Synthesis of **5**.

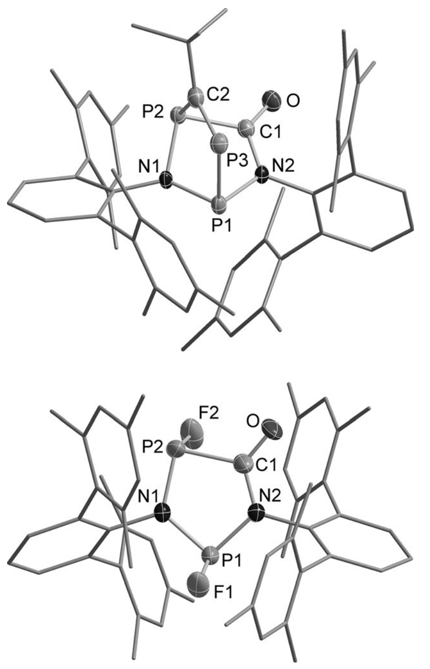
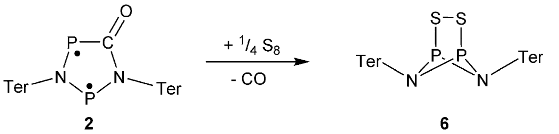


Figure 3. Molecular structure of **4** (top) and (*R*, *R*) isomer **5** (bottom).[39] Ellipsoids are set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: **4**: P1–N1 1.733(2), P1–N2 1.746(2), P1–P3 2.2855(8), P3–C2 1.680(2), O1–C1 1.209(3), N1–P2 1.749(2), P2–C2 1.870(2), P2–C1 1.875(2), P1···P2 2.8108(1); N1-P1-N2 92.83(8), N1-P1-P3 94.29(6), N2-P1-P3 96.77(6). **5**: P1–F2 1.588(3), P1–N1 1.691(3), P1–N2 1.716(2), P2–F1 1.596(3), P2–N1 1.708(2), P2–C1 1.870(8), C1–O1 1.236(9), C1–N2 1.341(8), P1···P2 2.943(3).



Scheme 5. Treatment of **2** with sulfur.

typically large $|^{1}J_{PF}|$ coupling constants of above 1000 Hz.[36–38] The $\delta[^{31}P]$ and $\delta[^{19}F]$ values, however, are considerably upfield shifted compared to the those of $[(\mu\text{-N}t\text{Bu})\text{P}-\text{F}]_2$ (cf. $\delta[^{31}P] = 165.5$, 247.9 ppm and $\delta[^{19}F] = -23.2$, -36.4 ppm).

Lastly, the reaction of **2** with elemental sulfur was studied (Scheme 5). The reaction quantitatively results in the expulsion of CO and the formation of $[(\text{TerNPS})_2]$ (**6**, $\delta[^{31}P] = 223.7$ ppm), which is already known from previous investigations.[20] This reversible binding of CO could provide an interesting approach towards catalytic activity of such singlet biradicaloids.

In conclusion, the first stable hetero-cyclopentane-1,3-diyl (**2**) was successfully prepared by insertion of CO into a P−N bond of diphosphadiazanediyl, isolated, and fully characterized. By irradiation the housane-type isomerization product could be spectroscopically characterized and these findings were rationalized with the aid of computations. Experimentally, the biradical character was confirmed by the addition reaction of a phosphaalkyne and CO as well as activation of S_8 and halogenation reactions, which are typical for main-group singlet biradicaloids.[18–20] Further investigations will be concerned with the activation of isolobal analogues of CO, namely isonitriles R−NC. We expect that this approach can be utilized to isolate more stable photochromic molecular switches, because introduction of R−NC instead of CO allows design by changing the R substituent.

