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Frustrated Lewis Pairs

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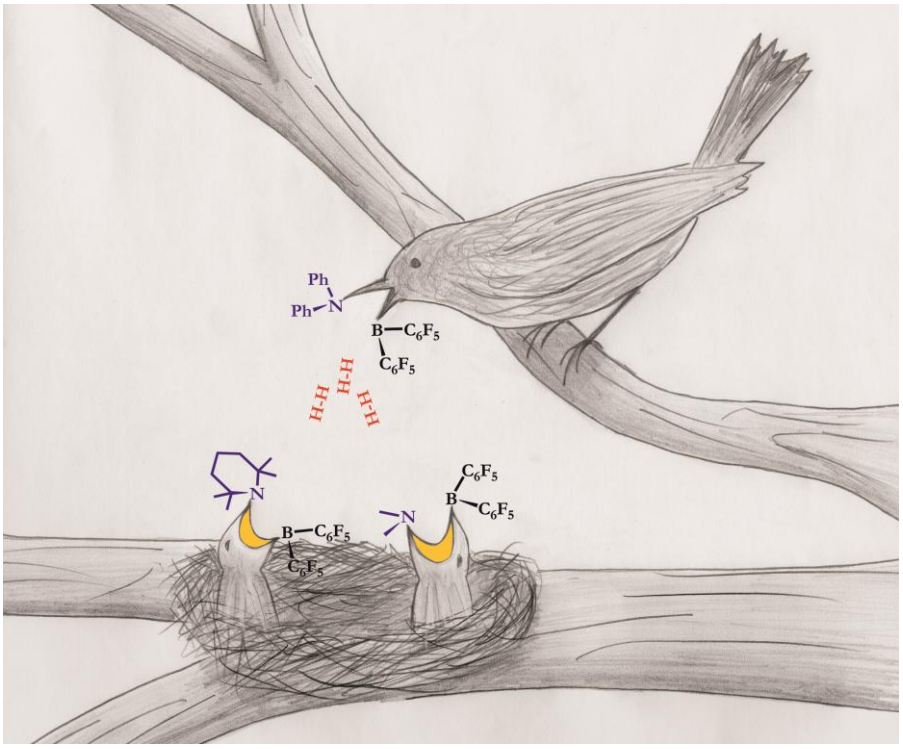

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PAPER

[2.2]Paracyclophane derived bisphosphines for the activation of hydrogen by FLPs: application in domino hydrosilylation/hydrogenation of enones†

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The heterolytic splitting of hydrogen by two types of [2.2]paracyclophane derived bisphosphines (**1**, **2a** and **2b**) in combination with tris(pentafluorophenyl)borane (**3**) at room temperature is described. The corresponding frustrated Lewis pairs (FLPs) exhibit different behavior in the activation of hydrogen. This results from diverse steric and electronic properties of the bisphosphines. The reactivity of the frustrated Lewis pairs was exploited in the first diastereoselective domino hydrosilylation/hydrogenation reaction catalyzed by FLPs.

Introduction

The metal-free hydrogenation of unsaturated compounds has emerged as powerful tool in synthetic organic chemistry.[1–4] Despite these great achievements, the direct utilization of hydrogen in metal free processes has only recently been described utilizing frustrated Lewis pairs[5] (FLPs).[6–8] The majority of these reactions utilize bulky monophosphines or monoamines[9] with $B(C_6F_5)_3$ (**3**) precluding the formation of a Lewis acid/Lewis base adduct. In contrast, the application of bisphosphines in FLP chemistry has found less attention. Clearly, this is attributed to the fact that apart from H_2-activation, multiple quenching or side reactions are observed as reported for flexible ferrocene,[10] zirconocene[6a] and dppe (diphenylphosphinoethane) derivatives.[11] One of the rare examples[10,11] of a rigid bisphosphine derived FLP capable for hydrogen activation was described by Erker *et al.*[7b] The FLP consisting of bis(diphenylphosphino)naphthalene (**4**)/**3** was capable of reversible uptake and release of hydrogen[7c–e,g–j] and was applied in the hydrogenation of silyl enol ethers. Hence, rigidity and steric bulk are key factors in the activation of hydrogen by bisphosphine-derived FLPs. Consequently, we focused on the activity of [2.2]paracylophane derived bisphosphines in the metal-free hydrogen activation. The highly rigid planar-chiral framework allows arrangement of the two phosphino groups in distances between 4.9 Å in **1**[12] or 4.0 Å in **2**[13] (Fig. 1) providing a unique setup to study their activity depending to the functional group distance. The FLPs were active in a novel domino hydrosilylation/hydrogenation reaction of enones, providing the silyl-protected alcohols in high yields and excellent diastereoselectivity in a single step (Scheme 1).

