



Cite this: *Org. Biomol. Chem.*, 2014, **12**, 9139

Received 28th June 2014,
Accepted 12th September 2014

DOI: 10.1039/c4ob01346h

www.rsc.org/obc

Frustrated Lewis pair catalyzed hydrosilylation and hydrosilane mediated hydrogenation of fulvenes†

Sergej Tamke,^a Constantin-G. Daniliuc^b and Jan Paradies*^a

The frustrated Lewis pair (FLP) mediated hydrosilylation of pentafulvenes is described yielding allyl silanes with high regioselectivity in excellent yields. While phenyl substituted allyl silanes undergo B(C₆F₅)₃-mediated rearrangement to vinyl silanes, dimethyl derivatives experience FLP-catalyzed hydrogenation followed by an unprecedented protodesilylation. This observation allowed the metal-free hydrogenation of 6,6-dimethylfulvene to iso-propyl cyclopentene according to a FLP-catalyzed triple domino reaction consisting of hydrosilylation, hydrogenation and protodesilylation. The mechanisms were investigated by deuteration experiments.

Introduction

Hydrogenations and hydrosilylations are two of the most applied processes in industrial chemistry.¹ Although both transformations are efficiently catalyzed by transition metal complexes,² research in the field of metal-free alternatives has flourished in the past few decades. Piers and co-workers demonstrated that the strong Lewis acid B(C₆F₅)₃ (**1**) is a powerful hydrosilylation catalyst of a number of substrates including aldehydes, ketones, imines and enones.³ Also, less polarized substrates such as olefins were susceptible to borane and phosphonium-mediated hydrosilylation.⁴ We have reported earlier⁵ that the B(C₆F₅)₃-catalyzed 1,4-hydrosilylation of enones^{3c} can be combined with frustrated Lewis pair (FLP) catalyzed hydrogenations^{6,7} of the *in situ* generated silylenol ethers.⁸ Also, allyl silanes were susceptible to FLP-catalyzed hydrogenation,^{7d,9} providing access to saturated silanes. We sought to expand this methodology to compounds bearing two or more non-polar double bonds. Particularly pentafulvenes are highly reactive, electron-rich compounds which readily undergo cycloaddition reactions¹⁰ to construct complex molecules.^{10a,d} In particular, this reactivity obstructs the use of pentafulvenes as cyclopentyl building blocks for natural products or fragrant syntheses.¹¹ Erker has shown that FLPs can influence

the fulvene-reactivity to yield unusual [6 + 4] cycloaddition products.¹²

Herein we report the FLP-catalyzed hydrosilylation and subsequent hydrogenation of pentafulvenes to access silylated cyclopentene-derivatives according to a domino reaction sequence.¹³

Results and discussion

Hydrosilylation of fulvenes

We initiated our investigations by reacting 6,6-dimethylfulvene (**2**) with 1 equiv. of methyl(diphenyl) silane (**3**) in the presence of 10 mol% of the Lewis-acid B(C₆F₅)₃ (**1**) (Table 1, entry 1).

Instantaneous conversion of the starting material was observed, yielding a mixture of hydrosilylation and oligomerization products. Remarkably, employing 10 mol% of the FLP consisting of P(1-naphthyl)₃ (**4**) and B(C₆F₅)₃ (**1**) (Table 1, entry 2) as the catalyst provided exclusively the hydrosilylation product **5** as a single regioisomer after 1 h in quantitative yield. The hydrosilylation product **5** was unambiguously characterized by NMR spectroscopy and X-ray crystallography¹⁴ as the addition product to the C2–C3 position (Fig. 1). Alternative products arising from FLP mediated cycloaddition¹² were not detected throughout our study. Evidently the choice of the Lewis base has a dramatic impact on the outcome of the reaction, and we expanded our investigation to other phosphines and amines (Table 1, entries 3–8). Indeed, the nature of the employed Lewis base has a significant influence on the reaction rate. In the presence of P(*t*-Bu)₃ (**6**)/**1** the fulvene **2** was not consumed even after prolonged reaction time (78 h, entry 3), most likely due to the formation of the stable silylium salt [(*t*-Bu)₃P-SiPh₂Me][HB(C₆F₅)₃].¹⁵ Phosphines or amines comprising less basic heteroatomic sites are viable Lewis bases for the

^aKarlsruhe Institute of Technology, Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany. E-mail: jan.paradies@kit.edu; Fax: +49 721 608 45637; Tel: +49 721 608 45344

^bWestfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstr. 40, 48149 Münster, Germany.

