Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A metal–amide dependent, catalytic C–H functionalisation of triphenylphosphonium methylide†

Adi E. Nako, Andrew J. P. White and Mark R. Crimmin*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report the $[Y\{N(SiMe_3)_2\}_3]$ catalysed dehydrocoupling of triphenylphosphonium methylide with phenylsilane to form the silylated ylide $Ph_3PCHSiH_2Ph$. Attempts to catalyse this reaction with the related group 2 hexamethyldisilazide base $[Ca\{N(SiMe_3)_2\}_2]$ led to the catalytic formation of the phosphine $Ph_2PCHSiH_2Ph$ along with Ph_2PMe in low selectivity, while group 1 bases $[M\{N(SiMe_3)_2\}]$ ($M = Li, Na, K$) proved ineffective for both transformations. The stoichiometric reactions of Ph_3PCH_2 with $[M\{N(SiMe_3)_2\}_n]$ have been investigated and allowed the isolation and characterisation of a cyclometallated phosphonium methylide complex of yttrium.

Introduction

In 1981 Watson reported the degenerate exchange of $^{13}CH_4$ with $[(Cp^*)_2Lu^{12}CH_3]$ to form $[(Cp^*)_2Lu^{13}CH_3]$ and $^{12}CH_4$.¹ In the following year Marks observed the C–H activation of benzene and tetramethylsilane with the thoracyclobutane derived from thermolysis of $[(Cp^*)_2Th\{CH_2CHMe_2\}_2]$.² These reactions are believed to proceed *via* σ -bond metathesis and provide a mechanistic counterpoint to C–H bond activation involving 1,2-addition across $M=X$ bonds ($M = NR, O$), oxidative addition to late-transition metals, electrophilic substitution at late-transition metals, and metalloradical mediated hydrogen-atom abstraction.^{3–5} More recently, *stoichiometric* methods for the C–H bond activation of hydrocarbons have given way to *catalytic* protocols and a large number procedures have been developed for the hydroalkylation and hydroarylation of substrates containing unsaturated carbon–carbon and carbon–nitrogen bonds.⁵ Despite these efforts, examples of *catalytic* C–H activation and functionalisation with d^0 and d^0f^n -complexes remain largely unexplored. For example, Jordan and co-workers reported the hydroarylation of alkenes with substituted pyridines catalysed by the cationic zirconium complex $[Cp_2ZrMe(THF)][BPh_4]$.⁶ The scope of this reaction has been improved by employing half-sandwich complexes of scandium and yttrium in the presence of $B(C_6F_5)_3$,⁷ while a pincer-supported scandium imide has been proposed as a catalyst for the hydroarylation of isonitriles with pyridine.⁸ In related studies, Tilley and Sadow documented $[(Cp^*)_2ScMe]$ as a catalyst for not only the hydromethylation of propene but also the dehydrocoupling of methane and Ph_2SiH_2 .⁹ A similar dehydrocoupling reaction was discovered by Hou and co-workers and applied to *ortho*-selective silylation of anisoles with arylsilanes catalysed by half-sandwich scandium alkyl complexes.¹⁰

Onium ylides represent an extremely important class of nucleophile for carbon–carbon bond forming reactions. Despite a number of studies documenting the stoichiometric cyclometallation of phosphonium ylides, the use of ylides as carbon–based directing groups in C–H functionalisation chemistry has limited precedent.^{1,11} We recently reported the coordination of triphenylphosphonium methylide to a “ $Y(I)\{N(SiMe_3)_2\}_2$ ” fragment.¹² Based on observations made during this study, we now report the C–H activation and dehydrocoupling of triphenylphosphonium methylide with phenylsilane catalysed by the simple metal amide complex $[Y\{N(SiMe_3)_2\}_3]$.

