

Preorganized Frustrated Lewis Pairs

Federica Bertini,[†] Volodymyr Lyaskovskyy,[†] Brian J. J. Timmer,[†] Frans J. J. de Kanter,[†] Martin Lutz,[‡] Andreas W. Ehlers,[†] J. Chris Slootweg,^{*,†} and Koop Lammertsma^{*,†}

[†]Department of Chemistry and Pharmaceutical Sciences, VU University Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

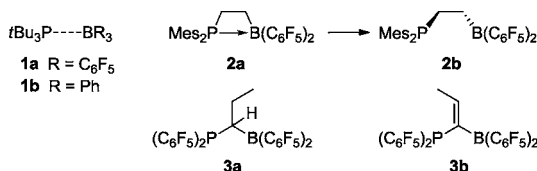
[‡]Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Supporting Information

ABSTRACT: Geminal frustrated Lewis pairs (FLPs) are expected to exhibit increased reactivity when the donor and acceptor sites are perfectly aligned. This is shown for reactions of the nonfluorinated FLP *t*Bu₂PCH₂BPh₂ with H₂, CO₂, and isocyanates and supported computationally.

Since their discovery, frustrated Lewis pairs (FLPs) have gained much attention because of their ability to activate small molecules.¹ This ability arises from the synergic effect of the donor and acceptor sites that polarizes the desired chemical bond.² FLPs react with molecules such as H₂,^{1,2} CO₂,^{3,4} alkenes,⁵ and alkynes,^{3,5b,6} thereby offering new synthetic entries. Their ability to cleave H₂ heterolytically makes them valuable metal-free catalysts for the hydrogenation of organic substrates,⁷ whereas activation of the greenhouse gas CO₂ holds potential for its conversion into products such as MeOH^{4b,8} and CH₄.^{8c} Mutual quenching of the Lewis acid and base sites in the FLPs is prevented by the bulky substituents that keep the donor and acceptor atoms sufficiently far apart, as is the case for the associated pair *t*Bu₃P---B(C₆F₅)₃ (**1a**) (Scheme 1).^{2a-c,9,10}

Scheme 1. Frustrated Lewis Pairs 1a,b, 2b, and 3a,b



Although weakly bonded Lewis pairs can be used,¹¹ the energy needed to separate the Lewis acid and base components reduces their reactivity. For example, whereas the strained four-membered ring **2a** can dissociate into the reactive open gauche form **2b** (Scheme 1),^{11a,12,13} the five- and six-membered rings Mes₂P(CH₂)_{*n*}B(C₆F₅)₂ (*n* = 3, 4) possess much stronger P–B bonds, rendering them unreactive.¹⁴

While many Lewis bases^{1,15,16} have been employed in FLP chemistry, the Lewis acid component is generally restricted to borane moieties bearing highly electron-withdrawing pentafluorophenyl substituents to enhance the acidity of the acceptor site. This effect is illustrated by the intermolecular FLP **1a**, which reacts smoothly with H₂ (rt, 13 h; 90% yield) while the nonfluorinated analogue *t*Bu₃P---BPh₃ (**1b**) requires a much

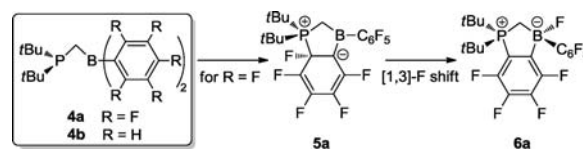
longer reaction time (25 h) and gives a much lower yield (33%).⁹

Enhanced reactivity can be expected for *preorganized* FLPs with *intramolecular* donor and acceptor sites,^{2a} particularly when the two sites are oriented in the same direction for optimal interaction with the substrate.¹⁷ We envisioned that geminal P/B-based FLPs might be ideally suited to activate small molecules, possibly to the extent that strongly electron-withdrawing substituents on B might not even be needed. We further reasoned that intramolecular self-quenching of the methylene-linked Lewis acid and base centers might be adequately countered by the inherent strain associated with the formation of the three-membered PCB ring.

