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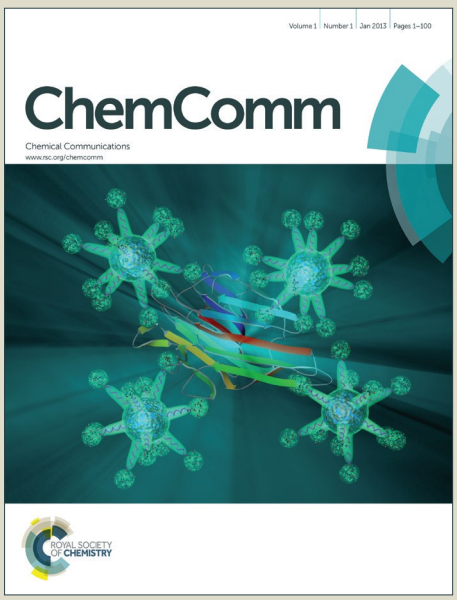

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Intramolecular Cooperativity in Frustrated Lewis Pairs

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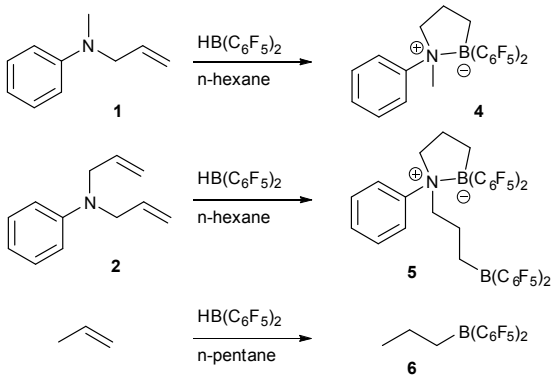
The doubly Lewis-acid functionalised aniline $PhN[(CH_2)_3B(C_6F_5)_2]_2$ features two competing boron functions in fast exchange for binding to the central Lewis base. It shows catalytic activity typical for FLPs in H/D-scrambling and catalytic hydrogenation experiments. By contrast, the singly acid-functionalised $PhMeN(CH_2)_3B(C_6F_5)_2$ reveals a dramatically smaller catalytic activity in analogous experiments.

Since the discovery of their enormous potential as hydrogenation catalysts as well as in the activation of small molecules by Stephan and co-workers,[1] the concept of frustrated Lewis pairs (FLPs) has shed new light onto numerous observations in chemistry.[2] The basic FLP principle is to combine sterically encumbered Lewis bases and acids such as $P(^tBu)_3$ and $B(C_6F_5)_3$, so that they are unable to form a classic Lewis adduct.[3] This principle was extended shortly after its discovery by the design of intramolecular FLPs.[4] In these systems adduct formation is disadvantaged by intramolecular ring strain. Erker *et al.* have demonstrated that $Mes_2P(CH_2)_2B(C_6F_5)_2$, a four-membered ring system, is highly active in hydrogenation, whereas the less strained five-membered ring system $Mes_2P(CH_2)_3B(C_6F_5)_2$ is not.[5] Other intramolecular FLPs include carbenes[6] as well as phosphidoboranes[7] with weak, frustrated interactions of two adjacent orbitals. Besides heterolytic hydrogen splitting, some of these systems are capable of activating small molecules like CO_2 and SO_2.[8] FLP reactivity was found for different types of acid/base combinations, mainly for group 15 Lewis bases (N, P) in combination with boron, aluminum,[9] silicenium,[10] silicon,[11] zinc[12] and zirconium[13] Lewis acids. Berke *et al.* prepared used the doubly Lewis acid functionalized naphthalene, also known as hydride sponge, in an intermolecular FLP and found cooperative hydride complexation.[14] All these FLPs are based on the same above mentioned principles of hindered Lewis adduct formation. Stephan and Pápai have shown, that classic Lewis adducts can also serve as hidden FLPs; e.g. by exposure to a hydrogen atmosphere at 80 °C the thermal bond dissociation of $PhCH_2NH(^tBu)B(C_6F_5)_3$ results in a system that cleaves hydrogen heterolytically.[15] Diethylether in combination with $B(C_6F_5)_3$ does not split hydrogen in a stoichiometric manner, but the small equilibrium concentration of split hydrogen in this mixture is capable of olefine hydrogenation.[16]

