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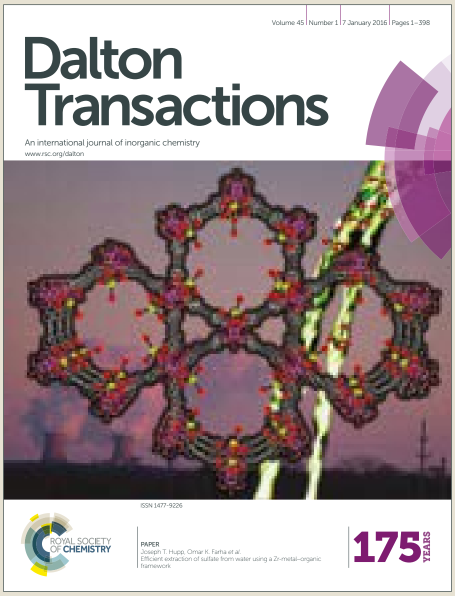

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COMMUNICATION

Catalytic N–Si Coupling as a Vehicle for Silane Dehydrocoupling via α-Silylene Elimination†

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Exploration of $(N_3N)ZrNMe_2$ (1, $N_3N = N(CH_2CH_2NSiMe_3)_3{}^{3-}$) as a catalyst for the cross-dehydrocoupling or heterodehydrocoupling of silanes and amines suggested silylene reactivity. Further study of the catalysis and stoichiometric modeling reactions hint at an α-silylene elimination as the pivotal mechanistic step, which expands the 3p elements known to engage in this catalysis and avails a new strategy for catalytic generation of low-valent fragments.

An increased premium has been placed on Si–N heterodehydrocoupling as a reaction that affords products of high synthetic utility and interest.[1] For example, silazanes have been of use as silylating agents,[2] bases,[3] ligands for catalysts, and as ceramic or polymer precursors.[4] While excellent work has been done in this area discovering and understanding metal and non-metal catalysts,[1] general catalysts for this reaction that tolerate both sterically encumbered substrates or that provide selectivity between a single or multiple Si–N bond forming events on the same substrate (one or two reactions at RNH_2 or $RR'SiH_2$, for example) remain challenges. Despite advances in from each Hill and Sadow in development of group 2 metal catalysts,[1c, 5] zirconium is an interesting potential candidate being relatively abundant while readily engaging in dehydrocoupling catalysis.[6] Supporting that hypothesis are reports of $Zr(NMe_2)_4$ reacting with silanes to give N–Si bonds,[7] though that chemistry is limited to stoichiometric N–Si bond formation and subsequent formation of a poorly soluble polymetallic hydride product. We report herein our exploration of catalytic N–Si bond formation by zirconium. Despite meeting limited success in improving upon literature catalysts, this work has led to suggestions of silylene reactivity which is unique within this field. Further studies within provide evidence that zirconium amido derivatives can liberate silylene fragments, an insight that may avail more facile routes to the catalytic generation of R_2Si: fragments and related synthetic chemistry.

Literature observations of $Zr(NMe_2)_4$ reactivity were readily replicated but no catalysis was identified.[7] For example, treatment of phenylsilane with 10 mol % of $Zr(NMe_2)_4$ gave $Ph(NMe_2)SiH_2$, $Ph(NMe_2)_2SiH$, and a yellow precipitate consistent with $[(Me_2N)_3Zr(\mu\text{-}H)(\mu\text{-}NMe_2)_2]_2Zr$.[7a] It was hypothesized that increased solubility of $Zr(NMe_2)_4$ may lead to catalysis, but replication of the above reaction with one equivalent of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) also gave stoichiometric N–Si products and a similar precipitate. Given the success of triamidoamine-supported zirconium in dehydrocoupling catalysis,[6, 8] we next considered this ligand to increase catalyst solubility.