Results and Discussion

C–H Functionalisation of triphenylphosphonium methylide:

Employing $[Y\{N(SiMe_3)_2\}_3]$ (10–20 mol%) as a pre-catalyst for the reaction of Ph_3PCH_2 with $PhSiH_3$ in C_6D_6 solution at 25 °C resulted in noticeable gas evolution and complete consumption of the ylide. Monitoring the reaction by 1H and ^{31}P NMR spectroscopy revealed the formation of a new product characterised by a diagnostic doublet of doublets in the silyl hydride region of the 1H NMR spectrum $\delta = 5.24$ ppm (dd, $^2J_{P-H} = 9.0$ Hz and $^3J_{H-H} = 4.5$ Hz) and a ^{31}P resonance consistent with a new four-coordinate phosphorus environment ($\delta = +23.8$ ppm) reminiscent of that reported for $Ph_3PCHSiMe_3$ in d_8 -THF ($\delta = +21.9$ ppm) and Ph_3PCH_2 in C_6D_6 ($\delta = +22.0$ ppm). These peaks are assigned to the silylated ylide **1a** formed in 88 % yield (Scheme 1 and Table 1) from the dehydrocoupling of Ph_3PCH_2 with $PhSiH_3$. While the by-product, H_2 , was observed at $\delta = 4.48$ ppm in C_6D_6 solution by 1H NMR spectroscopy, the assignment of **1a** was confirmed by multinuclear NMR spectroscopy, single crystal X-ray diffraction and high-resolution mass spectrometry, following a preparative scale experiment (Figure 1).

Scheme 1. The catalytic dehydrocoupling of Ph_3PCH_2 with PhSiH_3 to form $\text{Ph}_3\text{CHSiH}_2\text{Ph}$ **1a**

Figure 1. The crystal structure of one (**1a-A**) of the four independent molecules present in the crystals of **1a**. Selected bond lengths (Å) and angles (°) for the four independent molecules (in the form **1a-A**, **1a-B**, **1a-C**, **1a-D**) are; P(1)–C(2) 1.6771(19), 1.6790(19), 1.6757(19), 1.672(2); C(2)–Si(3) 1.797(2), 1.796(2), 1.804(2), 1.851(3); P(1)–C(2)–Si(3) 127.79(12), 126.70(12), 124.67(12), 123.84(15).

Table 1. The catalytic dehydrocoupling of Ph_3PCH_2 with PhSiH_3 with group 2 and 3 metal-amide catalysts

M	n	mol %	Time	Conversion	1a : 1b : 1c	Yield 1a ^a
–	–	–	1 h	95 %	1 : 0 : 1	47% ^b
Li	1	20	18 h	23 %	0 : 0.3 : 1	0%
Na	1	20	22 h	19 %	0 : 0.3 : 1	0%
K	1	20	22 h	32 %	0 : 0.7 : 1	0%
Ca	2	20	5.0 h	89 %	0 : 2.1 : 1	0%
Y	3	20	0.5 h	95 %	12 : 0 : 1	88%
2c ^c	30	3.5 h	97 %	7.7 : 1 : 1		77%
Lu	3	20	0.5 h	96 %	1.5 : 0 : 1	57%

a – reactions conducted at 0.22 M concentration of starting materials, yields recorded by ^1H NMR using 1,2,4,5-tetramethylbenzene and an internal standard, a – reaction conducted in triplicate in pre-silylated (HMDS) NMR tubes. c – conversion based on Ph_3PCH_2 .

Although the major product from the $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ catalysed reaction of Ph_3PCH_2 with PhSiH_3 , **1a** is not the sole product and Ph_2PMe (**1c**) along with trace amounts of $\text{Ph}_2\text{PCH}_2\text{SiH}_2\text{Ph}$ (**1b**) are observed as minor by-products by ^{31}P NMR spectroscopy. A background reaction conducted without a

catalyst resulted in production **1a** and **1c** in a 1:1 ratio. To investigate the possibility that the reaction is an example of general base catalysis, alternative silazide bases were examined as pre-catalysts (Table 1 and ESI Figure S1).