E-mail: constantin.daniliuc@uni-muenster.de; Fax: +49 251 83-39772;

Tel: +49 251 83-33293

† Electronic supplementary information (ESI) available: General information; synthetic procedures; NMR spectroscopic data. CCDC 1008790. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01346h



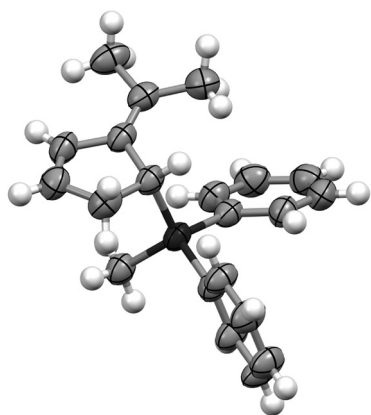
Table 1 Lewis base influence on the hydrosilylation of dimethylfulvene (**2**)^a

Entry	Lewis base	Time (h)	Yield (%)
1 ^b	—	—	—
2	P(1-naphth) ₃ (4)	1	>95
3 ^c	P(<i>t</i> -Bu) ₃ (6)	78	0
4	P(Mes) ₃ (7)	24	>95 (79%) ^d
5	P(C ₆ F ₅)Ph ₂ (8)	0.5	>95
6	PhNMe ₂ (9)	24	>95
7	(1-naphth)NMe ₂ (10)	1	>95
8 ^b	(<i>p</i> -tol) ₂ NMe (11)	1	<5

^a Reactions performed on a 0.1 mmol scale in CD₂Cl₂ (0.5 mL, 0.2 M) at r.t. using 1 equiv. of hydrosilane **3** and 10 mol% of B(C₆F₅)₃ (**1**) and the corresponding Lewis base. Yields were determined by ¹H NMR spectroscopy using the residual solvent signal as an internal standard.

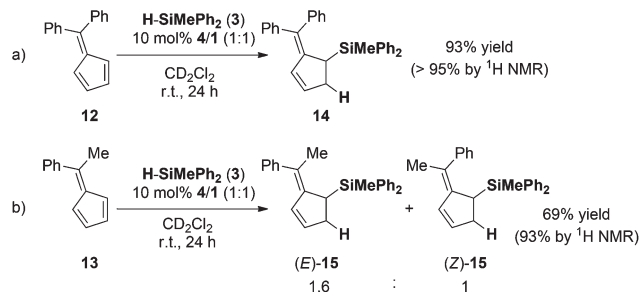
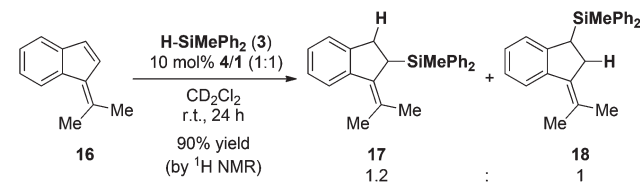
^b Significant amounts of the oligomerization product were observed.

^c No hydrosilylation was observed even at 70 °C. ^d Isolated yield.

**Fig. 1** Crystal structure of allyl silane **5**.

FLP-catalyzed hydrosilylation of **2** providing the product **5** in quantitative yield. The FLP consisting of P(Mes)₃ (**7**)/(**1**) required 24 h for the quantitative hydrosilylation of **2** whereas the corresponding P(C₆F₅)Ph₂ (**8**)/(**1**) needed only 0.5 h for completion. The electronic modification of the aniline derivatives exhibited even more drastic effects on the reaction rates (Table 1, entries 6–8). While *N,N*-dimethylaniline (**9**) as a Lewis base component gave **5** in 24 h (entry 6, >95%), the slightly less basic *N,N*-dimethyl-1-naphthylamine (**10**) provided the product in quantitative yield in 1 hour (Table 1, entry 7). In contrast, the FLP derived from *N,N*-di(*p*-toloyl)methylamine (**11**) and B(C₆F₅)₃ (**1**) furnished only traces of the hydrosilylation product **5** accompanied by significant amounts of oligomerization products (Table 1, entry 8). From these observations some tentative conclusions can be drawn.