Treatment of mixtures of silanes and amines with 10 mol % of $(N_3N)Zr$ derivatives resulted in limited in catalytic activity. For example, heating phenylsilane with excess dimethylamine in the presence of 10 mol % of $(N_3N)ZrNMe_2$[9] (**1**) to 80 °C in benzene-d_6 resulted in 60% formation of $Ph(NMe_2)SiH_2$ versus phenylsilane over 24 hours (~90% conversion after 48 hours) with apparent decomposition of $(N_3N)ZrNMe_2$ to a complex mixture of unidentified products (eqn (1)). The limited efficacy of $(N_3N)Zr$ derivatives for N–Si dehydrocoupling was not immediately clear given their past success in P–Si and P–Ge bond forming catalysis.[8c] The reaction of phenylsilane with isopropylamine in the presence of 10 mol % of **1** at 80 °C in benzene-d_6 produced minimal $Ph(NMe_2)SiH_2$.§ However, some diphenylsilane was also observed by ^1H NMR spectroscopy and confirmed in ^1H-^{29}Si HSQC experiments. Silane (SiH_4) was not identified in these reactions, and a similar phenyl migration has been reported by Tilley to proceed via a cationic Hf–Ph intermediate.[10] The possibility of a rare early transition-metal catalyzed redistribution was nevertheless intriguing because critical metal-mediated silicon catalysis, including the Direct Process and redistribution reactions,[11] appear to involve unsaturated silicon derivatives such as silylenes (R_2Si:). Aggressive study of such transition-metal silylene ($L_nM{=}SiR_2$)

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† Dedicated to Professor Phillip Power on the occasion of his 65th birthday.

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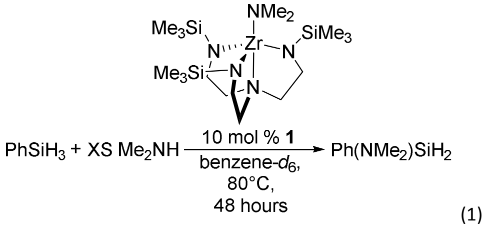
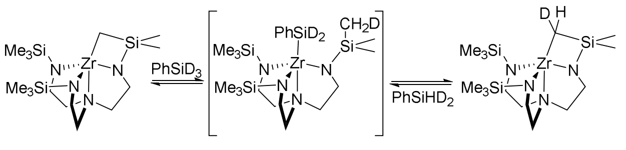
compounds has yielded substantial reactivity and new catalysts.[12] Likewise, useful organosilane products can be prepared utilizing silylene fragments generated via photolysis followed by trapping with organic reagents,[13] but the direct generation of silylene fragments via metal catalysis, such as α elimination, remains an untapped area.



(1)

Tilley identified that dehydropolymerization of stannanes appear to occur via α-stannylene elimination.[14] In group 15, α-stibine and α-arsinidene elimination reactions have also been reported, and form small rings or distibenes or disarsenes, respectively.[8b, 15] Layfield first realized catalytic trapping of a phosphinidene fragments using bis(NHC) iron and cobalt catalysts,[16] while we have expanded on α-phopshinidene elimination as a route to organophosphines via trapping.[17] These observations and the value of organosilanes argue for exploration of α-silylene elimination and the possibility of resultant organosilane synthesis.

The suggestion of silylene chemistry prompted investigation of zirconium-silyl derivatives supported by the triamidoamine ligand. Reaction of [κ^5-*N,N,N,N,C*-($Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2$]Zr (**2**) with one equivalent of primary or secondary aryl or alkyl silane failed to produce a silyl complex of the type $(N_3N)ZrSiR_nH_{3-n}$ (N_3N = $N(CH_2CH_2NSiMe_3)_3^{3-}$). Extended reactions resulted in the apparent decomposition of **2**. It was suspected that any silyl derivative may be unstable with respect to cyclometalation and restoration of **2**. It is already known that $(N_3N)ZrX$ derivatives can rapidly exchange the pseudoaxial X ligand, and that if X is of sufficient steric bulk, **2** is favored.[8b, 18] To test this hypothesis, **2** was treated with one equivalent of phenylsilane-d_3, which rapidly afforded a mixture of $PhSiHD_2$, $PhSiH_2D$, and $PhSiH_3$ as well as **2-*d*$_n$**,[19] illustrating equilibrium formation of a disfavored silyl derivative (Scheme 1).