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[1] F. Breher, *Coord. Chem. Rev.* **2007**, *251*, 1007–1043.
[2] J. S. Adams, R. B. Weisman, P. S. Engel, *J. Am. Chem. Soc.* **1990**, *112*, 9115–9121.
[3] D. Y. Zhang, D. A. Hrovat, M. Abe, W. T. Borden, *J. Am. Chem. Soc.* **2003**, *125*, 12823–12828.
[4] M. Abe, S. Kawanami, C. Ishihara, M. Nojima, *J. Org. Chem.* **2004**, *69*, 5622–5626.
[5] M. Abe, C. Ishihara, S. Kawanami, A. Masuyama, *J. Am. Chem. Soc.* **2005**, *127*, 10–11.
[6] M. Abe, H. Furunaga, D. Ma, L. Gagliardi, G. J. Bodwell, *J. Org. Chem.* **2012**, *77*, 7612–7619.
[7] M. Abe, J. Ye, M. Mishima, *Chem. Soc. Rev.* **2012**, *41*, 3808–3820.
[8] M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.
[9] W. Adam, J. Sendelbach, *J. Org. Chem.* **1993**, *58*, 5316–5322.
[10] M. Abe, W. Adam, W. M. Nau, *J. Am. Chem. Soc.* **1998**, *120*, 11304–11310.
[11] M. Abe, W. Adam, T. Heidenfelder, W. M. Nau, X. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 2019–2026.
[12] T. Nakamura, A. Takegami, M. Abe, *J. Org. Chem.* **2010**, *75*, 1956–1960.
[13] W. Adam, W. T. Borden, C. Burda, H. Foster, T. Heidenfelder, M. Heubes, D. A. Hrovat, F. Kita, S. B. Lewis, D. Scheutzow, J. Wirz, *J. Am. Chem. Soc.* **1998**, *120*, 593–594.
[14] M. Abe, W. Adam, M. Hara, M. Hattori, T. Majima, M. Nojima, K. Tachibana, S. Tojo, *J. Am. Chem. Soc.* **2002**, *124*, 6540–6541.
[15] T. Nakagaki, T. Sakai, T. Mizuta, Y. Fujiwara, M. Abe, *Chem. Eur. J.* **2013**, *19*, 10395–10404.
[16] M. Abe, M. Hattori, A. Takegami, A. Masuyama, T. Hayashi, S. Seki, S. Tagawa, *J. Am. Chem. Soc.* **2006**, *128*, 8008–8014.
[17] M. Abe, W. Adam, W. T. Borden, M. Hattori, D. A. Hrovat, M. Nojima, K. Nozaki, J. Wirz, *J. Am. Chem. Soc.* **2004**, *126*, 574–582.
[18] T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2011**, *50*, 8974–8978; *Angew. Chem.* **2011**, *123*, 9136–9140.
[19] S. Demeshko, C. Godemann, R. Kuzora, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2013**, *52*, 2105–2108; *Angew. Chem.* **2013**, *125*, 2159–2162.
[20] A. Hinz, A. Schulz, A. Villinger, *Chem. Eur. J.* **2014**, *20*, 3913–3916.
[21] M. Sajid, A. Lawzer, W. Dong, C. Rosorius, W. Sander, B. Schirmer, S. Grimme, C. G. Daniliuc, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2013**, *135*, 18567–18574.
[22] M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2013**, *52*, 2243–2246; *Angew. Chem.* **2013**, *125*, 2299–2302.
[23] The Supporting Information contains details of the synthesis, spectroscopic characterization, and computational details.
[24] E. Niecke, A. Fuchs, M. Nieger, *Angew. Chem. Int. Ed.* **1999**, *38*, 3028–3031; *Angew. Chem.* **1999**, *111*, 3213–3216.
[25] R. Streubel, E. Niecke, P. Paetzold, *Chem. Ber.* **1991**, *124*, 765–767.
[26] E. Niecke, A. Nickloweit-Lüke, R. Rüger, B. Krebs, H. Grewe, *Z. Naturforsch. B* **1981**, *36*, 1566–1574.
[27] E. C. Harvey, B. L. Feringa, J. G. Vos, W. R. Browne, M. T. Pryce, *Coord. Chem. Rev.* **2014**, 1–10.
[28] B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816.
[29] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779.
[30] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. V. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888.
[31] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 555–557; *Angew. Chem.* **1995**, *107*, 640–642.
[32] K. C. Mondal et al., *Inorg. Chem.* **2013**, *52*, 4736–4743.
[33] K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 1801–1805; *Angew. Chem.* **2013**, *125*, 1845–1850.
[34] Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrada, *J. Am. Chem. Soc.* **2013**, *135*, 12422–12428.
[35] M. S. Gordon, M. W. Schmidt, G. M. Chaban, K. R. Glaesemann, W. J. Stevens, C. Gonzalez, *J. Chem. Phys.* **1999**, *110*, 4199–4207.
[36] A. V. Cunliffe, E. G. Finer, R. K. Harris, W. McFarlane, *Mol. Phys.* **1967**, *12*, 497–499.
[37] J. F. Nixon, B. Wilkins, *Z. Naturforsch. B* **1970**, *B25*, 649–651.
[38] R. Keat, D. S. Rycroft, E. Niecke, H. Schäfer, H. Zorn, *Z. Naturforsch. B* **1982**, *37*, 1665–1666.
[39] CCDC 1042900 (**4**) and CCDC 1042899 (**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.