Group 1 metal amides, $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) inhibited methylde/silane dehydrocoupling, producing mixtures of **1b/1c** in low yield (19–32 % conversion). In contrast, $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ formed **1b** in high yields with modest selectivity. The C–H functionalized product **1a** was not formed under these reaction conditions (Table 1). Monitoring reactions of Ph_3PCH_2 with PhSiH_3 and 20 mol% $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in C_6D_6 by ^1H NMR revealed that the production of **1b** was accompanied by C_6H_6 as judged by an increase in the intensity of the resonance at 7.15 ppm relative to the internal standard.¹³ Exposing **1a** to these reaction conditions did not result in the formation of **1b**, furthermore attempts to effect the dehydrocoupling of MePPh_2 with PhSiH_3 to form **1b** failed. The former experiment demonstrates that **1a** is not a kinetic product on the pathway to the formation of **1b**.

Stoichiometric reactions of group 1–3 metal-amides with triphenylphosphonium methylide: In order to understand these observations further, we investigated the stoichiometric reactions of Ph_3PCH_2 with $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$, $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$. The results of these experiments are presented in Scheme 2. The reaction of $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ or $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with Ph_3PCH_2 both gave clean formation of a new product within the first 15 minutes of mixing at 25 °C in C_6D_6 solution as evidenced by ^{31}P NMR spectroscopy (**2a** $\delta = +27.9$; **2b** $\delta = +30.1$). Following preparative scale reactions, it was discovered that $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ reacts with Ph_3PCH_2 in a 1:1 stoichiometry to give **2a** in 49 % isolated yield, while $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ reacts with Ph_3PCH_2 in a 1:2 stoichiometry to give **2b** in 60 % isolated yield. Heating of C_6D_6 solutions of $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ or $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with 1 equiv. of Ph_3PCH_2 to 80 °C for 27 h did not result in any further reaction, and C–H activation of the ylide was not observed under these conditions. Furthermore heating isolated samples of **2a** and **2b** for 80 °C for 18 h resulted in no changes to the ^1H or ^{31}P NMR spectra.

In contrast, the reaction between $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and Ph_3PCH_2 in C_6D_6 solution at 80 °C for 3 h resulted in clean conversion to the cyclometallated complex **2c** along with $\text{HN}(\text{SiMe}_3)_2$. Although complex **2c** ($\delta = +28.3$ ppm, $d, {}^2J_{\text{P-Y-P}} = 11.2$ Hz) demonstrated ^{31}P NMR spectroscopy data that is consistent with **2a**, **2b** (see above) and the previously reported phosphonium methylide complex $[\text{Y}(\text{I})(\text{CH}_2\text{PPh}_3)\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\delta = +30.9$ ppm), ^{13}C NMR data were characteristic of C–H activation of an *ortho*-position of a phenyl group and a diagnostic resonance assigned to the carbon attached to yttrium was observed at $\delta = 195.9$ ppm. This value contrasts dramatically with that assigned to the metal bound carbon in $[\text{Cp}^*_2\text{Lu}\{\text{CH}_2\text{P}(\text{Ph})_2(o\text{-C}_6\text{H}_4)\}]$ ($\delta = 133.1$ ppm) but is reminiscent of that reported for $[\text{Cp}^*_2\text{Y}\{\text{CH}_2\text{P}(\text{Ph})_2(o\text{-C}_6\text{H}_4)\}]$ ($\delta = 208.00$ ppm).¹¹ Examining ^1H NMR data of the dehydrocoupling reaction to produce **1a** (Scheme 1) reveals that **2c** is present in the reaction mixture.