The dependence of the reaction rates may be attributed to the formation of the encounter complex.¹⁶ Precoordination of

**Scheme 1** Hydrosilylation of (a) 6,6-diphenylfulvene (**12**) and (b) 6-phenyl-6-methylfulvene (**13**).**Scheme 2** Hydrosilylation of dimethylbenzofulvene (the yield was determined by ¹H NMR spectroscopy using the residual solvent signal as an internal standard).

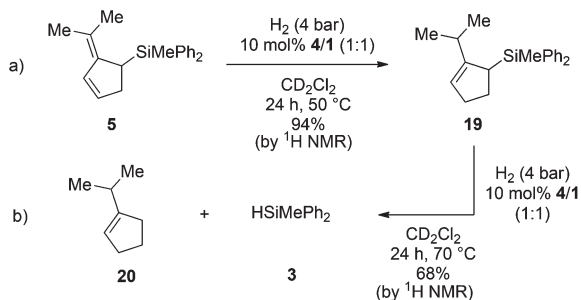
borane **1** by the corresponding Lewis base significantly decelerates the undesired oligomerization, thus favoring the hydrosilane activation.

In order to investigate the substrate scope of the reaction, different pentafulvenes were reacted with hydrosilane **3** in the presence of 10 mol% **4/1** at room temperature. The aryl substituted pentafulvenes, 6,6-diphenylfulvene (**12**) and 6-methyl-6-phenylfulvene (**13**), readily underwent regioselective 1,2-hydrosilylation in 98% and 93% yield for **14** and **15** respectively with remarkable C2 regioselectivity (Scheme 1). The hydrosilylation of the unsymmetric fulvene **13** provided a mixture of (*E*)-**15** and (*Z*)-**15** in a 1.6 : 1 ratio (Scheme 1b). As a fourth substrate we investigated the reactivity of 6,6-dimethylbenzofulvene (**16**) in the FLP-catalyzed hydrosilylation with **3** (10 mol% **4/1**). In accord with the previous examples the hydrosilylation was complete in 24 h in excellent yield (90%, Scheme 2). However, the reaction proceeds with low regioselectivity and a mixture of regioisomers (**17** : **18**; 1.2 : 1 ratio) was obtained.

Catalytic hydrogenation

The catalytic hydrosilylation of 6,6-disubstituted fulvenes was achieved using FLPs derived from P(1-naphth)₃ (**4**), P(C₆F₅)Ph₂ (**8**) and (*p*-tol)₂NMe (**11**) and B(C₆F₅)₃ (**1**) as Lewis acids. Our group has shown earlier that the same FLPs were active catalysts for the metal-free hydrogenation of allyl silanes^{7d,9} giving rise to a hydrosilylation/hydrogenation domino-reaction sequence.^{5a} Consequently we first investigated the reduction of the prepared allylic silanes using H₂ and **4/1** as catalysts. Indeed, when **5** was subjected to H₂-atmosphere in the presence of **4/1** the corresponding cyclopentenylsilane **19** together with small amounts of 1-iso-propylcyclopent-1-ene (**20**) and hydrosilane **3** as by-products were observed (Scheme 3a).





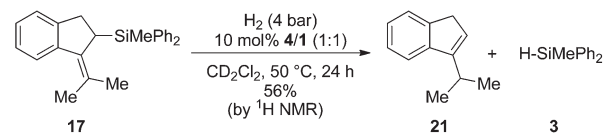
Scheme 3 FLP catalyzed hydrogenation of allylsilane **5** (yields were determined by ^1H NMR spectroscopy using the residual solvent signal as an internal standard).

Surprisingly the hydrogenation provided (2-iso-propylcyclopent-2-en-1-yl)trimethylsilane (**19**) as the sole isomer, indicating a double bond migration during the reaction (*vide infra* for mechanistic details). Since product **19** is once again an allyl silane a second reduction step to the saturated iso-propyl substituted cyclopentylsilane seems feasible. However, prolongation of the reaction time or increase of the reaction temperature (up to 70 °C) did not result in the reduction of the double bond but unexpectedly in the dehydrosilylation of **19** to produce iso-propyl-cyclopentene (**20**) and the hydrosilane **3** in 68% yield (Scheme 3b). Accordingly the by-product formation in the hydrogenation of **5** is a result of the over-hydrogenation of **19**. Such reactivity is known for allyl silanes when treated with strong Brønsted acids.¹⁷ However, these reactions usually require nucleophilic oxo-groups in order to cleave the silicon carbon bond. The unexpected protodesilylation prompted us to investigate the reactions in more detail. Therefore hydrogenation experiments of allyl silane **5** were conducted using 10 mol% of FLPs comprising different Lewis bases (Table 2). Lewis pairs consisting of electron rich phosphines P(*t*-Bu)₃ (**6**)/**1** and P(Mes)₃ (**7**)/**1** were not reactive (Table 2, entries 1 and 2). FLPs with a less electron releasing phosphine or amine *e.g.* **8** and **9** were able to catalyze the hydrogenation of **5** even at