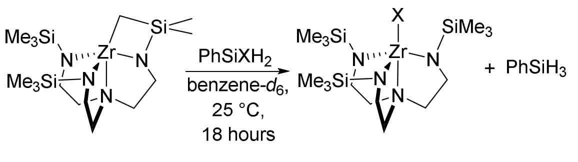
2

2-*d*$_1$

Scheme 1. Pathway for the incorporation of deuterium on **2** from phenylsilane via a presumed silyl intermediate, $(N_3N)ZrSiD_2Ph$.

With evidence for a transient silyl compound, more aggressive efforts to solicit reactivity were explored. Heating mixtures of **2** with excess (2–10 equiv.) phenylsilane resulted in the ultimate decomposition of **2** with trace quantities of hydrogen, 1,2-diphenyldisilane, and oligosilanes in conversions that were low and unreliable between experiments. Redistribution products were not observed.

Silanes featuring π-basic substituents gave different reactivity. Reaction of **2** with Ph(X)SiH_2 (X = NMe_2 or Cl) yielded known $(N_3N)ZrX$ (X = NMe_2 , **1**; Cl)[8d, 9] derivatives as the solely identifiable metal-containing product by ^1H NMR spectroscopy (eqn (2)). Significant decomposition of **2** was also observed. Phenylsilane was observed as a byproduct for both substrates.



2

X = NMe_2 (**1**)
Cl

(2)

Mass balance suggests that the byproduct from reactions of **2** with Ph(X)SiH_2 (X = NMe_2 or Cl) is phenylsilylene (PhHSi). The observation of phenylsilane, even in deuterated solvents, may be related to the low conversion and substantial degradation of zirconium compounds in the reaction. Nevertheless, such a transformation has precedent. Andersen and coworkers have shown that cerocene hydrides react with haloalkanes or ethers to give Ce–X (F, Cl, OR) bonds and the corresponding alkane.[20] These reactions appear to proceed via a two-step process involving C–H bond activation and H_2 formation followed by methylidene elimination and trapping by hydrogen—a stoichiometric α-carbene elimination reaction.[20] Based on the same arguments that Andersen has made, it is presumed that the formation of the strong Zr–N bond is a driving force for silylene elimination. Prior studies suggest that Zr–N bonds are among the strongest for $(N_3N)ZrX$ family of compounds based on structural evidence and computational models.[18]

While the relative stability of a Zr–N bond might appear to be detrimental to catalysis, **1** is already known to undergo stoichiometric N–Si bond formation,[8d] which suggested that *catalytic* α-silylene elimination may be possible. A testable hypothesis emerged: Does catalytic N–Si bond formation enable α-silylene elimination? Dehydrocoupling of silanes with **1**, a reaction that is unsuccessful with **2** (vide supra), would test this hypothesis.

Treatment of phenylsilane in benzene-d_6 at 80 °C with as little as 5 mol % of **1** gave a mixture of silicon-containing products, including predominately 1,2-diphenyldisilane $(PhSiH_2)_2$ (2%), Ph(NMe_2)SiH_2 (3%) and low molecular weight linear and cyclic oligosilanes (5%) as characterized by ^1H and ^{29}Si NMR spectroscopy (eqn (3)).[21] These reactions require heating for several days at 80 °C to achieve limited conversion of phenylsilane. With increased catalyst loading, typically to 20 mol %, Ph$(NMe_2)_2$SiH, a non-productive byproduct, is generated. Diphenysilane was far less reactive towards the catalysis. After five days of heating at 80 °C (20 mol % catalyst loading), 10% conversion to $Ph_2(NMe_2)SiH$, was measured. No reaction was observed between either $PhMeSiH_2$ or Ph_3SiH and the catalyst over five days at 80 °C.