To date, the only reported geminal P/B-based FLPs are **3a**¹⁸ and **3b**¹⁹ (Scheme 1), which were prepared by hydroboration of substituted phosphines in a manner similar to that used to synthesize **2**.²⁰ Both bear strongly electron-withdrawing C₆F₅ groups at P and at B. They react with unsaturated organic substrates but not with H₂, probably because of the reduced Lewis basicity of the P center.

Here we address the potential of simple, nonfluorinated geminal P/B-based FLPs to activate small molecules by comparing the reactivities of the methylene-bridged *t*Bu₂P-phosphinoboranes with pentafluorophenyl (**4a**) and phenyl substituents (**4b**) on B (Scheme 2). The enhanced reactivity

Scheme 2. Preorganized FLPs 4a,b and Rearrangement of 4a to 6a



was recently demonstrated by the intramolecular activation of transient perfluorinated **4a** to form the undesired five-membered heterocycle **6a**.²¹ Our M06-2X/6-31+G(d,p) calculations²² on the full system confirmed that **4a** undergoes intramolecular substitution via σ -complex **5a** [$\Delta E^\ddagger = 20.1$ kcal mol⁻¹, $\Delta E = 10.4$ kcal mol⁻¹; zero-point energy (ZPE)-corrected] and a facile [1,3]-F shift to the thermodynamically

Received: November 8, 2011

Published: December 13, 2011

avored **6a** ($\Delta\Delta E = -65.2$ kcal mol⁻¹; $\Delta E = -54.8$ kcal mol⁻¹; Scheme 2).

Interestingly, the “quenched” ring-closed FLP **4a'** with a P–B distance of 2.04 Å is slightly more stable ($\Delta E = -1.5$ kcal mol⁻¹) than the ring-opened isomer **4a** (P1–B1 = 2.89 Å),²³ but only the open form exists for the nonfluorinated derivative **4b** (P1–B1 = 2.69 Å), indicating reduced Lewis acidity of the acceptor site (Figure 1). Preorganized **4b** with Lewis base and

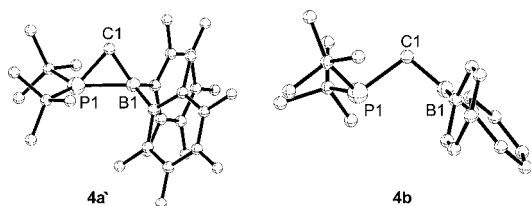


Figure 1. M06-2X/6-31+G(d,p) geometries of **4a'** and **4b**; H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4a'**: P1–B1, 2.04; P1–C1, 1.83; B1–C1, 1.59. For **4b**: P1–B1, 2.69; P1–C1, 1.90; B1–C1, 1.57; P1–C1–B1, 101.3.

acid sites perfectly oriented for small-molecule activation (see the HOMO and LUMO in Figure 2) became our target.

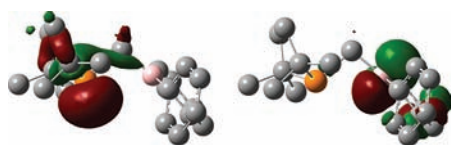
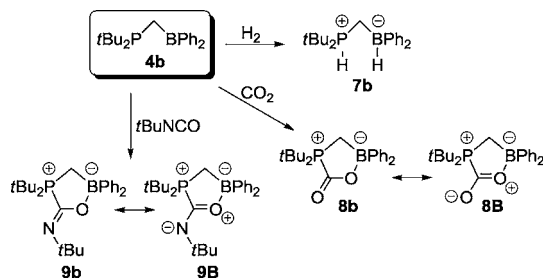


Figure 2. HOMO (left) and LUMO (right) of **4b**.