In order to investigate the possibility of cooperative effects in FLP chemistry, we prepared aniline based intramolecular FLP systems with one and two $B(C_6F_5)_2$ functions linked *via* 1,3-propandiyl units to the nitrogen atom. For this purpose, *N*-allyl-*N*-methylaniline (**1**) and *N*,*N*-diallylaniline[17] (**2**) were hydroborated with Piers' borane, $HB(C_6F_5)_2$ (**3**)[18] (Scheme 1), to afford $PhMeN[(CH_2)_3B(C_6F_5)_2]$ (**4**) and $PhN[(CH_2)_3B(C_6F_5)_2]_2$ (**5**), respectively. These were characterised by multinuclear NMR spectroscopy, mass spectrometry and CHN elemental analyses. For reasons of comparison, we also prepared bis(pentafluorophenyl)propylborane **6**, as a model for an independent Lewis-acid side-arm of **5** (Scheme 1).



Scheme 1. Hydroboration of mono **1** and diallylanilines **2** as well as propene with Piers' borane **3**.

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CCDC 1449801 contains the supplementary crystallographic data for this paper. These data can be obtained via www.ccdc.cam.ac.uk/data_request/cif. free of charge from The Cambridge Crystallographic Data Center.

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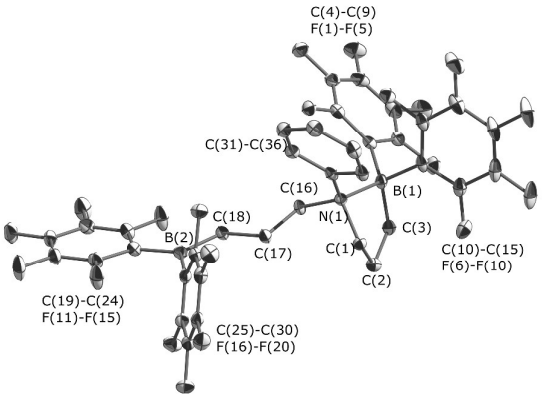

Figure 1. Molecular structure of dihydroboration product **5** in the solid state. Hydrogen atoms were omitted for clarity. Selected bond length [Å] and angles [°]. C(1)–N(1) 1.525(2), C(31)–N(1) 1.490(2), C(16)–N(1) 1.519(2), B(1)–N(1) 1.718(2), C(3)–B(1) 1.632(3), C(18)–B(2) 1.568(2), B(1)–N(1)–C(1) 99.0(1), C(1)–N(1)–C(31) 109.6(1), C(1)–N(1)–C(16) 107.4(1), N(1)–B(1)–C(3) 97.6(1), N(1)–C(1)–C(2) 106.9(1), C(1)–C(2)–C(3) 105.4(1), C(2)–C(3)–B(1) 108.3(1).

The molecular structure of **5** (Figure 1, for crystallographic details see ESI) in the solid state shows the formation of a five-membered heterocycle in envelope conformation, with the C(1)–C(2)–C(3)–B(1) unit (torsion angle = 2.7(1)°) being almost planar, N(1) lying above the plane. The torsion angle C(3)–C(2)–C(1)–N(1) is 33.1(2)°. The second Lewis-acid site points away from the heterocycle with the 1,3-propandiyl spacer in all-*anti* conformation. The B–N bond length [1.718(2) Å] is longer than in earlier reported analogous mono-hydroborated dialkylallylamines $R_2N(CH_2)_3B(C_6F_5)_2$ (R = CH_3, C_2H_5, R_2 = -$(CH_2)_5$-, 1.67–1.69 Å).[19] This is attributed to the lower basicity of the aniline derivative. Multiple crystallisation attempts to obtain suitable crystals of **4** for X-ray diffraction failed, but computational studies of **4** ($d_{B,N}$ = 1.722 Å) and **5** ($d_{B,N}$ = 1.728 Å) (PBEh-3c**,** for details see ESI) revealed only little effects of the second $(CH_2)_3B(C_6F_5)_2$ side-arm on the B–N distance. This indicates small to negligible steric effects by this second function.