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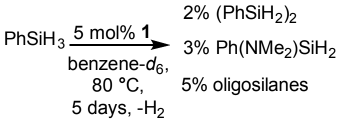
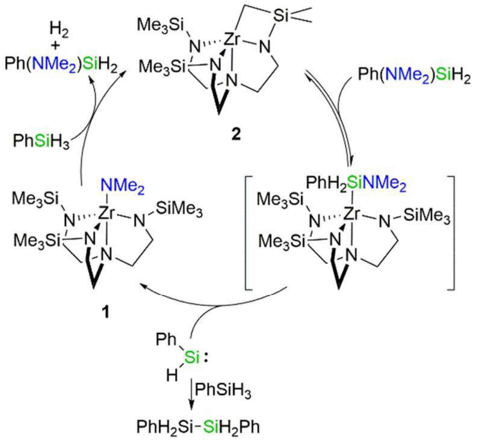


(3)

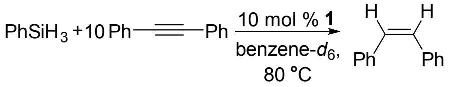
These observations and literature precedent lead to the proposed catalytic cycle (Scheme 2). The first step in the catalysis appears to be a Si–N heterodehydrocoupling reaction between **1** and phenylsilane resulting in Ph(NMe$_2$)SiH$_2$. This transformation necessarily produces a zirconium hydride that is known to rapidly dehydrogenate to the metallacycle **2**.[19] The stoichiometric reactions then suggest that Ph(NMe$_2$)SiH$_2$ ring opens **2**, resulting in a silyl intermediate (N$_3$N)ZrSiHPhNMe$_2$ that is poised for α-silylene elimination and restoration of **1**. The phenylsilylene fragment could then insert into the Si–H bond of another equivalent of phenylsilane to yield the disilane product, which is consistent with literature precedent.[13, 14c, 22]

In the catalysis, formation of Ph(NMe$_2$)$_2$SiH presumably results from the reaction of **1** with Ph(NMe$_2$)SiH$_2$ generated in situ. This process would be catalyst deactivating, consuming multiple equivalents of NMe$_2$ and leaving **2**, which is unstable in the presence of excess phenylsilane (vide supra). Decomposition of **1** limits consumption of starting phenylsilane. There is insufficient formation of Ph(NMe$_2$)SiH$_2$ to suggest that the decomposition occurs solely from **2**, but the complex mixture of decomposition products are similar in both the stoichiometric and catalytic reactions. The working hypothesis is that competitive N–Si bond formation occurs between phenylsilane and the amido arms of the triamidoamine ligand to strip the ligand off zirconium. While this is consistent with the formation of Si–NMe$_2$ derivatives, there is no direct evidence to support this pathway given the complex mixtures of decomposition products. The competitive degradation process and the apparent instability of (N$_3$N)Zr–silyl derivatives preclude a detailed mechanistic analysis of the system key to prior instances of α–elimination.[14b] There is, however, precedent for silylene elimination. Pannell and co-workers have reported photo-driven iron-catalyzed silylene elimination.[23]

Trapping was pursued as potential verification of silylene formation. Phenylsilane was treated with 10 equivalents of a trap in the presence of 10 mol % of **1** at 80 °C in benzene-d_6. For traps such as 2-butyne, terminal alkynes, dienes and disulfides, reactions failed to afford organosilanes products, and decomposition of **1** resulted. We attribute the lack of trapping to competitive reaction of **2** with these reagents, much of which has already been described.[18] In the case of diphenylacetylene as a trap, some formation of *cis*-stilbene (~24%) was observed (eqn (4)).[‡] Control reactions of H$_2$ and diphenylacetylene in the presence of **1** give much lower conversions to *cis*-stilbene than reactions with phenylsilane, which is unsurprising given that **1** and related derivatives are poor hydrogenation catalysts with H$_2$.[8a] The reduction of an alkyne by a silane is an unusual transformation, but a report by Marciniec indicates one potential route.[24]

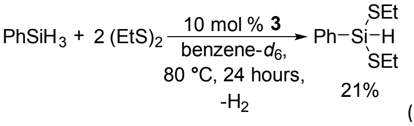


Scheme 2. Proposed catalytic cycle for the dehydrocoupling of phenylsilane using (N$_3$N)ZrNMe$_2$ (**1**).