Table 2 Lewis base influence on the hydrogenation and protodesilylation^a

Entry	Lewis base	<i>T</i> [°C]	Conv. [%]	Product ratio 19 : 20
1	6	70	0	—
2	7	70	0	—
3	4	50	>95	10.8 : 1
4	8	r.t.	76	5.3 : 1
5	9	r.t.	68	7.5 : 1

^a Reactions performed on a 0.1 mmol scale in CD₂Cl₂ (0.5 mL, 0.2 M) at the given temperature using 10 mol% of B(C₆F₅)₃ (**1**) and Lewis base under 4 bar of hydrogen atmosphere. Yields were determined by ^1H NMR spectroscopy after 24 h with the residual solvent signal as an internal standard.



Scheme 4 FLP mediated protodesilylation of allylsilane **17** (the yield was determined by ^1H NMR spectroscopy using the residual solvent signal as an internal standard).

room temperature (entries 4 and 5). Products resulting from protodesilylation were already generated in significant amounts even under these mild reaction conditions. The FLP-catalyzed protodesilylation was not only restricted to **19**. Exposure of the mixture of **17** and **18** (1.2 : 1) to H₂-atmosphere in the presence of **4/1** (10 mol%) resulted in the formation of the iso-propyl indene **21**. As expected, only the allyl silane **17** underwent protodesilylation (56%) while the homo allyl silane **18** remained unchanged (Scheme 4).

Finally the two allyl silanes **14** and *E/Z*-**15** were subjected to the hydrogenation (10 mol% **4/1**), but even after prolonged reaction time (48 h) at elevated temperatures (70 °C) the corresponding hydrogenation products were not identified. However, under the reaction conditions the allyl silanes underwent rearrangement to the corresponding vinyl silanes (compare Table 2). Subsequent control experiments revealed that this rearrangement is catalyzed by B(C₆F₅)₃ (**1**).¹⁸ The symmetrical diphenyl-derivative **14** was converted to the corresponding vinyl silane **22** in quantitative yield after 48 h at 70 °C (Table 3, entry 1 > 95% yield). Interestingly the two diastereomers *E/Z*-**15** displayed different rates for the rearrangement. In the mixture of *E/Z*-**15** (1.6 : 1) the *E*-diastereomer underwent the Lewis acid-catalyzed rearrangement more readily (entry 2: 40 °C, 24 h) than *Z*-**15** (entry 2: 70 °C, 92 h).

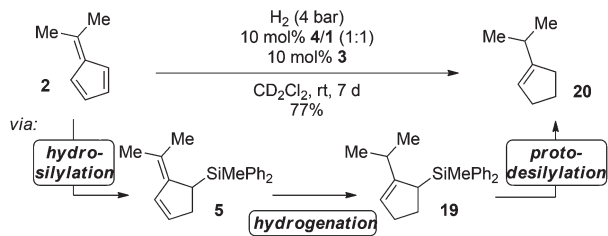
The combined data for the hydrosilylation of **2**, hydrogenation of **5** and final protodesilylation of **19** suggest that this sequence may be combined in a triple FLP-catalyzed domino-reaction cascade using hydrosilane **3** as the mediator (Scheme 5).

Table 3 Lewis acid-catalyzed double bond migration^a

Entry	Starting material		Product	Temp. (°C)	Time (h)	Yield (%)	
	R=	R'=					
1	Ph	Ph	14	22	70	48	>95
2	Ph	Me	<i>E</i> - 15	<i>E</i> - 22	40	24	>95
3	Me	Ph	<i>Z</i> - 15	<i>Z</i> - 22	70	92	78

^a Reactions performed on a 0.1 mmol scale in CD₂Cl₂ (0.5 mL, 0.2 M) at the given temperature and reaction time using 10 mol% of B(C₆F₅)₃ (**1**). Yields were determined by ^1H NMR spectroscopy with the residual solvent signal as an internal standard.