Results and discussion

Structure of frustrated Lewis pairs derived from bisphosphines 1 and 2 after hydrogen activation

We initiated our investigations by the reaction of commercially available PhanePhos (**1**) with $B(C_6F_5)_3$ (**3**). Indeed, **1**/**3** formed a

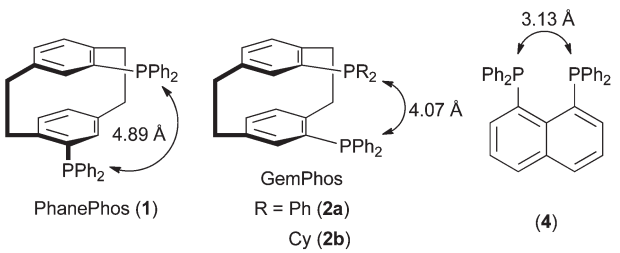
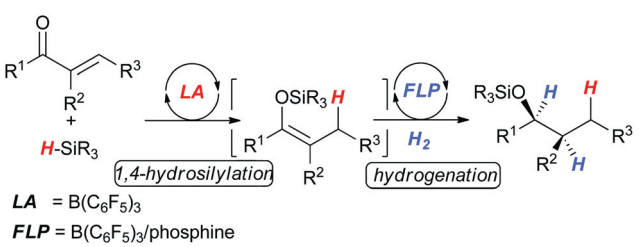


Fig. 1 Bisphosphines including relative P–P distances.



Scheme 1 Domino hydrosilylation/hydrogenation of enones.

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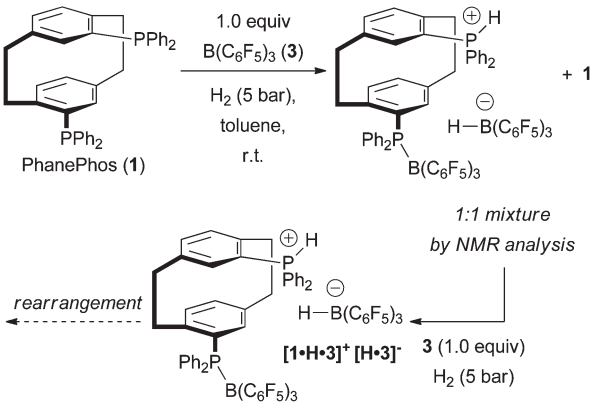
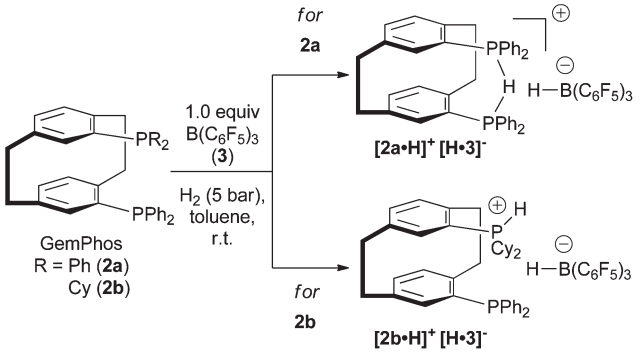
†Electronic supplementary information (ESI) available: synthetic details, NMR spectra and characterization. CCDC 867393 for $[\mathbf{2a}\cdot H]^+[BF_4]^-$ and 867456 for $[\mathbf{2b}\cdot H]^+[BF_4]^-$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30374d



Scheme 2 Activation of dihydrogen with PhanePhos (**1**).



Scheme 3 Hydrogen activation by GemPhos derivatives (**2**).

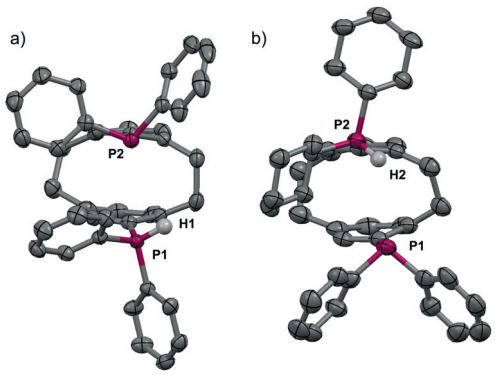


Fig. 2 Crystal structure of (a) $[\mathbf{2a}\cdot H]^+[BF_4]^-$ and (b) $[\mathbf{2b}\cdot H]^+[BF_4]^-$ (selected bond lengths for $[\mathbf{2a}\cdot H]^+[BF_4]^-$: P1–P2 3.681 Å, P2–H1 3.321 Å; for $[\mathbf{2b}\cdot H]^+[BF_4]^-$: P1–P2 4.040 Å, P1–H2 3.391 Å; peripheral hydrogen atoms and BF_4 anion were omitted for clarity).[14]