(4)

The limitations of **1** invited consideration of other catalysts, and Corey's report of phenylsilane dehydropolymerization using Cp$_2$Zr(NMe$_2$)$_2$ (**3**) was intriguing given their observations of high activity and formation of Ph(NMe$_2$)SiH$_2$ as a byproduct.[25] Because this catalysis is established, only trapping reactions were pursed. Reaction of phenylsilane with three equivalents of the organic trapping reagents diphenylacetylene or 2,3-dimethyl-1,3-butadiene in the presence of 10 mol % of **3** yielded no evidence of a silole and small quantities of PhH$_2$Si-SiH$_2$Ph and PhH$_2$SiNMe$_2$. Competitive silane polymerization was observed in the case of 2,3-dimethyl-1,3-butadiene, whereas diphenylacetylene stunted catalysis entirely. Replicating that reaction with diethyldisulfide as the trap afforded Ph(EtS)$_2$SiH[26] in 21% conversion as identified by NMR (^{1}H, ^{1}H/^{29}Si HSQC) spectroscopy and GC/MS (eqn (5)). Such a trapping reaction represents the microscopic reverse of known generation of silylene from dithiolsilanes.[23a]



$$PhSiH_3 + 2\,(EtS)_2 \xrightarrow[\text{80 °C, 24 hours, } -H_2]{\text{10 mol \% 3, benzene-}d_6} PhSiH(SEt)_2 \quad 21\%$$

(5)

A competition experiment was performed between phenylsilane and phenylsilane-d_3 under the same conditions using **1**. It was suspected that generation of PhHDSi–SiD$_2$Ph or PhH$_2$Si–SiHDPh must be the result of phenylsilylene or phenylsilylene-d_1 insertion into a Si–D or Si–H bond, respectively. In the ^{1}H and ^{2}H NMR spectra, respectively, broad multiplets at the chemical shift of 1,2-diphenyldisilane were identified, representing about 6% of the Si–H intensity by ^{1}H NMR integration. Attempts to accurately assign products using simulated spectra was hampered by poor simulation quality. A

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highly complex resonance was observed in the ^{29}Si NMR spectrum at approximately δ 61.2, indicative of multiple products and non-first order spin systems, but again, accurate simulations could not be made. While the observation of apparent crossover products is encouraging, these products may also arise from H/D exchange reactions, such as reaction of 1,2-diphenyldisilane and D_2 catalyzed by **2**. Therefore, this experiment represents, at best, supporting evidence of this reactivity rather than direct proof.

Table 1. Summary of observations and mechanistic implications

#	Observation	Implication(s)
1	$PhSiH_3 + Me_2NH + \mathbf{1}(cat) \rightarrow Ph(NMe_2)SiH_2$	Insufficient data for mechanistic suggestion, though prior work would suggest σ-bond metathesis.
2	$PhSiH_3 + {}^{i}PrNH_2 + \mathbf{1}(cat) \rightarrow Ph(NMe_2)SiH_2 + Ph_2SiH_2$	Absence of SiH_4 is inconsistent with redistribution, and Ph transfer from a Zr–Ph intermediate (a la Tilley) is possible.
3	$\mathbf{2} + PhSiD_3 \rightarrow \mathbf{2\text{-}}\boldsymbol{d_1}$	Deuterium incorporation on the trimethylsilyl substituent must arise from Si–D activation at **2**, which demonstrates that a Zr-silyl is unstable with respect to cyclometalation.
4	$PhSiH_3 + \mathbf{2}(cat) \rightarrow$ decomposition	This system is not competent for silane dehydrocoupling, despite transient Zr-silyl (#3).
5	$\mathbf{2} + Ph(NMe_2)SiH_2 \rightarrow \mathbf{1} + PhSiH_3$ $\mathbf{2} + PhClSiH_2 \rightarrow (N_3N)ZrCl + PhSiH_3$	Reactivity consistent with Andersen's methylidene elimination with cerocenes suggests a silylene intermediate.
6	$PhSiH_3 + \mathbf{1}(cat) \rightarrow (PhSiH_2)_2$	This catalysis may proceed via α-silylene elimination based on observation 5. An alternative is the generation of a hydride that would rapidly form **2** and a σ-bond metathesis pathway, but **2** is not catalytically active (# 4).
7	$PhSiH_3 + R_2S_2 + \mathbf{3}(cat) \rightarrow Ph(SR)_2SiH$	This reaction is consistent with silylene trapping by disulfide. An alternative may be disulfide splitting with adventitious hydrogen followed by two sequential Si–S heterodehydrocoupling events, but neither RSH nor $Ph(RS)SiH_2$ was observed by NMR.