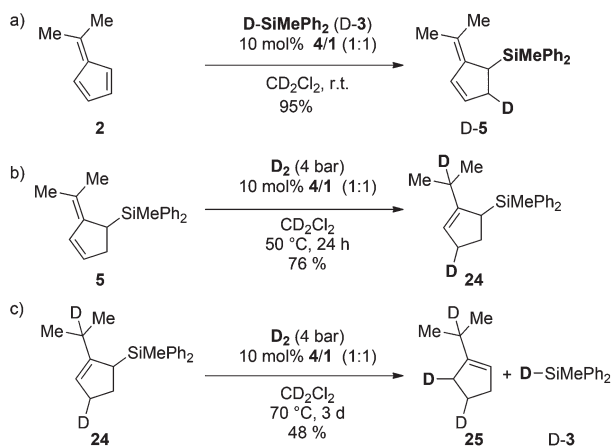
Scheme 5 FLP-catalyzed triple reaction cascade for the hydrosilane mediated hydrogenation of fulvene **2** (the yield was determined by ^1H NMR spectroscopy using the residual solvent signal as an internal standard).

Indeed, after reaction of **2** with 10 mol% FLP consisting of **4/1**, 10 mol% hydrosilane **3** in the presence of H_2 (4 bar) for 24 h at room temperature, complete consumption of the starting material was observed, yielding a mixture of cycloaddition and hydrosilylation products. However, after an additional 6 days the mixture was converted to iso-propylcyclopentene (**20**) in 77% yield. In this sequence the hydrosilane **3** enabled the FLP-catalyzed hydrogenation of 6,6-dimethylfulvene (**6**), which was not possible by direct metal-free hydrogenation as discussed earlier.

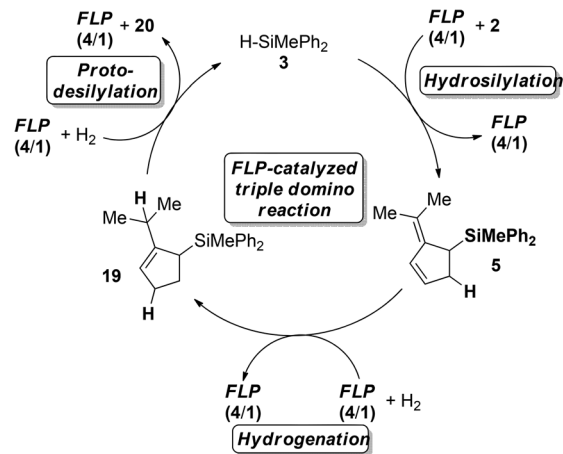
Mechanistic investigations

Finally we investigated the FLP-catalyzed triple cascade in more detail by deuteration experiments (Scheme 6).

Treatment of **2** with deuteriosilane **3** furnished the 2-(propan-2-ylidene)-5-deutero-cyclopent-3-en-1-yl)silane (**D-5**) selectively in quantitative yields (>95%, Scheme 6a). The exposure of **5** to D_2 -atmosphere in the presence of FLP **4/1** provided the 1,4-addition of deuterium to the diene with concomitant double bond migration, supporting a protonation/hydride addition mechanism (Scheme 6b). The resulting 3-cyclopentene **24** underwent deuterodesilylation in 48% yield with selective vicinal deuterium incorporation and formation of



Scheme 6 (a) Deuteriosilylation of dimethylfulvene (**2**), (b) deuteration of **5** and (c) deuterodesilylation of allylsilane **24** (yields were determined by ^1H NMR spectroscopy with the residual solvent signal as an internal standard).



Scheme 7 Catalytic cycle for the FLP-catalyzed triple reaction cascade.

equimolar amounts of deuteriosilane **D-3** (Scheme 6c). Accordingly, protodesilylation occurs *via* electrophilic attack of the double bond and nucleophilic deuteride-transfer from the borodeuteride to the silyl-group. Based on these observations a catalytic cycle for the FLP-catalyzed triple reaction cascade is proposed (Scheme 7). After the FLP-assisted hydrosilylation of **2** the allyl silane **5** is hydrogenated *via* metal-free H_2 -activation to the cyclopentene **19**. Finally hydrosilane **3** is regenerated by FLP-mediated H_2 -activation, and subsequent protodesilylation of **19** closes the catalytic cycle.