Phosphinoborane **4b** was readily obtained as a colorless oil in 94% isolated yield by a salt metathesis reaction between readily accessible *t*Bu₂PCH₂Li²⁴ and chlorodiphenylborane.²⁵ The broad ¹¹B{¹H} NMR resonance at 72.3 ppm is characteristic of a tricoordinated B center and supports the FLP nature of **4b** ($\delta^{31}\text{P} = 39.4$ ppm). Next, we examined its reactivity with H₂, CO₂, and isocyanates and studied the full systems computationally using ZPE-corrected M06-2X/6-31+G(d,p) energies.²²

Bubbling H₂ through a solution of **4b** in toluene under ambient conditions for 5 h afforded the H₂ adduct **7b** as a colorless solid in 28% isolated yield [$\delta^{31}\text{P} = 53.0$ ppm, ¹J(P,H) = 460.4 Hz; $\delta^{11}\text{B}\{\text{H}\} = -9.0$ ppm; Scheme 3). This process

Scheme 3. Reactions of **4b** with H₂, CO₂, and *t*BuNCO



reflects a modest increase in reactivity relative to **1b**.²⁶ The computations revealed that H₂ is delivered to the FLP cavity through van der Waals complexes [see the Supporting Information (SI)]. One of these results from the side-on interaction of H₂ with the B atom (**7b-vdW**, $\Delta E = -0.7$ kcal mol⁻¹), which leads via transition state **TS7b** ($\Delta E = 22.6$ kcal

mol⁻¹; Figure 3) to the phosphonium borate product **7b** ($\Delta E = -1.6$ kcal mol⁻¹). The computed covalent bond orders (bo's)

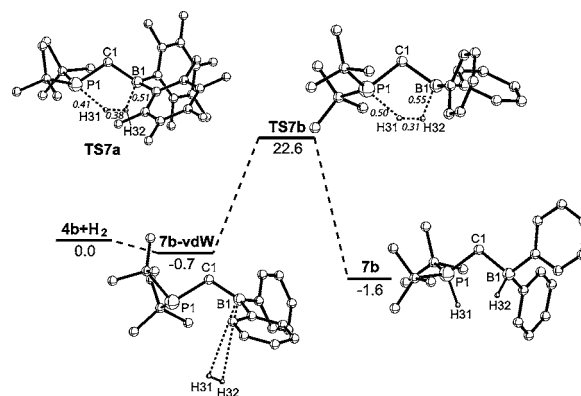


Figure 3. Relative M06-2X/6-31+G(d,p) energies (kcal mol⁻¹) for the reaction of **4b** with H₂ to give **7b**; the transition state for the H₂ uptake by **4a** is also shown. Computed bond orders for **TS7a** and **TS7b** are given in italics. Selected bond lengths (Å) and angles (deg) for **7b-vdW**: B1–H31, 3.61; B1–H32, 3.64; P1–C1–B1, 115.6; B1–H31–H32, 86.9; B1–H32–H31, 81.3. For **TS7b**: P1–H31, 1.70; H31–H32, 1.01; B1–H32, 1.40; P1–C1–B1, 104.3; P1–H31–H32, 135.5; B1–H32–H31, 107.2. For **7b**: P1–H31, 1.40; B1–H32, 1.23; P1–C1–B1, 108.2; H31–P1–C1–B1, -13.7; H32–B1–C1–P1, -47.1.

for **TS7b** show that heterolytic H₂ splitting occurs in a concerted manner, with the formation of the B–H bond (bo = 0.55) proceeding slightly earlier than that of the P–H bond (bo = 0.50) (Figure 3).^{2a} The significant barrier for the nearly thermoneutral H₂ splitting is consistent with our experimental findings. Apparently, pentafluorophenyl substituents may not be needed for FLPs to function. Their presence may even be detrimental, as illustrated in Scheme 2. Our calculations showed that heterolytic uptake of H₂ by **4a** to give **7a** is far more exothermic ($\Delta E = -14.8$ kcal mol⁻¹) and has only a modestly lower activation energy (**TS7a**, $\Delta E^\ddagger = 16.6$ kcal mol⁻¹; Figure 3), indicating that pentafluorophenyl substituents facilitate H–H bond cleavage while limiting the reversibility of this process.