In sum, **1** is a catalyst for the heterodehydrocoupling of amines and silanes with limited efficacy. It is also a poorly effective silane dehydrocoupling catalyst, but a series fo observations from stoichiometric and trapping reactions of **1** and zirconocene **3** (Table 1) support the idea that these zirconium compounds engage in α-silylene elimination. This reactivity is unique compared to prior reports of silane dehydrocoupling by group 4 metals, but the notion that N–Si coupling reaction prompts the α-silylene elimination avails new possibilities for promoting the generation of low-valent fragments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

§ Reaction of isolated $(N_3N)ZrNH^{i}Pr$ with $PhSiH_3$ fails to give any measurable N-Si products under similar conditions.

‡ It is known that photochemically generated phenylsilylene is trapped with diphenylacetylene to give 1,2,3,4,5-pentaphenylsilole.[36] In a limited set of reactions of phenylsilane and diphenylacetylene with catalytic **1**, 1,2,3,4,5-pentaphenylsilole was observed by ^{1}H NMR spectroscopy with confirmation by comparison to an authentic sample.[56] However, conditions that reliably favor this product could not be identified.

1(a) J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782; (b) J. L. Reichl and D. H. Berry, *Adv. Organomet. Chem.*, 1999, **43**, 197; (c) M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon and T. P. Robinson, *Chem. Sci.*, 2013, **4**, 4212; (d) L. Greb, S. Tamke and J. Paradies, *Chem Commun*, 2014, **50**, 2318; (e) J. X. Wang, A. K. Dash, J. C. Berthet, M. Ephritikhine and M. S. Eisen, *J. Organomet. Chem.*, 2000, **610**, 49; (f) W. Xie, H. Hu and C. Cui, *Angew. Chem. Int. Ed.*, 2012, **51**, 11141; (g) A. E. Nako, W. Chen, A. J. P. White and M. R. Crimmin, *Organometallics*, 2015, **34**, 4369; (h) F. Buch and S. Harder, *Organometallics*, 2007, **26**, 5132; (i) C. Bellini, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Angew. Chem. Int. Ed.*, 2015, **54**, 7679; (j) C. D. F. Konigs, M. F. Muller, N. Aiguabella, H. F. T. Klare and M. Oestreich, *Chem. Commun.*, 2013, **49**, 1506; (k) R. J. P. Corriu, D. Leclercq, P. H. Mutin, J. M. Planeix and A. Vioux, *J. Organomet. Chem.*, 1991, **406**, C1; (l) A. Pindwal, A. Ellern and A. D. Sadow, *Organometallics*, 2016, **35**, 1674; (m) N. Li and B.-T. Guan, *Adv. Synth. Catal.*, 2017, **359**, 3526; (n) A. Baishya, T. Peddarao and S. Nembenna, *Dalton Trans.*, 2017, **46**, 5880; (o) C. Bellini, T. Roisnel, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Chem. Eur. J.*, 2016, **22**, 15733; (p) L. K. Allen, R. Garcia-Rodriguez and D. S. Wright, *Dalton Trans.*, 2015, **44**, 12112; (q) M. Pérez, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *Proc. Natl. Acad. Sci. U.S.A.*, 2014, **111**, 10917.
2(a) A. Iida, A. Horii, T. Misaki and Y. Tanabe, *Synthesis*, 2005, **16**, 2677; (b) Y. Tanabe, M. Murakami, K. Kitaichi and Y. Yoshida, *Tet. Lett.*, 1994, **35**, 8409.
3 Y. Tanabe, T. Misaki, M. Kurihara, A. Iida and Y. Nishii, *Chem. Commun.*, 2002, 1628.
4 M. Birot, J.-P. Pillot and J. Dunogues, *Chem. Rev.*, 1995, **95**, 1443.
5 J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782.
6 R. Waterman, *Chem. Commun.*, 2013, **42**, 5629.

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DOI: 10.1039/C7DT04507G

7(a) X. Liu, Z. Wu, Z. Peng, Y.-D. Wu and Z. Xue, *J. Am. Chem. Soc.*, 1999, **121**, 5350; (b) X. Liu, Z. Wu, H. Cai, Y. Yang, T. Chen, C. E. Vallet, R. A. Zuhr, D. B. Beach, Z.-H. Peng, Y.-D. Wu, T. E. Concolino, A. L. Rheingold and Z. Xue, *J. Am. Chem. Soc.*, 2001, **123**, 8011.

8(a) K. A. Erickson, J. P. W. Stelmach, N. T. Mucha and R. Waterman, *Organometallics*, 2015, **34**, 4693; (b) A. J. Roering, J. J. Davidson, S. N. MacMillan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2008, 4488; (c) A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, **46**, 6855; (d) R. Waterman, *Organometallics*, 2007, **26**, 2492.

9 Z. Duan, A. A. Naiini, J.-H. Lee and J. G. Verkade, *Inorg. Chem.*, 1995, **34**, 5477.

10(a) A. D. Sadow and T. D. Tilley, *Organometallics*, 2001, **20**, 4457; (b) *Organometallics*, 2003, **22**, 3577.

11(a) K. M. Lewis and D. G. Rethwisch, eds., *Catalyzed Direct Reactions of Silicon*, Elsevier, Amsterdam, 1993; (b) B. Pachaly and J. Weis, in *Organosilicon Chemistry III: From Molecules to Materials*, eds. N. Auner and J. Weis, Wiley & Sons, New York, 1998; (c) L. N. Lewis, ed., Wiley & Sons, Chichester, UK, 1998; (d) M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000.

12 R. Waterman, P. G. Hays and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712.

13 D. N. Lee, H. S. Shin, C. H. Kim and M. E. Lee, *J. Korean Chem. Soc.*, 1993, **37**, 757.

14(a) N. R. Neale and T. D. Tilley, *Tetrahedron*, 2004, **60**, 7247; (b) N. Neale and T. D. Tilley, *J. Am. Chem. Soc.*, 2005, **127**, 14745; (c) N. Neale and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 3802.

15(a) R. Waterman and T. D. Tilley, *Angew. Chem. Int. Ed.*, 2006, **45**, 2926; (b) T. Pugh, N. F. Chilton and R. A. Layfield, *Chemical Science*, 2017, **8**, 2073.

16 K. Pal, O. B. Hemming, B. M. Day, T. Pugh, D. J. Evans and R. A. Layfield, *Angew. Chem. Int. Ed.*, 2016, **55**, 1690.

17 J. K. Pagano, B. J. Ackley and R. Waterman, Chem. Eur. J. 10.1002/chem.201704954.

18 A. J. Roering, A. F. Maddox, L. T. Elrod, S. M. Chan, M. B. Ghebreab, K. L. Donovan, J. J. Davidson, R. P. Hughes, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2009, **28**, 573.

19 S. E. Leshinski, C. A. Wheaton, H. Sun, A. J. Roering, J. M. Tanski, D. J. Fox, P. G. Hayes and R. Waterman, *RSC Adv.*, 2016, **6**, 70581.

20(a) E. L. Werkema, E. Messines, L. Perrin, L. Maron, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 7781; (b) E. L. Werkema, R. A. Andersen, A. Yahia, L. Maron and O. Eisenstein, *Organometallics*, 2009, **28**, 3173.

21 J. L. Huhmann, J. Y. Corey and N. P. