ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c6cc02607a

Received 27th March 2016,
Accepted 13th April 2016

DOI: 10.1039/c6cc02607a

www.rsc.org/chemcomm

Cooperative Lewis acidity in borane-substituted fluorophosphonium cations†

Juri Möbus,‡ Thorsten vom Stein‡ and Douglas W. Stephan*

A series of aryl-difluorophosphoranes are converted to give fluorophosphonium salts $[Ph_2PF(o\text{-}C_6X_4BR_2)]^+$ (X = H, F; R = Cy, Mes). The proximity of the two weakly Lewis acidic fluorophosphonium and borane moieties results in enhanced Lewis acid catalytic reactivity.

Since the articulation of the concept of frustrated Lewis pairs (FLPs),[1] there has been considerable interest in the chemistry and development of potent Lewis acidic species.[2] While a number of investigations have focused on group 13 compounds as well as some examples of group 14 Lewis acids,[3] we have focused recent attention on a range of group 15 Lewis acids, exploiting the low energy σ* orbital of electrophilic phosphonium cations (EPCs) as Lewis acids.[4] These systems have been employed in a series of catalyses including hydrodefluorination,[4a] dehydrocoupling,[5] hydrosilylation,[6] FLP hydrogenations,[7] ketone deoxygenations[8] and phosphine-oxide reductions.[9] Since this work, we have probed strategies to enhance the Lewis acidity at phosphorus. While the incorporation of electron deficient substituents is an obvious approach, the introduction of positively charged centers has also shown to improve Lewis acidity.[10] In a related sense, the pioneering work of Gabbaï and others showed that the introduction of two Lewis acidic moieties into one molecule showed significantly increased binding constants for hydride and fluoride ions.[11] Using this strategy, Gabbaï developed systems in which the proximity of a phosphonium cation enhanced fluoride binding to a neutral boron center yielding highly effective fluoride ion sensors **A** (Fig. 1).[11h,j,k]

We sought to employ a similar approach to enhance Lewis acidity for catalytic applications. To this end, we have recently described the facile conversion of common bidentate phosphines to bis-fluorophosphonium dication Lewis acid catalysts.[10b–d] Exploring an alternative approach, we now report the synthesis

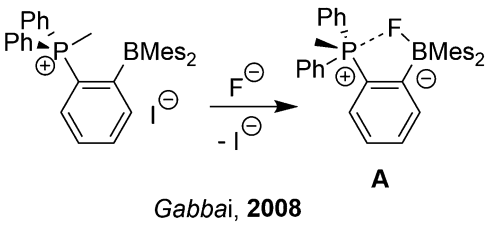
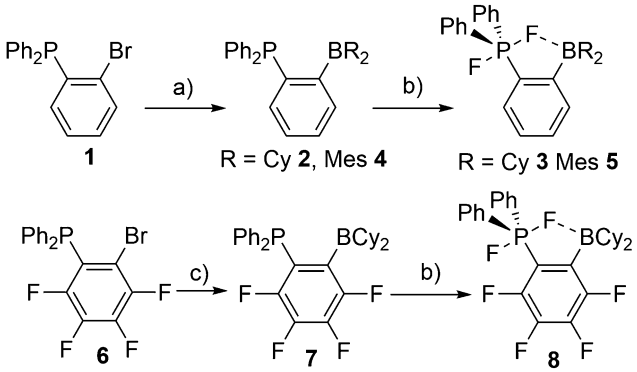


Fig. 1 A Gabbai fluoride ion sensor.

of aryl-fluorophosphonium cations in which a neutral borane fragment is placed *ortho-* to the phosphonium fragment. The nature of the impact of proximity of the two Lewis acidic centers on the catalytic chemistry is probed and discussed in comparison with known systems.

The species $Ph_2P(o\text{-}C_6H_4BCy_2)$ **2** was prepared as a colorless oil in 64% isolated yield *via* lithiation of the commercially available $Ph_2P(o\text{-}C_6H_4Br)$ **1**[12] in THF at −30 °C followed by quenching with $ClBCy_2$ (Scheme 1). Subsequent oxidation of **2** with XeF_2 in CH_2Cl_2 generates the corresponding pure difluorophosphorane $Ph_2PF_2(o\text{-}C_6H_4BCy_2)$ **3** which was crystallized from pentane



Scheme 1 Synthesis of **2–5** and **7–8**. (a) 1.1 eq. *n*-BuLi, THF, −30 °C, 1 h, then 1 eq. R_2BCl (R = Cy, Mes), −30 °C to RT, 20 h. (b) XeF_2, CH_2Cl_2, RT, 20 h. (c) 1.1 eq. i-PrMgCl LiCl, Et_2O, −60 °C, 4 h, then 1 eq. Cy_2BCl, −60 °C to RT, 20 h.

Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, M5S 3H6, Canada. E-mail: dstephan@chem.utoronto.ca

† Electronic supplementary information (ESI) available: Experimental details and spectral data have been deposited. CCDC 1470769–1470772. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02607a

‡ These authors contributed equally.

solution at −30 °C in 82% yield. In a similar fashion, the analogous species $Ph_2P(o\text{-}C_6H_4BMes_2)$ **4** was prepared in 87% yield and converted to $Ph_2PF_2(o\text{-}C_6H_4BMes_2)$ **5** (Scheme 1). In addition, magnesiation of 1,2-dibromotetrafluorobenzene employing Knochel's "Turbo-Grignard" reagent[13] followed by quenching with $ClPPh_2$ gave the known species $Ph_2P(o\text{-}C_6F_4Br)$ **6**[14] in 84% yield. This product was subsequently converted to the phosphine–borane **7** in 90% yield. Oxidation with XeF_2 proceeds smoothly at −35 °C affording the difluorophosphorane $Ph_2PF_2(o\text{-}C_6F_4BCy_2)$ **8** in 95% yield (Scheme 1).

In the case of **3**, the room temperature ^{11}B NMR spectrum shows a resonance at $\delta^{11}B$ +29.7 ($\nu_{1/2} \sim 710$ Hz) clearly indicating an interaction of a fluorine atom with the boron center. This is also evident in the corresponding broad ^{19}F NMR resonances at δ −76.0 and −76.8 (see ESI†). Cooling to −80 °C, the ^{19}F NMR spectrum shows two distinct doublets at δ −75.3 ($^1J_{PF}$ = 725 Hz) and δ −83.1 ($^1J_{PF}$ = 267 Hz), while the ^{31}P NMR spectrum showed the corresponding doublet of doublets, at δ −9.7 (see ESI†). By comparison, the room temperature spectra of compound **8** ($\delta^{11}B$ +30.7) exhibit a sharp doublet of doublets resonance in the ^{19}F NMR spectrum at $\delta^{19}F$ −66.6 ($^1J_{PF}$ = 547 Hz, J_{FF} = 71 Hz) and a corresponding triplet resonance in the ^{31}P NMR spectrum (δ −9.8), typical for a difluorophosphorane unit. Upon cooling, the NMR spectra of compound **8** exhibit similar features to those of the system **3**. These data are consistent with slow rotation about the P–C bond to the aryl linker thus differentiating the two P–F bonds as a result of a weak interaction of one of the fluorine atoms with the boron center.[15] The corresponding ^{11}B NMR resonances were not observed due to temperature induced broadening of the signals at low temperatures.

X-ray crystallographic analyses confirmed the structures of **3** and **8** as difluorophosphoranes with *ortho*-BCy_2 fragments (Fig. 2). The coordination geometries about the P-atoms are distorted trigonal bipyramidal with the sum of the C–P–C angles being 358.0(1)° in **3** and 358.4(1)° in **8**, while the F–P–F angles are 179.0(1)° and 178.76(8)° in **3** and **8** respectively. The boron centers approach tetrahedral geometry with the sum of the C–B–C angles being 346.0(1)° in **3** and 350.5(1)° in **8**. In each case, one of the fluorine atoms on P interacts with the proximal B atom, accounting for the distortion from trigonal planarity. The P–F bond proximal to boron is significantly elongated in comparison to the *trans*-P–F bond. In compound **3**, the P–F(2) distance is 1.9381(8) Å while the other P–F distance amounts to 1.6206(9) Å. In comparison, in **8** the corresponding distances are slightly different at 1.854(1) Å and 1.609(1) Å. The corresponding B–F contacts are 1.640(2) Å and 1.665(2) Å in **3** and **8**, respectively.

Subsequent reaction of **3**, **5** and **8** with $[Et_3Si][B(C_6F_5)_4]$ (Scheme 2) resulted in fluoride abstraction and the *ortho*-boryl substituted fluorophosphonium compounds $[Ph_2PF(o\text{-}C_6H_4BR_2)][B(C_6F_5)_4]$ (R = Cy **9**, Mes **10**) and $[Ph_2PF(o\text{-}C_6F_4BCy_2)][B(C_6F_5)_4]$ **11** were obtained in 76%, 82% and 93% yield. NMR data for compounds **9–11** showed the expected, significant increase in the $^1J_{PF}$ coupling constants (**9:** 980 Hz, **10:** 1000 Hz and **11:** 977 Hz) in comparison to the precursor difluorophosphoranes. Interestingly these coupling constants are lower than those observed

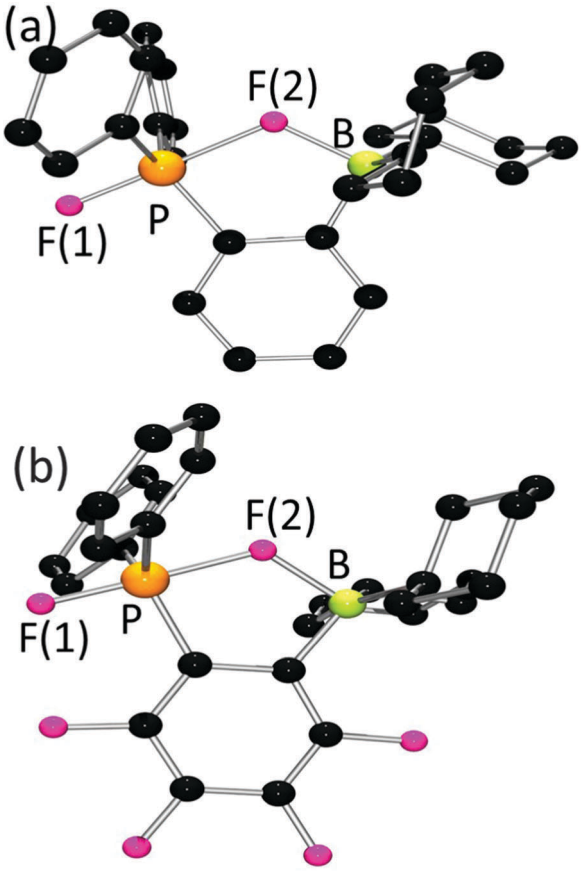
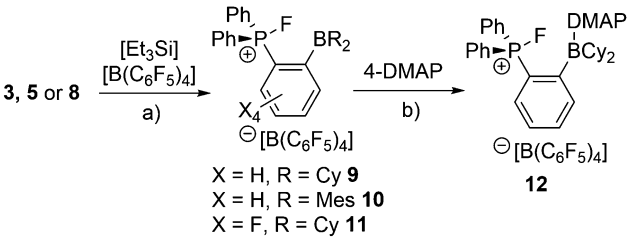


Fig. 2 Solid-state structures of the difluorophosphoranes (a) **3** and (b) **8**, H-atoms are omitted for clarity. Carbon: black; fluorine: pink; phosphorus: orange; boron: yellow-green. Selected bond lengths (Å) and angles (°): **3**: P–F(1): 1.6206(9), P(1)–F(2): 1.9381(8), B–F(2): 1.640(2), F(1)–P–F(2): 178.96(4), P–F(2)–B: 119.43(7), **8**: P–F(1): 1.609(1), P–F(2): 1.854(1), B–F(2): 1.665(2), F(1)–P–F(2): 178.76(8), P–F(2)–B: 122.2(1).



Scheme 2 Preparation of **9–12**: (a) 0.9–0.95 eq. $[Et_3Si][B(C_6F_5)_4]$, −35 °C to RT, 1–3 h, toluene; (b) 1.0 eq. 4-DMAP, CD_2Cl_2, RT, 1 h.

for the unsubstituted analogs.[16] The ^{11}B NMR shifts for **9–11** range from 73.5–84.8 ppm consistent with three coordinate boron centers.

Single crystals of compounds **9** and **11** were characterized by X-ray diffraction. Both solid-state structures (Fig. 3) show a distorted tetrahedral environment around phosphorus with P–F bond distances of 1.554(2) Å and 1.555(2) Å in **9** and **11**, respectively. These values are typical for fluorophosphonium cations.[17] In the solid state, geometries at boron are distorted trigonal planar with the sum of the angles about boron being

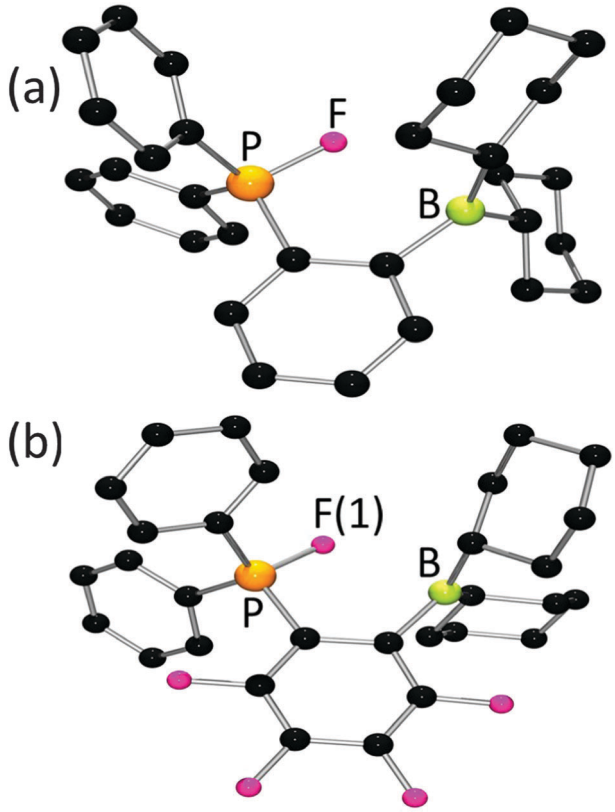
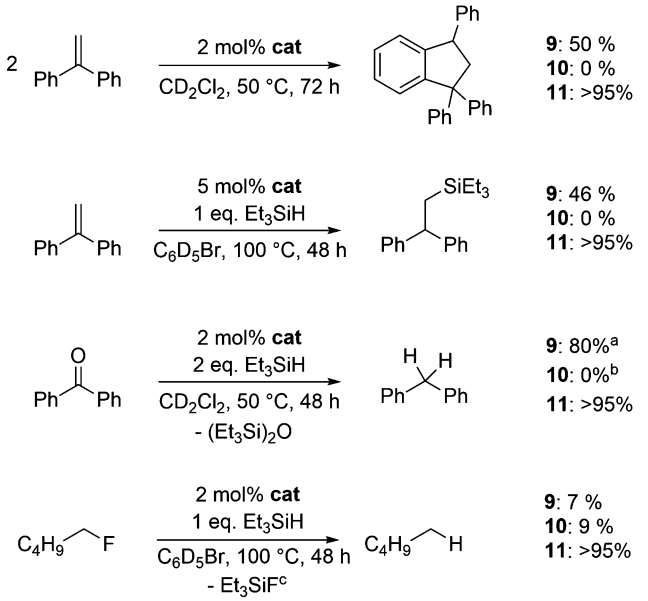


Fig. 3 Solid state structures of compounds (a) **9** and (b) **11**. Hydrogen atoms and the $[B(C_6F_5)_4]^-$ counterions are omitted for clarity. Carbon: black; fluorine: pink; phosphorus: orange; boron: yellow-green. Selected bond lengths (Å) and angles (°): **9**: P(1)–F(1): 1.555(2), B(1)–F(1): 2.639(1). **11**: P(1)–F(1): 1.555(2), B(1)–F(1): 2.491(1).

358.8(3)° in **9** and 359.9(2)° in **11**. The BCCC plane is oriented almost perpendicular to the plane of the bridging aryl substituent (**9:** θ 86.3(1)°; **11:** θ 82.2(1)°). The F-atoms on phosphorus are in the corresponding PCCB planes oriented towards the empty p_z-orbital at boron with B–F distances of 2.637(1) Å and 2.491(1) Å in **9** and **11**, respectively.

Upon addition of a stoichiometric amount of 4-dimethylaminopyridine (4-DMAP) to **9**, formation of the nitrogen–boron adduct **12** ($^1J_{PF}$ = 1025 Hz) was observed.[18] Interestingly, this adduct exhibits an increase in the $^1J_{PF}$ coupling constant which is in the range of fluorophosphonium compounds where boron substituents are absent. This suggests that the proximal tricoordinate boron centers in compound **9** influence the P–F bond and the resulting Lewis acidity at P.

To probe this further, the utility of compounds **9–11** in a series of reactions, typically catalyzed by fluorophosphonium compounds,[4a] was assessed (Scheme 3). In the reaction with 1,1-diphenylethylene, 2 mol% of **9** afforded a 50% yield of the Friedel–Crafts dimer in 72 h at 50 °C. In contrast, utilizing compound **10** as catalyst resulted in no reaction whereas **11** gives quantitative conversion to the dimer under the same conditions. For the hydrosilylation of 1,1-diphenylethylene, a similar trend was observed. Again, with 2 mol% catalyst, compound **9** gave 46% of the hydrosilylation product while **10** is inactive and



Scheme 3 Catalytic reactivity of **9–11**. Reaction conditions: 0.1 mmol substrate, 0.5 ml solvent. Conversion determined by ^{1}H NMR integration. [a]15% of $Ph_2CHOSiEt_3$ was observed. [b]8% of $Ph_2CHOSiEt_3$ were observed. [c]Conversion determined by ^{19}F NMR integration.

11 affords >95% conversion to $Et_3SiCH_2CHPh_2$ in 48 h at 100 °C. The deoxygenation of benzophenone to diphenylmethane in the presence of two equivalents of triethylsilane and 2 mol% catalyst (**9**, **10**, **11**) proceeds with 80%, 0% and >95% conversion (48 h, 50 °C). Lastly, in the case of hydrodefluorination of 1-fluoropentane, the catalysts **9–11** gave rise to 7%, 9% and >95% conversion of starting material (Scheme 3).

As a further point of comparison, the P-methylated phosphonium compound $[Ph_2PMe(o\text{-}C_6H_4BCy_2)][B(C_6F_5)_4]$ **13** was prepared by alkylation of **2** with MeOTf and subsequent anion exchange with $[Et_3Si][B(C_6F_5)_4]$ (see ESI†). This species shows no catalytic activity in all of the above reactions described for **9–11** (Scheme 3). This finding suggests that the site of Lewis acidic reactivity of compounds **9–11** is the fluorophosphonium center, not the borane moiety.

The above catalyst efficiencies were also compared to those derived from $[Ph_3PF][B(C_6F_5)_4]$ **14**, $[Ph_2(C_6F_5)PF][B(C_6F_5)_4]$ **15** and $[Ph(C_6F_5)_2PF][B(C_6F_5)_4]$ **16**. In the hydrosilylation of 1,1-diphenylethylene **14–16** gave 0%, 60% and >95% yields respectively. Comparing **11** and **15** after a reaction time of 12 h at 100 °C showed conversions of 55% (**11**) and 5% (**15**). This clearly illustrates a reactivity enhancement which results from the presence of the *ortho*-boryl substituent. Compound **16** showed virtually full conversion at 12 h, consistent with previous observation that reactivity of the phosphonium cations increases significantly with each additional C_6F_5 group. The reactivity difference between **9** and **11** follows this trend. For the other reactions depicted in Scheme 3, similar observations of reactivity were made for compounds **9–11** and **14–16** (see the ESI†).

It is worth noting that the bulky substituents at boron in compound **10** basically shut down reactivity, despite the presence of a more electron deficient B center. This implies that the impact

of the borane center on the reactivity of the adjacent phosphonium center is not merely inductive but rather it plays a cooperative role in enhancing Lewis acid catalyst activity. Indeed, the structural data for the above fluorophosphonium cations support the notion that presence of the borane does not impact the Lewis acidity of the fluorophosphonium cations by direct interaction with fluoride. Rather the boron center stabilize transiently generated phosphorane-type intermediates analogous to those previously proposed for the reaction mechanisms.[4a] In this way, the combination of two relatively weak Lewis acids leads to increased catalytic activity. It is interesting to note that use of even stronger boron Lewis acids is not expected to improve reactivity further as the stronger B-Lewis acid binds fluoride irreversibly leading to the formation of zwitterionic phosphonium-fluoroborates. This notion has been previously illustrated with the isolation of $Ph_2PFC(tol)=C(C_6F_5)BF(C_6F_5)_2$.[19]

While there is no doubt that the presence of electron-withdrawing substituents enhances the Lewis acidity of electrophilic phosphonium cations, this strategy offers limited options for tailoring these main group Lewis acids. Herein, we have presented a conceptual alternative that enhances catalytic reactivity of fluorophosphonium compounds. The incorporation of weakly acidic boron centers enhance the reactivity at the P-based σ*-orbital by providing an avenue to stabilize hypervalent phosphoranes reaction intermediates *via* an intramolecular P–F–B interaction. This finding is an interesting twist on Gabbaï's strategy in which a proximal phosphonium center enhanced fluoride binding at boron. In our case, a proximal boron center enhances the reactivity at an adjacent fluorophosphonium center. Current efforts are directed towards exploiting this new strategy to libraries of group 15 Lewis acid catalysts en route to a range of new synthetic applications.

D. W. S. gratefully acknowledges the financial support of the NSERC of Canada and the award of a Canada Research Chair. J. M. is grateful to the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. T. v. S. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Research Fellowship. J. M. is grateful to the DFG for a postdoctoral fellowship.

Notes and references

1 (*a*) G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881; (*b*) J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968–4971; (*c*) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126.

2 (*a*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441; (*b*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76; (*c*) D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032; (*d*) D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306–316.

3 S. A. Weicker and D. W. Stephan, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1003–1016.

4 (*a*) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374–1377; (*b*) F. P. Gabbaï, *Science*, 2013, **341**, 1348–1349; (*c*) J. M. Bayne and D. W. Stephan, *Chem. Soc. Rev.*, 2016, **45**, 765–774.

5 M. Pérez, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 10917–10921.

6 (*a*) M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308–18310; (*b*) M. Pérez, Z. W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovetsky, S. Grimme and D. W. Stephan, *Chem. – Eur. J.*, 2015, **21**, 6491–6500.

7 T. v. Stein, M. Pérez, R. Dobrovetsky, D. Winkelhaus, C. B. Caputo and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2015, **54**, 10178–10182.

8 M. Mehta, M. H. Holthausen, I. Mallov, M. Pérez, Z. W. Qu, S. Grimme and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2015, **54**, 8250–8254.

9 M. Mehta, I. G. d. l. Arada, M. Pérez, D. Porwal, M. Oestreich and D. W. Stephan, *Organometallics*, 2016, **35**, 1030–1035.

10 (*a*) J. M. Bayne, M. H. Holthausen and D. W. Stephan, *Dalton Trans.*, 2016, **45**, 5949–5957; (*b*) M. H. Holthausen, R. R. Hiranandani and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2016–2021; (*c*) M. H. Holthausen, J. M. Bayne, I. Mallov, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 7298–7301; (*d*) M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538–6541; (*e*) E. R. Clark and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2014, **53**, 11306–11309; (*f*) E. R. Clark and M. J. Ingleson, *Organometallics*, 2013, **32**, 6712–6717; (*g*) J. M. Farrell, R. T. Posaratnanathan and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2010–2015; (*h*) J. M. Farrell, J. A. Hatnean and D. W. Stephan, *J. Am. Chem. Soc.*, 2012, **134**, 15728–15731; (*i*) S. Litters, M. Ganschow, E. Kaifer and H. J. Himmel, *Eur. J. Inorg. Chem.*, 2015, 5188–5195; (*j*) P. Eisenberger, B. P. Bestvater, E. C. Keske and C. M. Crudden, *Angew. Chem., Int. Ed.*, 2015, **54**, 2467–2471; (*k*) Y. Kim, H. Zhao and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2009, **48**, 4957–4960; (*l*) C. W. Chiu, Y. Kim and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 60–61; (*m*) Y. Kim and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 3363–3369; (*n*) K. C. Song, K. M. Lee, N. V. Nghia, W. Y. Sung, Y. Do and M. H. Lee, *Organometallics*, 2013, **32**, 817–823.

11 (*a*) H. E. Katz, *J. Am. Chem. Soc.*, 1985, **107**, 1421–1423; (*b*) H. E. Katz, *J. Org. Chem.*, 1985, **50**, 5027–5032; (*c*) V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3244–3245; (*d*) H. Y. Zhao and F. P. Gabbaï, *Organometallics*, 2012, **31**, 2327–2335; (*e*) M. Melaïmi, S. Solé, C.-W. Chiu, H. Wang and F. P. Gabbaï, *Inorg. Chem.*, 2006, **45**, 8136–8143; (*f*) W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, 2131–2142; (*g*) C. Jiang, O. Blacque and H. Berke, *Chem. Commun.*, 2009, 5518–5520; (*h*) T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, **130**, 10890–10891; (*i*) Y. Li, Y. Kang, J.-S. Lu, I. Wyman, S.-B. Ko and S. Wang, *Organometallics*, 2014, **33**, 964–973; (*j*) C. R. Wade and F. P. Gabbaï, *Organometallics*, 2011, **30**, 4479–4481; (*k*) M. Hirai and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2014, **54**, 1205–1209.

12 M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir and D. Bourissou, *Inorg. Chem.*, 2010, **49**, 3983–3990.

13 A. Krasovskiy and P. Knochel, *Angew. Chem., Int. Ed.*, 2004, **43**, 3333–3336.

14 P. G. Eller and D. W. Meek, *J. Organomet. Chem.*, 1970, **22**, 631–636.

15 (*a*) G. S. Reddy and R. Schmutzler, *Z. Naturforsch., B: J. Chem. Sci.*, 1970, **25**, 1199–1214; (*b*) K. M. Doxsee, E. M. Hanawalt and T. J. R. Weakley, *Inorg. Chem.*, 1992, **31**, 4420–4421.

16 (*a*) C. B. Caputo, D. Winkelhaus, R. Dobrovetsky, L. J. Hounjet and D. W. Stephan, *Dalton Trans.*, 2015, **44**, 12256–12264; (*b*) L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 2629–2635.

17 L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2012, **51**, 4714–4717.

18 The DMAP adducts of **10** and **11** were not observed; presumably a result of steric and alternate reactivity respectively.

19 O. Ekkert, C. B. Caputo, C. Pranckevicius, C. G. Daniliuc, G. Kehr, G. Erker and D. W. Stephan, *Chem. – Eur. J.*, 2014, **20**, 11287–11290.