Scheme 2. Reactions of triphenylphosphonium methylenes with $[M\{N(SiMe_3)_2\}_n]$ ($M = Li$, $n = 1$; $M = Ca$, $n = 2$; $M = Y$, $n = 3$)

The structure of **2c** was confirmed unambiguously by X-ray crystallography (Figure 2c). While similar cyclometallated complexes are known, in all cases a rare-earth alkyl reagent is used to deprotonate the ylide. For example, $[Cp^*_2LuMe]$ reacts with Ph_3PCH_2 to produce $[Cp^*_2Lu\{CH_2P(Ph)_2(o-C_6H_4)\}]$.¹

Comparison of solid-state data: Examples of crystallographically characterised onium ylide adducts of group 1 and 2 are rare. In the solid-state, the lithium complex **2a** exists with two molecules in the asymmetric unit, these molecules differ only slightly from one another. Complex **2a** forms a dimer and the lithium centres are bridged by the silazide ligands with additional coordination being provided by the ylide. The Li–N bond lengths in **2a** are unremarkable while the short Li–C bond lengths (2.302(8) and 2.285(9) Å) are consistent with that reported by Davidson and co-workers for the only other known lithium adduct of a neutral phosphonium ylide $[Li\{\mu-NBn-2\}(CH_2PPh_3)_2]$ (2.207(4) Å).¹⁴ In the solid-state, the calcium complex **2b** demonstrates crystallographic C_2 symmetry. While calcium onium ylide adducts have little precedent a number of alkyls have been crystallographically characterised, and the Ca–C bond length of the coordinated ylide (2.6413(14) Å) is longer

than that observed in the four-coordinate alkyl $[Ca\{CH(SiMe_3)_2\}_2(THF)_2]$ (2.4930(18) Å).¹⁵

Similarly, a minor lengthening of the yttrium–carbon bond to the zwitterionic ligand in comparison to the anionic ligand is observed in complex **2c**, the Y–C_{ylide} and Y–C_{aryl} bond lengths being 2.4835(17) and 2.4346(18) Å respectively. Comparison of the C–P bond lengths and the M–C–P bond angles across the series reveals that in each of the complexes the carbon–phosphorus bond is elongated with respect to the free ylide (**1a**, 1.672(2) to 1.6790(19) Å; **2a**, 1.698(4) to 1.707(4) Å; **2b**, 1.7178(4) Å; **2c**, 1.7373(19) Å). While the M–C–P bond angle is similar for complexes **2a** (133.6(3) to 136.7(3)°) and **2b** (134.26(7)°), constraining the ylide in a five-membered metallocycle tightens this angle to 107.17(8)°. Complex **2c** is kinetically competent for the dehydrocoupling of Ph_3PCH_2 with $PhSiH_3$ producing **1a** in 77% conversion employing 30 mol% catalyst after 3.5h at 25 °C (Table 1).

Possible mechanisms of C–H functionalisation, including isotope labelling and DFT studies: At least four distinct mechanistic pathways for the C–H silylation step can be envisioned, (i) direct addition of the Si–H bond across the ylide in **2c** (or a non-cyclometallated adduct) via a σ -bond metathesis mechanism followed by decomposition of a zwitterionic intermediate with loss of H_2 , (ii) C–H silylation of the aryl ring followed by 1,4-silyl migration to the methylene position, (iii) generation of a transient yttrium alkylidene from **2c** (or a non-cyclometallated adduct) followed by 1,2-addition of the Si–H bond across the M=CHPPh₃ moiety, and (iv) Si–H bond activation followed by α -elimination to form a silylene that inserts into the C–H bond of Ph_3PCH_2 .