Conclusions

In conclusion, we have shown that FLPs are potent catalysts for the hydrosilylation of pentafulvenes in excellent yields. Here the FLPs not only catalyzed the hydrosilylation with remarkable regioselectivity but also suppressed undesired side reactions *e.g.* the Lewis acid catalyzed oligomerization of fulvenes. Dimethyl-substituted allyl silanes underwent FLP-catalyzed hydrogenation and protodesilylation. The latter observation led to the development of the triple reaction cascade consisting of hydrosilylation/hydrogenation/protodesilylation, allowing for the metal-free hydrogenation of 6,6-dimethyl fulvene to iso-propyl cyclopentene. The mechanisms of the individual reactions were investigated by deuteration experiments.

Acknowledgements

The authors acknowledge the Landesgraduiertenförderung of the State of Baden-Württemberg for a Ph.D. grant to S. T. We would also like to acknowledge the German research foundation (DFG) for a Heisenberg fellowship to J. P.

Notes and references

- (a) J. G. de Vries and C. J. Elsevier, *The handbook of homogeneous hydrogenation*, Wiley-VCH, 2007; (b) I. Ojima,



- in *Organic Silicon Compounds*, John Wiley & Sons, Ltd, 1989, p. 1479.
- 2 (a) M. E. Fasulo, M. C. Lipke and T. D. Tilley, *Chem. Sci.*, 2013, **4**, 3882; (b) C. D. F. Königs, H. F. T. Klare and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 10076; (c) E. P. Plueddemann, *Silane Coupling Agents*, Springer, US, 2013; (d) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567; (e) D. Troegel and J. Stohrer, *Coord. Chem. Rev.*, 2011, **255**, 1440; (f) B. Marciniak, *Hydrosilylation: A Comprehensive Review on Recent Advances*, Springer, 2010; (g) A. K. Roy, in *Adv. Organomet. Chem*, ed. A. F. H. Robert West and J. F. Mark, Academic Press, 2007, vol. 55, p. 1; (h) M. Oestreich and S. Rendler, *Angew. Chem., Int. Ed.*, 2005, **44**, 1661; (i) P. B. Glaser and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 13640; (j) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant and J.-P. Declercq, *Science*, 2002, **298**, 204; (k) R. M. Hill, *Silicone Surfactants*, Taylor & Francis, 1999; (l) B. Marciniak, *Comprehensive handbook on hydrosilylation*, Pergamon Press, 1992; (m) M. Voronkov, L. I. Kopylova, E. Lukevics and V. B. Pukhnarevitch, *Perspectives of Hydrosilylation*, Institute of Organic Synthesis, Riga, Latvia, 1992; (n) P. B. Hitchcock, M. F. Lappert and N. J. W. Warhurst, *Angew. Chem., Int. Ed.*, 1991, **30**, 438; (o) S. Patai and Z. Rappoport, *The chemistry of organic silicon compounds*, Wiley, 1989; (p) A. Mortreux, F. Petit and Commission of the European Communities, *Industrial Applications of Homogeneous Catalysis*, Springer, 1988; (q) J. L. Speier, in *Adv. Organomet. Chem*, ed. F. G. A. Stone and W. Robert, Academic Press, 1979, vol. 17, p. 407.
 - 3 (a) J. Hermeke, M. Mewald and M. Oestreich, *J. Am. Chem. Soc.*, 2013, **135**, 17537; (b) W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, **50**, 12252; (c) J. M. Blackwell, D. J. Morrison and W. E. Piers, *Tetrahedron*, 2002, **58**, 8247; (d) J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921; (e) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440.
 - 4 (a) M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538; (b) A. Simonneau and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 11905; (c) M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308; (d) M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936.
 - 5 (a) L. Greb, P. Ona-Burgos, A. Kubas, F. C. Falk, F. Breher, K. Fink and J. Paradies, *Dalton Trans.*, 2012, **41**, 9056; (b) L. Greb and J. Paradies, *Topics in Current Chemistry: Frustrated Lewis Pairs II: Expanding the Scope*, 2013, vol. 334, p. 81.