FLP since the corresponding NMR spectra of a 1 : 1 mixture did not differ from the individual spectra. After the solution was reacted with hydrogen (2 bar) at room temperature the NMR spectra changed significantly. The ^{31}P NMR spectrum displayed two new resonances at 4.3 and −1.2 ppm (^{31}P NMR resonance of free **1** δ = −0.7 ppm). The resonance at lower frequencies was split into a doublet (J_{P-H} = 510 Hz) accounting for a protonated phosphine species. However, the spectrum also displayed the signal of free bisphosphine **1** in a 1 : 1 ratio to the phosphonium compound. The ^{11}B NMR and the ^{19}F NMR spectrum indicated a borohydride anion with its characteristic signals (^{11}B NMR δ = −24.3 ppm, ^{19}F NMR δ = −132 (*o*-), −163 (*p*-) and −166 (*m*-C_6F_5); ^{1}H NMR resonance at δ = 4.40 ppm ((C_6F_5)$_3$B–H)) together with the formation of a P–B Lewis adduct (^{11}B NMR δ = 0.4 ppm, ^{19}F NMR δ = −132 (*o*-), −158 (*p*-) and −164 (*m*-C_6F_5)). The subsequent addition of a second equivalent of **3** and reaction with hydrogen resulted in conversion to the phosphonium cation together with a borohydride species ($[\mathbf{1}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$, Scheme 2).

Consequently, the activation of hydrogen by PhanePhos (**1**) required two equivalents of Lewis acid **3**, while only one borohydride anion was formed. This might be the result of a geometrical reorganisation in $[\mathbf{1}\cdot H]^+$ making the second phosphine unit more accessible (**3**) (*vide infra* for theoretical considerations) thus providing a binding/reaction site for the Lewis acid **3**. The product $[\mathbf{1}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$ was prone for concurrent attack of the phosphine unit to the *para*-position in **3** (see ESI† for details).[10] Surprisingly, the *pseudo-geminal* bisphosphine GemPhos derivatives **2** displayed different stoichiometry for H_2-activation compared to **1**. The NMR spectra of a 1 : 1 mixture of **2a** or **2b** with **3** displayed no changes compared to the individual spectra, hence both GemPhos phosphines **2** in combination with **3** form FLPs. Exposure of these mixtures to hydrogen formed the corresponding phosphonium–borohydride salts as clearly determined by NMR spectroscopy (Scheme 3). The symmetrical bisphosphine **2a** provided a binding motive for the proton, which is similar to **4**.[7b] Accordingly, upon lowering the temperature to −60 °C the ^{31}P NMR resonance separated into a resonance at high (−0.42 ppm, J_{P-H} = 515 Hz, J_{P-P} = 86 Hz) and at low frequencies (−4.75 ppm, J_{P-P} = 86 Hz), indicating slow exchange of the proton between the two phosphorous atoms on the NMR time scale. The ^{11}B NMR spectrum revealed a doublet centered at −24.6 ppm with a coupling constant of J_{B-H} = 92 Hz, which accounts for a borohydride anion. On the contrary, the phosphonium motive derived from **2b** is structurally different from **2a**. When the unsymmetrical bisphosphine **2b** was subjected to hydrogen activation the PCy_2H^+ species was provided (Scheme 3) and the resonance for a free PPh_2-unit was observed by ^{31}P NMR (H-PCy_2: −14.3 ppm, J_{P-H} = 473 Hz, J_{P-P} = 47 Hz; PPh_2: 2.79 ppm, J_{P-P} = 47 Hz; regioselective protonation was proved by ^{31}P^{1}H COSY). All attempts to obtain suitable crystals for single crystal analysis were unsuccessful. However, the structures of the protonated phosphonium species $[\mathbf{2a}\cdot H]^+$ and $[\mathbf{2b}\cdot H]^+$ as BF_4^--salts were determined (Fig. 2a and b). The solid state structure of $\mathbf{2a}\cdot HBF_4$ reveals the monoprotonation of one phosphino-unit. Additionally, the proton is hydrogen bonded to the second phosphino-group (P2–H1 3.321 Å). The P1–P2 distance is reduced by 0.387 Å to 3.681 Å compared to unprotonated **2a** (4.068 Å).[13] The crystal structure of $[\mathbf{2b}\cdot H]^+[BF_4]^-$ displays the selective protonation of the PCy_2-unit confirming the NMR spectroscopic results. The two phosphorous moieties are separated by 4.040 Å, which is significantly larger than in the $[\mathbf{2a}\cdot H]^+$ cation. Clearly, the *pseudo-geminal* bisphosphines **2a** and **2b** offer more efficient activation of dihydrogen compared **1** since only one equivalent of **3** is needed. However, the requirement of two equivalents of **3** for exhaustive H_2-activation by **1** prompted us to investigate this system in more detail, since it is a potential deactivation pathway for bisphosphines. Therefore the