Precedent exists for each of the proposed C–H silylation mechanisms. Hence, α -elimination reactions of fluoroalkyl and stannyl d^0f^n -complexes are known to generate carbene and stannylene reactive intermediates respectively,¹⁶ while the insertion of a base-stabilised silylene into a C–H bond of a ylide has been observed.¹⁷

Figure 2. (Left) The crystal structure of one (**2a-A**) of the two independent molecules present in the crystals of **2a**. (Centre) The crystal structure of the C_2 symmetric complex **2b**. Atoms labelled with an “A” after the number are related to their counterparts without the letter by the C_2 axis that passes through the calcium centre and bisects the N(1)–Ca(1)–N(1A) and C(10)–Ca(1)–C(10A) angles. (Right) The crystal structure of **2c**. Selected bond lengths (Å) and angles (°): For **2a** (in the form **2a-A**, **2a-B**), Li(1)–C(1) 2.302(8), 2.264(8); Li(2)–C(32) 2.285(9), 2.254(8); P(1)–C(1) 1.698(4), 1.701(4); P(2)–C(32) 1.705(4), 1.707(4); Li(1)–C(1)–P(1) 136.6(3), 135.0(3); Li(2)–C(32)–P(2) 133.6(3), 136.7(3). For **2b**, Ca(1)–C(10) 2.6413(14), Ca(1)–N(1) 2.3596(11), Ca–C(10)–P(11) 1.7178(14). For **2c**, Y–C(1) 2.4835(17), Y–C(4) 2.4346(18), P(2)–C(1) 1.7373(19), Y–N(21) 2.2381(14), Y–N(31) 2.2454(15), Y–C(1)–P(2) 107.17(8), C(4)–Y–C(1) 78.80(6)

The addition of chlorosilanes across N-heterocyclic carbene adducts of the rare-earth metals to form zwitterionic organometallic complexes highlights the possibility of a direct functionalisation of the ylide.¹⁸ Furthermore, C–H bond activation by 1,2-addition of the C–H bond across a Y=C moiety is known.¹⁹ Finally, recent studies have shown that *ortho*-silylated phosphonium methylides are kinetically labile and undergo 1,4-silyl migration at temperatures as low as –78 °C to form the more stable silylated ylides.²⁰ DFT studies conducted with the B3LYP functional and 6,31G+(d,p) basis-set implemented in Gaussian09 imply a *thermodynamically favourable* process, with $\Delta_r G^\circ = -12.3 \text{ kcal mol}^{-1}$ for the isomerisation of **A** to **1a** (see supporting information for further details).

Scheme 3. 1,4-silyl migration of *ortho*-silylated triphenylphosphonium ylides

In an attempt to shed light on the possible mechanism of C–Si bond formation, a series of isotopic labelling experiments were conducted. The reaction of Ph_3PCD_2 with PhSiH_3 catalyzed by $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ in benzene was monitored by ^1H , ^2H and ^{31}P NMR spectroscopy. Following 1 h at 25 °C $\text{Ph}_3\text{PCDSiH}_2\text{Ph}$ was present in 77 % yield. Examination of the ^1H and ^2H NMR data revealed no detectable D-incorporation into either the *ortho* sp^2C –H of the triphenylphosphonium moiety or the silyl hydrides of the product. These data argue against mechanisms (ii) and (iv).

Reaction of Ph_3PCD_2 with $\text{Ph}_3\text{PCHSiH}_2\text{Ph}$ in the presence of 20 mol% $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ for 1 week at 80 °C did not result in H/D exchange of the Si–H positions and also militates against a reversible silylene insertion mechanism. The fate of the isotopic label was determined by conducting a transfer hydrogenation experiment. Hence, the reaction was repeated in a closed double-chamber system with a benzene solution of Ph_3PCD_2 and PhSiH_3 in one vial and a benzene solution of 5 mol % $[\text{RhCl}(\text{PPh}_3)_3]$ and 1 equiv. styrene in a second vial (see ESI for experimental details). Consistent with the formation of H–D from the reaction of Ph_3PCD_2 with PhSiH_3 , non-selective D-incorporation into both the methylene and methyl positions of the styrene hydrogenation product, ethylbenzene was observed by ^1H and ^2H NMR spectroscopy.