 - 6 (a) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124; (b) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050, (*Angew. Chem., Int. Ed.*, 2007, **119**, 8196–8199); (c) G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880; (d) 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; (e) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem., Int. Ed.*, 2008, **47**, 7543, (*Angew. Chem., Int. Ed.*, 2008, **120**, 7654–7657); (f) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Froehlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072.
 - 7 (a) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46; (b) D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535; (c) D. W. Stephan, *Org. Biomol. Chem.*, 2012, **10**, 5740; (d) J. Paradies, *Angew. Chem., Int. Ed.*, 2014, **53**, 3552; (e) J. Paradies, *Synlett*, 2013, 777.
 - 8 For the FLP-catalyzed hydrogenation of silylenol ethers see: H. D. Wang, R. Frohlich, G. Kehr and G. Erker, *Chem. Commun.*, 2008, 5966.
 - 9 (a) L. Greb, S. Tussing, B. Schirmer, P. Ona-Burgos, K. Kaupmees, M. Lokov, I. Leito, S. Grimme and J. Paradies, *Chem. Sci.*, 2013, **4**, 2788; (b) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan and J. Paradies, *Angew. Chem., Int. Ed.*, 2012, **124**, 10311, (*Angew. Chem. Int. Ed.*, 2012, **51**, 10164).
 - 10 (a) S. S. Bhojgude, T. Kaicharla, A. Bhunia and A. T. Biju, *Org. Lett.*, 2012, **14**, 4098; (b) N. Coskun, J. Ma, S. Azimi, C. Gärtner and I. Erden, *Org. Lett.*, 2011, **13**, 5952; (c) B.-C. Hong, F.-L. Chen, S.-H. Chen, J.-H. Liao and G.-H. Lee, *Org. Lett.*, 2005, **7**, 557; (d) B.-C. Hong, Y.-J. Shr and J.-H. Liao, *Org. Lett.*, 2002, **4**, 663; (e) V. Nair, G. Anilkumar, K. V. Radhakrishnan, M. V. Nandakumar and S. Kumar, *Tetrahedron*, 1997, **53**, 15903; (f) P. Bickert, B. Hildebrandt and K. Hafner, *Organometallics*, 1984, **3**, 653; (g) E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.
 - 11 (a) D. M. Whitehead, P. A. Helliwell, S. C. McKeown and A. Routledge, *React. Funct. Polym.*, 2009, **69**, 884; (b) J. A. Bajgrowicz, T. B. Bourdin and P. Gyax, *Eur. Patent*, 1067118A1, 2001; (c) J. E. Nystroem and P. Helquist, *J. Org. Chem.*, 1989, **54**, 4695; (d) A. Steinmeyer, W. Schwede and F. Bohlmann, *Liebigs Ann. Chem.*, 1988, 925.
 - 12 C. M. Momming, G. Kehr, R. Frohlich and G. Erker, *Chem. Commun.*, 2011, **47**, 2006.
 - 13 (a) L. F. Tietze, G. Brasche and K. M. Gericke, *Domino Reactions in Organic Synthesis*, Wiley-VCH Verlag, Weinheim, 2006; (b) P. von Zezschwitz and A. de Meijere, *Top. Organomet. Chem.*, 2006, **19**, 49; (c) A. de Meijere, P. von Zezschwitz and S. Bräse, *Acc. Chem. Res.*, 2005, **38**, 413; (d) A. de Meijere, P. von Zezschwitz, H. Nuske and B. Stulgies, *J. Organomet. Chem.*, 2002, **653**, 129; (e) L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115.
 - 14 (a) Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307; (b) Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2003, **59**, 228; (c) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 467; (d) G. M. Sheldrick,



- Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112; CCDC 1008790.
- 15 (a) D. Chen, V. Leich, F. Pan and J. Klankermayer, *Chem. – Eur. J.*, 2012, **18**, 5184; (b) C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 325.
- 16 (a) T. A. Rokob, A. Hamza, A. Stirling and I. Papai, *J. Am. Chem. Soc.*, 2009, **131**, 2029; (b) L. Rocchigiani, G. Ciancaleoni, C. Zuccaccia and A. Macchioni, *J. Am. Chem. Soc.*, 2013, **136**, 112.
- 17 (a) I. Fleming and J. A. Langley, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1421; (b) I. Fleming, D. Marchi and S. K. Patel, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2518.
- 18 The rearrangement was not observed in the presence of $4/H_2$, pure **4** or pure H_2 .