^{1}H and ^{19}F NMR spectra of the mono-functionalised compound **4** reveal B–N adduct formation in a five-membered ring structure in solution. Spectra recorded at ambient temperature show broadened resonances for the 1,3-propandiyl spacer and the C_6F_5 groups due to inversion of the five-membered B/N heterocycle. At 363 K, these averaged resonances are sharp due to fast flipping on the NMR timescale. The well-resolved ^{11}B resonance at 363 K at 4.6 ppm is typical for tetra-coordinate boron atoms. The observations are consistent with a closed-ring structure of **4** undergoing endothermic ring opening only to a very minor extent as described by Boltzmann distribution.

A different situation is observed for the doubly $B(C_6F_5)_2$-substituted compound **5**. Variable temperature NMR measurements of CD_2Cl_2 solutions revealed fast exchange of the two boron Lewis acids competing for binding to the central Lewis base (Figure 2). At ambient temperature, this fast exchange leads to only one set of signals with averaged chemical shifts for both 1,3-propandiyl spacers, for the boron nuclei as well as for the four C_6F_5 groups. The ^{11}B NMR resonance at 40.6 ppm represents an averaged chemical shift of three- and tetra-coordinate boron (compare 75.2 ppm in **6** and 3.7 ppm in **4**). The averaged ^{1}H resonances split at low temperatures. This is best seen for the two CH_2 groups bonded to the central nitrogen atom (Figure 2, •). Due to the formation of a stereocenter at nitrogen, when exchange is slow at 193 K, four resonances are observed for these CH_2 protons. As the coalescence method only applies for two site systems, thermodynamic data could not be obtained from these measurements.[20] The resonances of the other CH_2 groups are also split, but a full assignment was hampered by mutual overlap of the signals. Low-temperature ^{11}B NMR measurements were impeded by the temperature dependence of the quadrupole broadening of the I = 1 nucleus, precluding the observation of resonances.[21] Determination of thermodynamic data from ^{11}B NMR spectra using the coalescence method was thus also excluded.

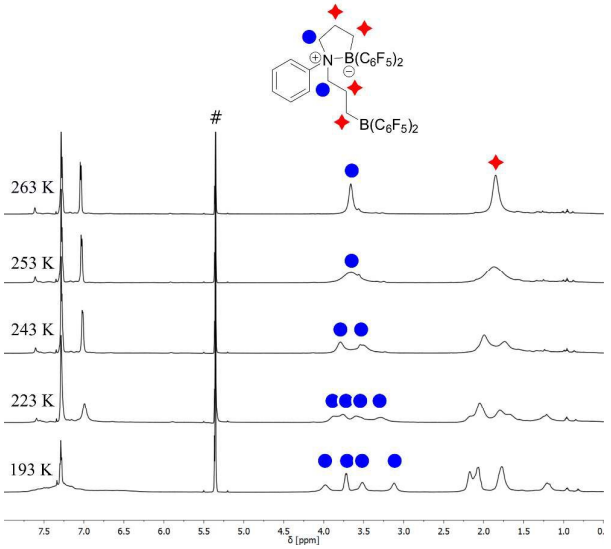

Figure 2. Excerpt of the variable temperature NMR spectra of compound 5 (600 MHz, CD_2Cl_2 #). The coalescence resonance of the two CH_2 groups • bonded to nitrogen split at low temperature when dynamic exchange is slow on the NMR timescale.

Treatment of the doubly Lewis-acid functionalised compound **5** with one atmosphere of hydrogen, carbon dioxide, CS_2 and SO_2 led to no observable reactions in NMR experiments. Anyhow, FLPs which do not show stoichiometric hydrogen splitting can still serve as "hidden" FLPs, providing the hydrogen splitting products in a small equilibrium concentration. This can be proven in H/D-scrambling experiments.[16,22] Unexpectedly, **5** was found to be catalytically active in H/D-scrambling ^{1}H NMR experiments, i.e. the conversion of a H_2/D_2 mixture into HD at ambient temperature (0.04 M solution of **5** in CD_2Cl_2 + 1 atm H_2/D_2(1:1)). Formation of HD was observed as a characteristic triplet at 4.57 ppm with a coupling constant $^1J_{D,H}$ of 42.7 Hz. After 15 minutes 12% of HD were formed and complete isotopic equilibration of H_2/HD/D_2 at a ratio of 1:2:1 (100% HD formation) was observed after 18 hours (for NMR spectra see ESI). This clearly proves the equilibrium existence of the hydrogen splitting products of **5** in solution.

The question arises, whether the observed activity is simply thermal activation of a classic Lewis pair, or has to be attributed to the presence of the second Lewis-acid function in **5**. Therefore, the H/D-scrambling experiment was repeated with the singly acid-functionalised compound **4**. It revealed a drasti-

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cally lower activity: no formation of HD was observable within the first days and after two weeks only about 6% HD were formed (for spectra see ESI). This represents a very low catalytic activity of the mono acid-functionalised Lewis pair **4** at room temperature. Consequently, the much higher activity of compound **5** has to be addressed to the presence of its second Lewis-acid function. A further question arises: does the second Lewis-acid function need to be present in an intramolecular fashion, or will additional free Lewis acids also result in the same reactivity pattern? Addition of bis(pentafluorophenyl)-propylborane (**6**), representing the "cut-off" second Lewis-acid side-arm of **5**, or $B(C_6F_5)_3$ (**7**) to Lewis pair **4** does not change its NMR spectra. This indicates that substitution or exchange of the internal Lewis acid in **5** by an external one does not take place in solution to an appreciable extent, certainly for entropic reasons. H/D-scrambling experiments with these mixtures, **4**+**6** and **4**+**7**, resulted in no formation of HD within the first days and only about 8% within two weeks. Being practically the same activity as observed solely for Lewis pair **4**, this proves the presence of the intramolecular bound second Lewis-acid side-arm in **5** to be responsible and necessary for the H/D-scrambling activity.

To elucidate the observed reactivity difference between singly and doubly acid-functionalised **4** and **5**, we performed quantum-chemical calculations. As HD-formation proceeds *via* intermolecular H/D-exchange, the activity difference of the singly and doubly acid-functionalised catalysts **4** and **5** in scrambling experiments is addressed to different concentrations and lifetimes of the hydrogen splitting products **4-H_2/4-D_2** and **5-H_2/5-D_2** in solution. These are correlated with the free reaction energies of hydrogen splitting, which are, in good approximation, accessible *via* quantum-chemical calculations.[22] Differences in the reaction energies are expected to occur in either the B–N-ring opening or the heterolytic hydrogen addition to the ring-opened forms of **4** and **5**. Gibbs free energies of the closed forms **closed-4/5**, the open-chain forms **open-4/5** and the hydrogen splitting products **4/5-H_2** were calculated at the PW6B95-D3/def2-TZVP/COSMO(CH_2Cl_2)//PBEh-3c level of theory (details see ESI). The calculated thermodynamic data indicated no significant difference in reactivity towards hydrogen splitting between **4** and **5** (Figure 3).

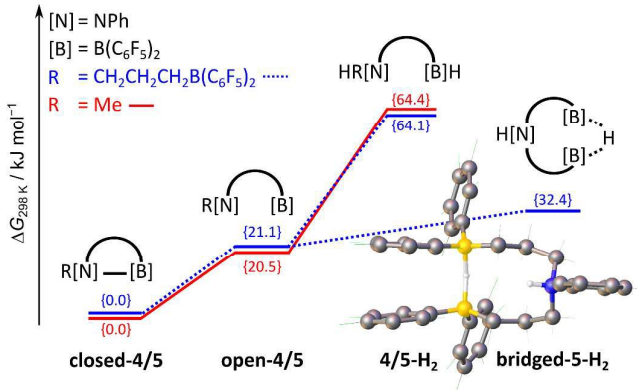


Figure 3. Calculated Gibbs free reaction energies (PW6B95-D3/def2-TZVP/COSMO(CH_2Cl_2)//PBEh-3c) of the relevant species of hydrogen splitting by singly **4** (red) and doubly acid functionnalised FLP **5** (blue).

However, as **5** contains an additional Lewis-acid function, an alternative hydride binding motif, the intramolecular complexation by two boron atoms, was explored. This structure **bridged-5-H_2** was found to be a minimum on the potential energy surface of the hydrogen adduct of **5**, 32 kJ mol^{-1} lower in energy than the open-chain form. Thus, the high H/D-scrambling activity of **5**, in contrast to **4**, can essentially be attributed to the cooperative hydride stabilisation by the second Lewis-acid site.

The catalytic activity of **5** was also tested in hydrogenation experiments of 1,1-diphenyl ethylene (**8**), 1-(cyclopent-1-en-1-yl)piperidine (**9**), *N*-benzylidene-*tert*-butylamine (**10**) and (β-styryloxy)trimethylsilane (**11**), as benchmark for the most common substrates used in FLP chemistry. The hydrogenations were performed in high-pressure NMR tubes (6 Mol% catalyst, 6 bar H_2). No catalytic reduction was observed for diphenyl ethylene (**8**) and enamine **9**, but imine **10** (58% conversion in 24 h) and silylenol ether **11** (63% conversion in 20 h) were hydrogenated at ambient temperature.

In order to obtain insights into the effect of the second Lewis-acid function and the nature of the substrate on the catalytic activity, four parallel hydrogenation experiments with each, imine **10** and silylenol ether **11**, were performed employing the following catalyst systems (Table 1):

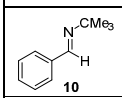
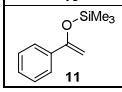
(a) singly Lewis-acid functionalised Lewis pair **4**, to identify a possible catalytic activity of the mono-acid functionalised derivative,

(b) bifunctional catalyst **5**, to determine the catalytic activity induced by its second acid function,

(c) a 1:1 mixture of Lewis pair **4** and propylborane **6**, to see whether intermolecular cooperativity plays a role, and

(d) sole propylborane **6**, to mimic the dangling Lewis-acid arm in **5** and to identify its possible independent activity in combination with a substrate.

Table 1. Catalytic reduction of imine **10** and silylenol ether **11** with the different catalyst systems **4**-**6**.

Substrate	Time	(a) 4	(b) 5	(c) 4+6	(d) 6
 **10**	4 h	<1%	42%	49%	49%
	18.5 h	<1%	100%	100%	100%
 **11**	4 h	<1%	42%	25%	<1%

For each substrate all four experiments, (a) – (d), (6 Mol% catalyst, 6 bar H_2) were simultaneously performed in one steel autoclave to ascertain identical conditions concerning hydrogen pressure and quality. Table 1 shows **5** to be an active catalyst in all cases. In contrast, compound **4** is practically inactive as catalyst for both substrates. This proves that the second acid function is also essential to the activity of **5** in hydrogenation reactions. Not unexpectedly, sole Lewis acid **6**, mimicking the dangling Lewis-acid side-arm of **5**, is catalytically active for imine **10**. This parallels earlier observations[15] of sole $B(C_6F_5)_3$ catalysing the reduction of **10**, i.e. imine **10** acts simultaneously as substrate and part of the catalyst. As expected from these

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results, a mixture of **4** and **6** also shows catalytic activity towards reduction of imine **10**. Consequently, imine system **10** is not suitable to distinguish between a catalytic activity of **5** due to (a) cooperative hydride complexation, as observed in H/D-scrambling experiments, and (b) due to an effect of the sole dangling acid of **5**. Anyhow, the latter point is clarified as unimportant as the sole Lewis acid **6** is inactive in hydrogenation of silylenol ether **11** (Table 1, line 2), probably due to its poor basicity. The catalytic activity of catalyst **5** towards reduction of **11** has therefore to be addressed to a cooperativity of both Lewis acids. Interestingly, a mixture of **4**+**6** is active in the hydrogenation of silylenol ether **11**, although its activity is somewhat less than that of **5**. This observation possibly indicates a more complex intermolecular cooperative mechanism in the reduction experiments of the silylenol ether.

In essence, the above facts show, that the presence of two $B(C_6F_5)_2$ acid groups in catalyst **5** leads to catalytic activity in H/D-scrambling as well as in hydrogenation experiments, whereas the singly acid-functionalised compound **4** is much less active. Quantum-chemical investigations revealed that the hydrogen-splitting product of FLP **5** is stabilised by a chelate-type hydride binding by both boron Lewis-acid functions. As a result, this concept decreases the hydrogen splitting reaction energy without increasing the Lewis acidity. The latter would counterproductively increase the barrier to thermal activation of B–N cleavage. In this way the described cooperative effect can be used to tune the activity of FLP systems.

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Notes and references

1 a) G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126. b) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 8050–8053.

2 For a detailed overview, see the following reviews: a) D. W. Stephan, *Dalton Trans.*, 2009, 3129–3136; b) D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46–76; c) D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400–6441; d) D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032.

3 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881.

4 a) K. Chernichenko, M. Nieger, M. Leskela and T. Repo, *Dalton Trans.*, 2012, **41**, 9029–9032; b) S. Schwendemann, R. Fröhlich, G. Kehr and G. Erker, *Chem. Sci.*, 2011, **2**, 1842–1849; c) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskelä, T. Repo, P. Pyykkö and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117–14119.

5 a) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem. Int. Ed.*, 2008, **47**, 7543–7546. b) P. Spies, R. Fröhlich, G. Kehr, G. Erker and S. Grimme, *Chem. Eur. J.*, 2008, **14**, 333–343; c) P. Spies, G. Kehr, K. Bergander, B. Wibbeling, R. Fröhlich and G. Erker, *Dalton Trans.*, 2009, 1534–1541; d) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.,* 2007, 5072–5074; e) T. Özgun, K-Y. Ye, C. Daniliuc, B. Wibbeling, L. Liu, S. Grimme, G. Kehr and G. Erker, *Chem. Eur. J.*, 2016, **22**, 5988-5995.

6 a) G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439–441; b) P. A. Chase and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2008, **47**, 7433–7437.

7 S. J. Geier, T. M. Gilbert and D. W. Stephan, *J. Am. Chem. Soc.*, 2008, **130**, 12632–12633.

8 a) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643–6646, b) M. Sajid, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 213-219.

9 a) G. Ménard, J. A. Hatnean, H. J. Cowley, A. J. Lough, J. M. Rawson and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 6446–6449; b) C. Appelt, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed.*, 2013, **52**, 4256–4259; c) L. Keweloh, H. Klöcker, E.-U. Würthwein and W. Uhl, *Angew. Chem. Int. Ed.*, 2016, **55**, 3212–3215.

10 a) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann and T. Müller, *Chem. Eur. J.*, 2014, **20**, 9381–9386; b) M. Reißmann, A. Schäfer, S. Jung and T. Müller, *Organometallics*, 2013, **32**, 6736–6744.

11 a) S. A. Weicker and D. W. Stephan, *Chem. Eur. J.*, 2015, **21**, 13027–13034; b) B. Waerder, M. Pieper, L. A. Körte, T. A. Kinder, A. Mix, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Angew. Chem. Int. Ed.*, 2015, **54**, 13416–*13419.*

12 a) R. Dobrovetsky and D. W. Stephan, *Isr. J. Chem.*, 2015, **55**, 206–209; b) P. Jochmann and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9831–9835.

13 a) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 8826-8829; b) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 18463-18478; c) O. J. Metters, S. J. K. Forrest, H. A. Sparks, I. Manners and D. F. Wass, *J. Am. Chem. Soc.*, 2016, **138**, 1994-2003.

14 C. Jiang, O. Blacque and H. Berke, *Chem. Commun.*, 2009, 5518-5520.

15 P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701–1703; b) T. Rokob, A. Hamza, A. Stirling and I. J. Pápai, *J. Am. Chem. Soc.*, 2009, **131**, 2029-2036;

16 L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2013, **52**, 7492–7495.

17 B. Schmidt, S. Krehl and E. Jablowski, *Org. Biomol. Chem.*, 2012, **10**, 5119–5130.

18 a) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503; b) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed.*, 1995, **34**, 809–811.

19 D. Winkelhaus, B. Neumann, H.-G. Stammler, R. J. F. Berger, Yu. V. Vishnevskiy and N. W. Mitzel, *Chem. Eur. J.*, 2012, **18**, 9312–9320.

20 a) J. Sandström, *Dynamic NMR spectroscopy*, Academic Press, London, New York, 1982; b) M. Ōki, *Applications of dynamic NMR spectroscopy to organic chemistry*, VCH Publishers, Deerfield Beach, FL, 1985.

21 a) J. P. Kintzinger and J. M. Lehn, *Mol. Phys.*, 1968, **14**, 133–145; b) H. C. Brown, U. S. Racherla and P. J. Pellechia, *J. Org. Chem.*, 1990, **55**, 1868–1874.

22 L. A. Körte, R. Warner, Yu. V. Vishnevskiy, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Dalton Trans.*, 2015, **44**, 9992–10002.

23 T. A. Rokob, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2009, **131**, 10701–10710.