While the complexity of this system does not allow unambiguous deconvolution of the C–Si bond forming step, based upon the aforementioned experiments and the metal-amide dependence of the reaction (Table 1), we favour a mechanism in which the Si–H bond undergoes a σ -bond metathesis reaction with the M–C bond in **2c**, or a non-cyclometallated analogue. Subsequent decomposition of the corresponding zwitterionic intermediate would liberate H_2 , ultimately yielding **1a** and allowing catalytic turnover.

Conclusions

In summary, we have discovered that the C–H activation and dehydrocoupling of triphenylphosphonium methylide with phenylsilane occurs selectively in the presence of $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$. Initial studies suggest that the reaction is metal dependent and while $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ and $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ both form coordination complexes with Ph_3PCH_2 these compounds do not undergo C–H functionalisation under the conditions observed for $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$. We are continuing to explore the application of d⁰-organometallic complexes to C–H bond functionalization.

Acknowledgements

We are grateful to the Royal Society for the provision of a University Research Fellowship (MRC) and Imperial College for the funding of a PhD studentship (AEN). Peter Haycock is acknowledged for variable temperature and multinuclear NMR experiments. We are grateful to the reviewers for insightful comments.

Notes and references

^a Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, SW7 2AZ. Tel: +44(0)2075942846 ; E-mail:

[†] m.crimmin@imperial.ac.uk

[†] Electronic Supplementary Information (ESI) available: Full experimental details for catalytic procedures and the synthesis of **1a**, **2a-c**. CIF files for **1a**, **2a-c** and details of the DFT calculations. See DOI: 10.1039/b000000x/

- (a) P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1983, 276-277. (b) P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491-6493. (c) P. L. Watson, G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51.
- (a) T. J. Marks, J. W. Bruno and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7357-7360. (b) T. J. Marks and C. M. Fendrick, *J. Am. Chem. Soc.*, 1984, **106**, 2214-2216. (c) T. J. Marks, J. W. Bruno, G. M. Smith, C. K. Fair, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 40-56. (d) T. J. Marks, C. M. Fendrick, *J. Am. Chem. Soc.* 1986, **108**, 425.
- For book chapters on C–H activation see, (a) A. E. Shilov, G. B. Shul'pin, *Activation of Saturated Hydrocarbons by Transition Metal Complexes* (Reidel, Dordrecht, Netherlands, 1984). (b) B. L. Conely, W. J. Tenn III, K. J. H. Young, S. Ganesh, V. Z. Meier, O. Mironov, J. Oxgaard, J. Gonzales, W. A. Goddard, III, R. A. Periana, *Methane functionalization in Activation of small molecules: Organometallic and bioinorganic perspectives*, Ed. W. B. Tolman (Wiley-VCH, Weinheim, Germany, 2006).
- For review articles on C–H activation see, (a) B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154. (b) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879. (c) J. A. Labinger, and J. E. Bercaw, *Nature* 2002, **417**, 507. (d) R. A. Periana, G. Bhalla, W. J. Tenn, III, K. J. H. Young, X. Y. Liu, O. Mironov, C. J. Jones, V. R. Ziatdinov, *J. Mol. Cat. A* 2004, **220**, 7. (e) R. H. Crabtree, *J. Organomet. Chem.* 2004, **689**, 4083. (f) R. G. Bergman, *Nature* 2007, **446**, 391.
- (a) J. C. Lewis, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2008, **41**, 1013. (c) D. A. Colby, J. A. Ellman, R. G. Bergman, *Chem. Rev.*, 2010, **110**, 624. (c) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.*, 2011, ASAP, DOI: 10.1021/ar200190g.
- (a) R. F. Jordan, D. F. Taylor, *J. Am. Chem. Soc.*, 1989, **111**, 778. (b) S. Rodewald, R. F. Jordan, *J. Am. Chem. Soc.*, 1994, **116**, 4491. (c) S. Bi, Z. Li, R. F. Jordan, *Organometallics*, 2004, **23**, 4882.
- B. –T. Guan and Z. Hou, *J. Am. Chem. Soc.* 2011, **133**, 18086.

- 8 (a) B. F. Wicker, J. Socct, A. R. Fout, M. Pink and D. J. Mindiola, *Organometallics* 2011, **30**, 2453. (b) B. F. Wicker, M. Pink, D. J. Mindiola, *Dalton Trans.* 2011, **40**, 9020.
- 9 (a) A. D. Sadow and T. D. Tilley, *J. Am. Chem. Soc.* 2003, **125**, 7971. (b) A. D. Sadow and T. D. Tilley, *J. Am. Chem. Soc.*, 2005, **127**, 643.
- 10 J. Oyamada, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* 2011, **45**, 10720.
- 11 For the *ortho*-metalation of ylides with complexes of the rare-earth metals see ref. 1 and (a) M. Booi, B.-J. Deelman, R. Duchateau, D. S. Postma, A. Meetsma, J. H. Teuben, *Organometallics*, 1993, **12**, 3531. (b) K. A. Ruffanov, B. H. Mueller, A. Spannenberg, U. Rosenthal, *N. J. Chem.*, 2006, **30**, 29.
- 12 M. R. Crimmin, A. J. P. White, *Chem. Commun.* 2012, **48**, 1745.
- 13 The formation of **1b** proceeds with *catalytic* P–C bond cleavage and C–Si bond formation. Related *stoichiometric* reactions of calcium and yttrium complexes with triphenylphosphonium oxide are known and are proposed to proceed *via* P–C/M–H σ -bond metathesis see for example, (a) M. S. Hill, M. F. Mahon, T. P. Robinson, *Chem. Commun.* 2010, **46**, 2498. (b) E. Lu, Y. Chen, J. Zhou, X. Leung, *Organometallics* 2012, **31**, 4574. In the latter case, the yttrium hydride complex $[\kappa^3\text{-}\{\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{CH}_2)_2\text{NMe}_2\}\text{Y}(\text{NHA}r)(\mu\text{-H})_2]$ (Ar = 2,6-di-*iso*-propylaniline) reacts with Ph_3PO to form C_6H_6 along with $[\kappa^3\text{-}\{\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{CH}_2)_2\text{NMe}_2\}\text{Y}(\text{NHA}r)(\kappa^1\text{-P}(\text{O})\text{Ph}_2)]$; a complex which possess a formal “ $\text{Ph}_2\text{P}(\text{O})$ ” anion
- 14 D. R. Armstrong, M. G. Davidson, D. Moncrieff, *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 478.
- 15 M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon, P. A. Procopiou, *Chem. Eur. J.* 2008, **14**, 11292.
- 16 For carbene generation see (a) E. L. Werkema, E. Messines, L. Perrin, L. Maron, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* 2005, **127**, 7781. (b) E. L. Wekema, R. A. Andersen, A. Yahia, L. Maron, O. Eisenstein, *Organometallics* 2009, **28**, 3173. For stannylene generation see (c) N. R. Neale, T. D. Tilley, *J. Am. Chem. Soc.* 2002, **124**, 3802. (d) N. R. Neale, T. D. Tilley, *J. Am. Chem. Soc.* 2005, **127**, 14745.
- 17 R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* 2011, **30**, 2897.
- 18 (a) Z. R. Turner, R. Bellabarba, R. P. Tooze and P. L. Arnold, *J. Am. Chem. Soc.*, 2010, **132**, 4050–4051. (b) P. L. Arnold, Z. R. Turner, R. Bellabarba and R. P. Tooze, *J. Am. Chem. Soc.*, 2011, **133**, 11744–11756.
- 19 D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* 2010, **132**, 14379.
- 20 (a) A. Kawachi, T. Yoshioka and Y. Yamamoto, *Organometallics*, 2006, **25**, 2390. (b) E. Vedejs, O. Daugulis, S. T. Diver and D. R. Powell, *J. Org. Chem.*, 1998, **63**, 2338.

50