The reactivity of **4b** toward H₂ encouraged us to examine the capture of CO₂, which is unprecedented for nonfluorinated borane-based FLPs. Bubbling CO₂ through a solution of **4b** in toluene under ambient conditions for 30 s quantitatively formed **8b**, which was isolated as a colorless solid in 89% yield ($\delta^{31}\text{P} = 48.0$ ppm; $\delta^{13}\text{C}\{\text{H}\}$ (CO₂) = 167.8 ppm, ¹J(C,P) = 89.7 Hz; $\delta^{11}\text{B}\{\text{H}\} = 5.0$ ppm; Scheme 3). CO₂ fixation by **4b** was confirmed by the X-ray structure of **8b** (Figure 4), which displays an almost planar five-membered ring with P–C and B–O distances of 1.8690(12) and 1.5645(15) Å, respectively, and C=O/C–O lengths of 1.2098(15)/1.2938(14) Å, which are comparable to those observed for **2-CO₂**.^{4a} The short endocyclic C22–O1 bond suggests double-bond character, as in all previously reported FLP–CO₂ adducts [i.e., 1.2988(15) Å for **1-CO₂**; 1.284(4) Å for **2-CO₂**],^{4a} underlining the contribution of resonance structure **8B** (Scheme 3).

The calculations revealed that the generation of **8b** ($\Delta E = -20.3$ kcal mol⁻¹) starts with the formation of a van der Waals complex (**8b-vdW**, $\Delta E = -4.1$ kcal mol⁻¹; Figure 5) with an almost linear CO₂ fragment (177.4°) and long P–C (3.34 Å) and B–O (3.81 Å) distances. In contrast to the reaction with H₂, the computed bo's show that CO₂ uptake occurs via facile nucleophilic attack on the CO₂ C atom by the P atom (**TS8b**,

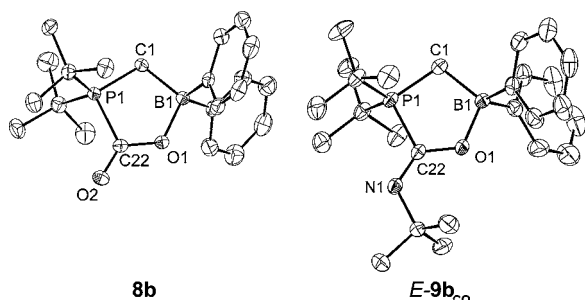


Figure 4. Molecular structures of **8b** and *E*-**9b_{CO}**. Ellipsoids are set at 50% probability; H atoms and disordered solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **8b**: P1–C22, 1.8690(12); C22–O1, 1.2938(14); C22–O2, 1.2098(15); O1–B1, 1.5645(15); P1–C1, 1.7791(13); C1–B1, 1.6893(18); O2–C22–O1, 125.85(11); P1–C1–B1, 105.22(8); P1–C22–O1, 110.04(8); C22–O1–B1, 120.40(9). For *E*-**9b_{CO}**: P1–C22, 1.8341(11); C22–O1, 1.3198(13); O1–B1, 1.5514(15); P1–C1, 1.7812(12); B1–C1, 1.6719(16); C22–N1, 1.2708(15); P1–C22–N1, 120.01(8); P1–C22–O1, 110.08(8); N1–C22–O1, 129.84(10); C22–O1–B1, 119.64(9); C22–P1–C1, 97.93(5); P1–C1–B1, 105.32(8); C1–B1–O1, 106.79(9).

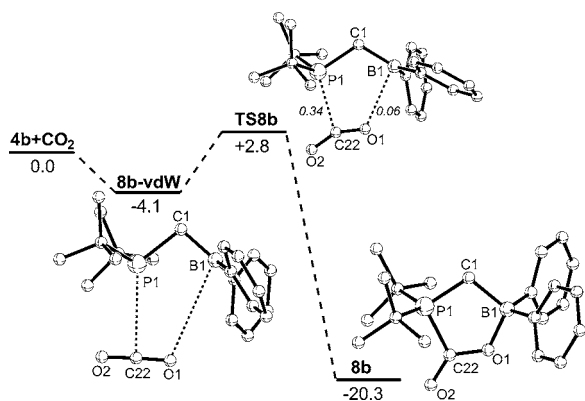


Figure 5. Relative M06-2X/6-31+G(d,p) energies (kcal mol⁻¹) for the reaction of **4b** with CO₂. Selected bond lengths (Å) and angles (deg) for **8b-vdW**: P1–C22, 3.34; B1–O1, 3.81; C22–O1, 1.16; C22–O2, 1.16; P1–C22–O1, 95.7; B1–O1–C22, 107.8; P1–C1–B1, 100.9; O1–C22–O1, 177.4. For **TS8b**: P1–C22, 2.40; C22–O1, 1.19; C22–O2, 1.19; B1–O1, 2.66; P1–C1–B1, 113.6; P1–C22–O1, 99.6; B1–O1–C22, 114.4; O1–C22–O2, 153.0. For **8b**: P1–C22, 188.14; C22–O1, 1.29; C22–O2, 1.21; B1–O1, 1.55; P1–C1–B1, 104.1; O1–C22–O2, 128.5; P1–C22–O1, 109.0; B1–O1–C22, 121.5.

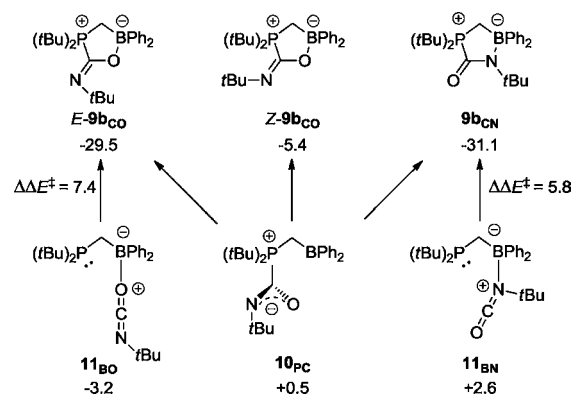
$\Delta\Delta E^\ddagger = 6.9$ kcal mol⁻¹; P–C bo = 0.34, B–O bo = 0.06; Figure 5) followed by ring closure.^{4a} The CO₂ adduct **8b** was thermally stable at 100 °C under vacuum (5×10^{-2} mbar) and showed no release of CO₂. This reaction underscores the fact that nonfluorinated FLPs can capture small molecules.

Finally, we examined the reaction of **4b** with isocyanates. To date, three C=O adducts for the reaction of phenyl isocyanate with FLPs have been reported,²⁷ whereas with the electron-poor FLPs **3a** and **3b**, C=N adducts were obtained.^{18,19} For the reaction of PhNCO with **4b**, we observed two ³¹P NMR resonances (47.2 and 58.5 ppm) in a 1:1 ratio that we attribute to the CO and CN adducts. Reaction of **4b** with *t*BuNCO instead yielded only the CO adduct, which was isolated as a colorless solid in 76% yield ($\delta^{31}\text{P} = 50.5$ ppm; $\delta^{13}\text{C}\{^1\text{H}\}$ (*t*BuNCO) = 155.3 ppm, $^1\text{J}(\text{C},\text{P}) = 115.1$ Hz; $\delta^{11}\text{B}\{^1\text{H}\} = 6.3$ ppm; Scheme 3). Single-crystal X-ray analysis revealed the formation of *E*-**9b_{CO}** having P–C and B–O bond lengths of

1.8341(11) and 1.5514(15) Å, respectively, and a short endocyclic C22–O1 bond [1.3198(13) Å] (Figure 4). Thus, the substrate substituents also influence the product formation.

To address the selectivity of the reaction of **4b** with *t*BuNCO, we calculated the relative energies of *E*-**9b_{CO}** and the feasible but unobserved *Z*-**9b_{CO}** and **9b_{CN}** (Scheme 4). Steric

Scheme 4. Possible Reaction Products of **4b** + *t*BuNCO with Their Connectivities and Calculated Energies (kcal mol⁻¹)



repulsion between the *tert*-butyl groups on N and P appears to underlie the lower exothermicity of *Z*-**9b_{CO}** ($\Delta E = -5.4$ kcal mol⁻¹) relative to the experimentally obtained *E*-**9b_{CO}** ($\Delta E = -29.5$ kcal mol⁻¹). The analogous but sterically less hindered Ph-substituted adducts show a less pronounced *E*/*Z* difference ($\Delta\Delta E = 10.0$ kcal mol⁻¹; see the SI). Whereas the calculations gave an energetic preference of 2.4 kcal mol⁻¹ for CN adduct **9b_{CN}** over *E*-**9b_{CO}**, no changes in the ³¹P{¹H} and ¹H NMR spectra were observed upon heating a solution of *E*-**9b_{CO}** in C₆D₆ for 1 h at 100 °C, indicating the irreversibility of the isocyanate capture by **4b**.

To unravel the reaction mechanism, we computationally compared (a) nucleophilic attack of the P atom on the electrophilic isocyanate C atom to generate ylide **10_{PC}**, (b) formation of the Lewis adduct **11_{BN}** by coordination of *t*BuNCO's N atom, and (c) formation of B–O Lewis adduct **11_{BO}** by coordination of *t*BuNCO's O atom (Scheme 4).

Phosphine–isocyanate adducts like **10_{PC}** have been proposed as intermediates in the phosphine-catalyzed oligomerization of isocyanides,²⁸ but no such ylides have been isolated to date. Our computations showed that the formation of **10_{PC}** with the isocyanate unit orthogonal to the PCB plane is endothermic by 0.5 kcal mol⁻¹. Rotation of the isocyanate along the P–C axis results in the barrierless formation of *E*-**9b_{CO}** (clockwise) and **9b_{CN}** (counterclockwise) by B–O and B–N bond formation, respectively. As both pathways are equally facile, this mechanism cannot account for the observed exclusive formation of the less stable *E*-**9b_{CO}**. N-Coordination of *t*BuNCO to give Lewis adduct **11_{BN}** is even more endothermic (2.6 kcal mol⁻¹) despite the favorable energetics for ring closure to give **9b_{CN}** ($\Delta\Delta E^\ddagger = 0.6$ kcal mol⁻¹, $\Delta\Delta E = -34.5$ kcal mol⁻¹). In contrast, O-coordination of the isocyanate to give Lewis adduct **11_{BO}** is exothermic ($\Delta E = -3.2$ kcal mol⁻¹). Subsequent ring closure by P–C bond formation gives *E*-**9b_{CO}** ($\Delta\Delta E^\ddagger = 7.4$ kcal mol⁻¹, $\Delta\Delta E = -26.3$ kcal mol⁻¹; Scheme 4). Consequently, we conclude that the formation of *E*-**9b_{CO}** is kinetically controlled with **11_{BO}** as the key intermediate.

In summary, this work underscores the potential of geminal methylene-bridged phosphinoboranes as preorganized FLPs

and shows that remarkable reactivity can be achieved without the need for strongly electron-withdrawing substituents on B.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, Cartesian coordinates and energies of all stationary points, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

j.c.slootweg@vu.nl; k.lammertsma@vu.nl

■ ACKNOWLEDGMENTS

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) and benefitted from interactions within the European PhoSciNet (COST Action CM0802). We thank J. W. H. Peeters for measuring the high-resolution mass spectra.