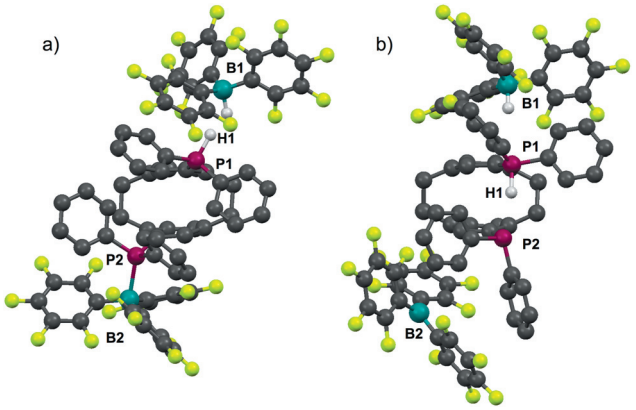


Fig. 3 Calculated phosphonium-borohydride salts of (a) **1** and (b) **2a** with one additional $B(C_6F_5)_3$ molecule; (selected interatomic distances: (a) $[\mathbf{1}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$: B1–P1 3.766 Å, B2–P2 2.283 Å; (b) $[\mathbf{2a}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$: B1–P1 4.347 Å, B2–P2 5.673 Å; selected hydrogen atoms were omitted for clarity).

structures of the phosphonium–borohydride salts derived from **1** and **2a** with one additional $B(C_6F_5)_3$ (**3**) molecule were studied by theoretical methods. The corresponding lowest energy structures optimized at BP86/def2-SVP[15] level of theory including Grimme's dispersion corrections[16] as implemented in the Turbomole[17] package are depicted in Fig. 3 (see ESI† for more details).

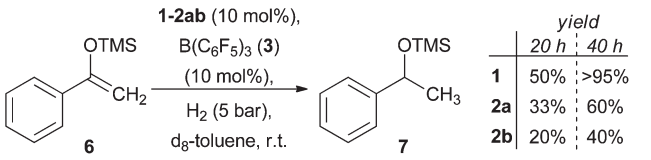
The two calculated structures show distinctly different binding modes: (1) the arrangement in $[\mathbf{1}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$ exhibits a short B2–P2 distance (Fig. 3a, 2.283 Å), which confirms our experimental observation that one Lewis acid molecule is consumed by adduct formation (see Scheme 1); (2) the structure of $[\mathbf{2a}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$ shows an *intramolecular* hydrogen bond of H1 to P2 (Fig. 3b). This hydrogen bond prevents the *intermolecular* adduct formation with **3** and is in agreement with the NMR data and solid-state structure of $\mathbf{2a}\cdot HBF_4$. Additionally this study rationalizes why reaction product $[\mathbf{1}\cdot H\cdot\mathbf{3}]^+[H\cdot\mathbf{3}]^-$ is prone for rearrangement.

Catalytic application

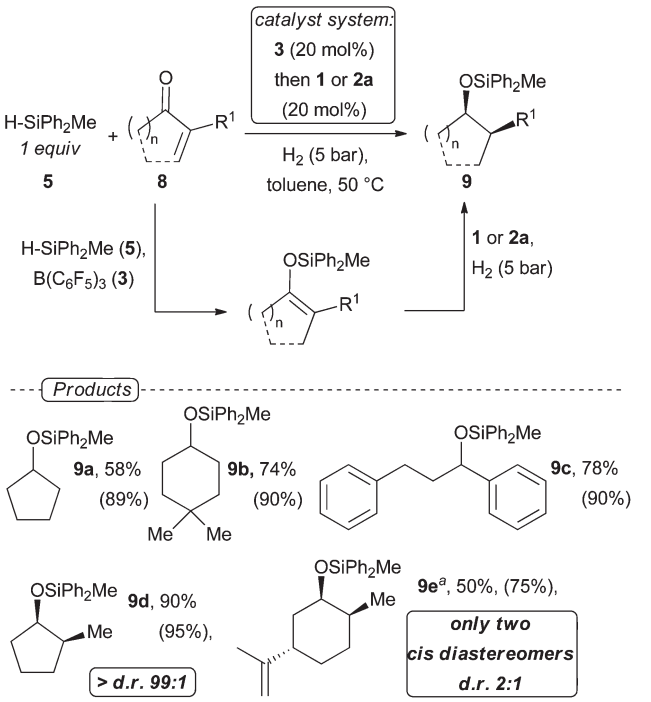
Since the three bisphosphines **1**, **2a** and **2b** display different reactivity when exposed to **3** and H_2, we were curious how these structural features would affect their catalytic potential. We envisioned the application of the new catalyst system in a novel domino reaction[18] consisting of two processes: the $B(C_6F_5)_3$-catalyzed 1,4-hydrosilylation of enones providing silyl enol ethers and their subsequent hydrogenation by a FLP consisting of a bisphosphine and $B(C_6F_5)_3$ (Scheme 1).

Although both reactions have been reported separately by Piers *et al.*[19] and Erker *et al.*,[7b] the application of such transformations in a sequence employing only one single catalyst system has not been reported so far.

First we established that the $B(C_6F_5)_3$-catalyzed 1,4-hydrosilylation reaction is not affected by the presence of phosphine. To our delight, when 4,4-dimethyl cyclohexenone was reacted with one equivalent of diphenylmethylsilane (**5**) in the presence of 20 mol% **3**/**1** the silyl enol ether was provided instantaneously. Next, we turned our attention to the hydrogenation of silyl enol



Scheme 4 Hydrogenation of silyl enol ether **6** by bisphosphine derived frustrated Lewis-pairs (yields were determined by ^1H NMR).



Scheme 5 Domino hydrosilylation/hydrogenation of α,β-unsaturated ketones (numbers in parentheses are NMR yields, [a]reaction was performed at 100 °C).

ethers. Accordingly we subjected the three bisphosphines in combination with **3** to the hydrogenation of silyl enol ether **6** at room temperature (10 mol% cat. loading, Scheme 4).

The saturated product **7** was obtained in variable yields dependent on the nature of the bisphosphine. When PhanePhos (**1**) was reacted with one equivalent **3** (1 : 1 mixture, 10 mol%) in the presence of silyl enol ether **6** and hydrogen, the previously observed adduct formation was prevented due to the lower concentration of free borane. This was evidenced by the ^{31}P NMR spectrum of the reaction displaying only resonances for the corresponding FLP. The hydrogenation of **6** with 10 mol% **1**/**3** (1 : 1) provided the product in highest yield (>95%). The *pseudo-geminal* isomer **2a** proved less efficient (60% yield) and the unsymmetrical bisphosphine **2b** provided **7** in 40% yield after 40 h at room temperature. The notable difference in reactivity might be explained by the increasing basicity of the phosphine moieties in the order $PPh_2\text{-}H^+ < PPh_2\text{-}H^+\text{-}PPh_2 < PCy_2\text{-}H^+$. Encouraged by the fact that each step of the domino reaction was affected by the catalyst system consisting of the planar-chiral bisphosphines (**1** and **2a**) and **3**, we directed our interest to the catalytic domino 1,4-hydrosilylation/hydrogenation of α,β-unsaturated ketones (Scheme 5). The domino

reaction of cyclic and acyclic enones with one equivalent of silane **5** and hydrogen was efficiently catalyzed by **1**/**3** employing 20 mol% catalyst loading at 50 °C. Generally, the corresponding silyl-protected secondary alcohols were obtained in good yields (50–90% for isolated products after column chromatography; 75–95% determined by NMR from crude material). Notably, the saturated products derived from tetra-substituted silyl enol ethers (**9d**, **9e**) were obtained with highest yield and exclusively as *cis* diastereomers, which can be rationalized according to the well established mechanistic model for $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds.[20] Such products are commonly not easily accessed, which underscores the potential of this transition metal free hydrogenation process.

Conclusions

We have shown that planar-chiral bisphosphines are viable Lewis bases for the activation of hydrogen by frustrated Lewis pairs and exhibit distinct reactivity to more flexible ferrocene derived bisphosphines. The two isomeric [2.2]paracylophane-derived bisphosphines **1** and **2a** allowed to study steric aspects without altering electronic properties. Especially PhanePhos (**1**) exhibited significant features for the use of bisphosphines in hydrogen activation: Although **1** and **3** forms a FLP, one phosphine moiety is quenched by **3** upon exposure to hydrogen. However, in the presence of an unsaturated substrate the adduct formation was not observed and a 1 : 1 ratio of **1**/**3** can be applied.

A novel domino hydrosilylation/hydrogenation reaction was developed providing silyl protected alcohols in one step. The hydrogenation proceeded in high yields and high diastereoselectivity.

Experimental section

General procedure for the reduction of enones 8

In a glovebox, $B(C_6F_5)_3$ (**3**) (10–20 mol%), Ph_2MeSiH (**5**, 1.0 eq.) and the corresponding enone **9** (25 mg, 1.0 eq.) were dissolved in toluene (2 ml) followed by immediate addition of PhanePhos (**1**) (10–20 mol%) (in case of **9e** GemPhos **2a** was used). The solution was transferred to a sealable flask equipped with a Teflon tap and magnetic stirbar. The solution was freeze–pump thawed for 2 cycles, charged with H_2 at 77 K and stirred for 24–48 h at 50 °C. The reaction mixture was directly subjected to column chromatography (cyclohexane–EtOAc 99 : 1) yielding the corresponding silylether as a colorless oil.

Cyclopentyloxy(methyl)diphenylsilane (9a)

24 h, 50 mg, yield 58% (10% silane impurity), R_f = 0.20. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.56 (m, 4H, H_{Ar}), 7.42–7.32 (m, 6H, H_{Ar}), 4.40–4.30 (m, 1H, C*H*), 1.86–1.46 (m, 8H, CH_2), 0.93 (s, 3H, CH_3) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 137.1 (2 × $C_{quart\ Ph}$), 134.5 (4 × CH_{Ph}), 129.7 (2 × CH_{Ph}), 127.9 (4 × CH_{Ph}), 75.3 (CH), 35.7, 23.3, −2.2 ppm.

4,4-Dimethylcyclohexyloxy(methyl)diphenylsilane (9b)

24 h, 48 mg, yield 74%, R_f = 0.15. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.58 (m, 4H, H_{Ar}), 7.43–7.32 (m, 6H, H_{Ar}), 3.73 (sept, J = 4.7 Hz, 1H, C*H*), 1.73–1.50 (m, 4H, CH_2), 1.48–1.36 (m, 2H, CH_2), 1.19–1.05 (m, 2H, CH_2), 0.93 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 0.67 (s, 3H, CH_3) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 137.2 (2 × $C_{quart\ Ph}$), 134.5 (4 × CH_{Ph}), 129.8 (2 × CH_{Ph}), 127.9 (4 × CH_{Ph}), 71.9 (CH), 36.9, 31.6, 30.8, 29.7, 26.2, −2.1 ppm.

1,3-Diphenylpropoxy(methyl)diphenylsilane (9c)

48 h, 38 mg, yield 78%, R_f = 0.1. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–6.92 (m, 20H, H_{Ar}), 4.68 (dd, J = 6.7 Hz, 5.6 Hz, 1H, C*H*), 2.68–2.39 (m, 2H, CH_2), 2.15–1.83 (m, 2H, CH_2), 0.36 (s, 3H, CH_3) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.6, 142.2, 134.7, 134.5, 129.9, 128.8, 128.5, 128.4, 128.3, 127.9, 127.9, 127.3, 126.4, 125.8, 75.3, 42.0, 31.8, −2.3 ppm.

cis-2-Methylcyclopentyloxy(methyl)diphenysilane (9d)

24 h, 69 mg, yield 90%, R_f = 0.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.56 (m, 4H, H_{Ar}), 7.45–7.32 (m, 6H, H_{Ar}), 4.16 (q, J = 4.6 Hz, 1H, C*H*), 1.88–1.61 (m, 5H), 1.59–1.38 (m, 2H), 1.00 (d, J = 7.0 Hz, 3H, CH_3), 0.66 (s, 3H, CH_3) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 137.3 (2 × $C_{quart\ Ph}$), 134.5 (4 × CH_{Ph}), 129.7 (2 × CH_{Ph}), 127.8 (4 × CH_{Ph}), 40.0, 34.8, 31.0, 21.9, 14.6, −2.3 ppm [*C*H(O) was not observed]. The NMR data agrees with the literature.[21]

(1*S*,2*R*,5*S*)-2-Methyl-5-(prop-1-en-2-yl)cyclohexyloxy(methyl)-diphenylsilane and (1*R*,2*S*,5*S*)-2-methyl-5-(prop-1-en-2-yl)-cyclohexyloxy(methyl)diphenylsilane (9e)

100 h, 29 mg, yield 50%, R_f = 0.6; d : r = 2 : 1; (1*S*,2*R*,5*S*)-**9e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.55 (m, 4H, H_{Ar}), 7.44–7.32 (m, 6H, H_{Ar}), 5.09 (s, 1H), 4.89 (s, 1H), 3.94 (m_c, 1H), 2.75–2.62 (m, 1H), 1.83–1.68 (m, 2H), 1.57 (s, 3H, CH_3), 1.33–1.11 (m, 5H), 0.91 (d, J = 6.6 Hz, 3H, CH_3), 0.66 (s, 3H, CH_3) ppm; (1*R*,2*S*,5*S*)-**9e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.54 (m, 4H, H_{Ar}), 7.45–7.30 (m, 6H, H_{Ar}), 4.62 (br s, 2H), 3.95 (br s, 1H), 2.49–2.36 (m, 1H), 1.80–1.66 (m, 2H), 1.62 (s, 3H, CH_3), 1.31–1.13 (m, 5H), 0.89 (d, J = 6.4 Hz, 3H, CH_3), 0.65 (s, 3H, CH_3) ppm.

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Notes and references

1 For comprehensive reviews see: (*a*) C. Zheng and S.-L. You, *Chem. Soc. Rev.*, 2012, **41**, 2498; (*b*) B. List, *Tetrahedron*, 2002, **58**, 5573; (*c*) G. Lelais and D. W. C. MacMillan, *Aldrichimica Acta*, 2006, **39**, 79; (*d*) A. Erkkila, I. Majander and P. M. Pihko, *Chem. Rev.*, 2007, **107**, 5416; (*e*) S. G. Ouellet, A. M. Walji and D. W. C. Macmillan, *Acc. Chem. Res.*, 2007, **40**, 1327.

2 Transferhydrogenation catalyzed by sec amines: (*a*) J. W. Yang, M. T. H. Fonseca and B. List, *Angew. Chem., Int. Ed.*, 2004, **43**, 6660; (*b*) J. W. Yang, M. T. H. Fonseca, N. Vignola and B. List, *Angew. Chem., Int. Ed.*, 2005, **44**, 108; (*c*) S. G. Ouellet, J. B. Tuttle and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2005, **127**, 32.

3 Transferhydrogenation catalyzed by phosphoric acid derivatives: (*a*) G. L. Li, Y. X. Liang and J. C. Antilla, *J. Am. Chem. Soc.*, 2007, **129**, 5830; (*b*) Q. Kang, Z. A. Zhao and S. L. You, *Adv. Synth. Catal.*, 2007, **349**, 1657; (*c*) Q. Kang, Z. A. Zhao and S. L. You, *Org. Lett.*, 2008, **10**, 2031; (*d*) M. Rueping, A. P. Antonchick and T. Theissmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 6751; (*e*) M. Rueping, A. R. Antonchick and T. Theissmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 3683; (*f*) M. Rueping, E. Sugiono, C. Azap, T. Theissmann and M. Bolte, *Org. Lett.*, 2005, **7**, 3781; (*g*) M. Rueping, T. Theissmann and A. P. Antonchick, *Synlett*, 2006, 1071.

4 Transferhydrogenation catalyzed by thiourea derivatives: (*a*) D. Menche and F. Arikan, *Synlett*, 2006, 841; (*b*) D. Menche, S. Bohm, J. Li, S. Rudolph and W. Zander, *Tetrahedron Lett.*, 2007, **48**, 365; (*c*) D. Menche, J. Hassfeld, J. Li, G. Menche, A. Ritter and S. Rudolph, *Org. Lett.*, 2006, **8**, 741; (*d*) Z. G. Zhang and P. R. Schreiner, *Synlett*, 2007, 1455; (*e*) J. Paradies, J. F. Schneider, M. B. Lauber, V. Muhr and D. Kratzer, *Org. Biomol. Chem.*, 2011, **9**, 4323; (*f*) N. J. A. Martin, X. Cheng and B. List, *J. Am. Chem. Soc.*, 2008, **130**, 13862.

5 D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535.

6 For reviews see: (*a*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46; (*b*) G. Erker, *Dalton Trans.*, 2011, **40**, 7475.

7 For selected examples see: (*a*) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072; (*b*) H. D. Wang, R. Fröhlich, G. Kehr and G. Erker, *Chem. Commun.*, 2008, 5966; (*c*) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124; (*d*) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050; (*e*) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 9136; (*f*) J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968; (*g*) P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701; (*h*) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117; (*i*) V. Sumerin, F. Schulz, M. Nieger, M. Leskela, T. Repo and B. Rieger, *Angew. Chem., Int. Ed.*, 2008, **47**, 6001; (*j*) M. Ullrich, A. J. Lough and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 52.

8 For asymmetric hydrogenation employing frustrated Lewis pairs see: (*a*) D. J. Chen, Y. T. Wang and J. Klankermayer, *Angew. Chem., Int. Ed.*, 2010, **49**, 9475; (*b*) D. J. Chen and J. Klankermayer, *Chem. Commun.*, 2008, 2130.

9 (*a*) F. Schulz, V. Sumerin, S. Heikkinen, B. Pedersen, C. Wang, M. Atsumi, M. Leskela, T. Repo, P. Pyykko, W. Petry and B. Rieger, *J. Am. Chem. Soc.*, 2011, **133**, 20245; (*b*) V. Sumerin, K. Chernichenko, M. Nieger, M. Leskela, B. Rieger and T. Repo, *Adv. Synth. Catal.*, 2011, **353**, 2093; (*c*) C. F. Jiang, O. Blacque and H. Berke, *Chem. Commun.*, 2009, 5518; (*d*) S. J. Geier, P. A. Chase and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 4884; (*e*) C. F. Jiang, O. Blacque, T. Fox and H. Berke, *Organometallics*, 2011, **30**, 2117; (*f*) C. F. Jiang, O. Blacque, T. Fox and H. Berke, *Dalton Trans.*, 2011, **40**, 1091.

10 For other examples see: A. Ramos, A. J. Lough and D. W. Stephan, *Chem. Commun.*, 2009, 1118.

11 D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, **50**, 12338.

12 (*a*) K. Rossen, P. J. Pye, A. Maliakal and R. P. Volante, *J. Org. Chem.*, 1997, **62**, 6462; (*b*) P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. P. Volante and P. J. Reider, *J. Am. Chem. Soc.*, 1997, **119**, 6207; (*c*) M. N. Cheemala, M. Gayral, J. M. Brown, K. Rossen and P. Knochel, *Synthesis*, 2007, 3877; (*d*) J. Almena, S. Klaus, H. Neumann, A. Zapf, D. Strubing, S. Hubner, T. Riemeier, P. Gross, M. Sarich, W. R. Krahnert, K. Rossen and M. Beller, *Angew. Chem., Int. Ed.*, 2006, **45**, 154.

13 F. C. Falk, R. Fröhlich and J. Paradies, *Chem. Commun.*, 2011, **47**, 11095.

14 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

15 Becke-Perdew (BP86) functional: (*a*) P. A. M. Dirac, *Proc. R. Soc. (London)*, 1929, **A123**, 714; (*b*) J. C. Slater, *Phys. Rev.*, 1951, **81**, 385; (*c*) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (*d*) A. D. Becke, *Phys. Rev.*, 1988, **A38**, 3098; (*e*) J. P. Perdew, *Phys. Rev.*, 1986, **B33**, 8822; def2-SVP basis set: (*f*) A. Hellweg, C. Hättig, S. Höfener and W. Klopper, *Theor. Chem. Acc.*, 2007, **117**, 587; (*g*) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297; (*h*) F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143.

16 (*a*) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (*b*) S. Grimme, H. Kruse, L. Goerigk and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 1402.

17 TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com

18 (*a*) L. F. B. Tietze, G. Brasche and K. M. Gericke, Wiley-VCH, Verlag, Weinheim, 2006; (*b*) P. v. Zezschwitz and A. de Meijere, *Top. Organomet. Chem.*, 2006, **19**, 49; (*c*) P. V. Zezschwitz, A. de Meijere and S. Bräse, *Acc. Chem. Res.*, 2005, **38**, 413; (*d*) P. v. Zezschwitz, A. de Meijere, H. Nuske and B. Stulgies, *J. Organomet. Chem.*, 2002, **653**, 129; (*e*) L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115.

19 J. M. Blackwell, D. J. Morrison and W. E. Piers, *Tetrahedron*, 2002, **58**, 8247.

20 (*a*) W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, **50**, 12252; (*b*) D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090; (*c*) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440.

21 S. Y. Chang, W. T. Jiaang, C. D. Cherng, K. H. Tang, C. H. Huang and Y. M. Tsai, *J. Org. Chem.*, 1997, **62**, 9089.