■ REFERENCES

- (1) Reviews of FLPs: (a) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46. (b) Stephan, D. W. *Dalton Trans.* **2009**, 3129. (c) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
- (2) Computational work on H₂ activation: (a) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 1402. (b) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 2435. (c) Hamza, A.; Stirling, A.; Rokob, T. A.; Pápai, I. *Int. J. Quantum Chem.* **2009**, *109*, 2416. (d) Erős, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. *Angew. Chem., Int. Ed.* **2010**, *122*, 6709. (e) Kim, H. W.; Rhee, Y. M. *Chem.—Eur. J.* **2009**, *15*, 13348. (f) Schirmer, B.; Grimme, S. *Chem. Commun.* **2010**, 46, 7942. (g) Guo, Y.; Li, S. *Inorg. Chem.* **2008**, *47*, 6212. (h) Rokob, T. A.; Hamza, A.; Stirling, A.; Pápai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029. (i) Rokob, T. A.; Hamza, A.; Pápai, I. *J. Am. Chem. Soc.* **2009**, *131*, 10701.
- (3) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 3925.
- (4) (a) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643. (b) Menard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796.
- (5) (a) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968. (b) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280. (c) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594. (d) Geier, S. J.; Dureen, M. A.; Ouyang, E. Y.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 988. (e) Geier, S. J.; Dureen, M. A.; Ouyang, E. Y.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 3005. (f) Chen, C.; Eweiner, F.; Wibbeling, B.; Fröhlich, R.; Senda, S.; Ohki, Y.; Tatsumi, K.; Grimme, S.; Kehr, G.; Erker, G. *Chem.—Asian J.* **2010**, *5*, 2199.
- (7) (a) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543. (b) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem.* **2007**, *119*, 8196; *Angew. Chem., Int. Ed.* **2007**, *46*, 8050. (c) Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, 5966. (d) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117. (e) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701. (f) Chen, D.; Klankermayer, J. *Chem. Commun.* **2008**, 2130. (g) Chen, D.; Wang, Y.; Klankermayer, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 9475. (h) Xu, B.-H.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 7183. (i) Erős, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 6559. (j) Jiang, C. F.; Blacque, O.; Berke, H. *Chem. Commun.* **2009**, 5518.
- (8) (a) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem.* **2009**, *121*, 10023; *Angew. Chem., Int. Ed.* **2009**, *48*, 9839. (b) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 13559. (c) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660.
- (9) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.
- (10) Kim, H. W.; Rhee, Y. M. *Chem.—Eur. J.* **2009**, *15*, 13348.
- (11) (a) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072. (b) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396. (c) Welch, G. C.; Prieto, R.; Dureen, M. A.; Lough, A. J.; Labeodan, O. A.; Höltrichter-Rössmann, T.; Stephan, D. W. *Dalton Trans.* **2009**, 1559. (d) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2011**, *30*, 2117. (e) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476.
- (12) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643.
- (13) (a) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2010**, 39, 7556 and refs 9, 13, and 15–18 cited therein. (b) Spies, P.; Kehr, G.; Bergander, K.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2009**, 1534.
- (14) Spies, P.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *Chem.—Eur. J.* **2008**, *14*, 333.
- (15) (a) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001. (b) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117. (c) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476. (d) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 10466. (e) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050.
- (16) (a) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7428. (b) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433. (c) Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 5788.
- (17) (a) Lu, G.; Li, H.; Zhao, L.; Huang, F.; Wang, Z. *Inorg. Chem.* **2010**, *49*, 295. (b) Wang, Z.; Lu, G.; Zhao, L. *Chin. Sci. Bull.* **2010**, *55*, 239. (c) Lu, G.; Li, H.; Zhao, L.; Li, H.; Huang, F.; Wang, Z. *Eur. J. Inorg. Chem.* **2010**, 2254.
- (18) Stute, A.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2011**, 47, 4288.
- (19) Rosorius, C.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Organometallics* **2011**, *30*, 4211.
- (20) Geminal P/Al-based FLPs: see ref 3. Geminal S/B-based FLPs: Tanur, C. A.; Stephan, D. W. *Organometallics* **2011**, *30*, 3652.
- (21) (a) Zhao, X.; Gilbert, T. M.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 10304. (b) Schnurr, A.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2010**, *29*, 6012.
- (22) (a) Zaho, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Janesco, B. G. *J. Chem. Theory Comput.* **2010**, *6*, 1825.
- (23) Ring closure occurred upon geometry optimization of the open form.
- (24) Eisenräger, F.; Göthlich, A.; Gruber, I.; Heiss, H.; Kiener, C. A.; Krüger, C.; Notheis, J. U.; Rominger, F.; Scherhag, G.; Schultz, M.; Straub, B. F.; Volland, M. A. O.; Hofmann, P. *New J. Chem.* **2003**, *27*, 540.
- (25) Thomas, J. C.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5055.
- (26) We did not attempt to increase the yield with prolonged reaction times since we observed that other side reactions took place during the course of the H₂ uptake.
- (27) (a) Moebs-Sanchez, S.; Bouhadir, G.; Saffon, N.; Maron, L.; Bourissou, D. *Chem. Commun.* **2008**, 3435. (b) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2010**, 39, 7556. (c) Axenov, K. V.; Mömming, C. M.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem.—Eur. J.* **2010**, *16*, 14069.
- (28) (a) Pusztai, Z.; Vlád, G.; Bodor, A.; Horváth, I. T.; Laas, H. J.; Halpaap, R.; Richter, F. U. *Angew. Chem., Int. Ed.* **2006**, *45*, 107. (b) Tang, J.; Verkade, J. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 896. (c) Tang, J.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931.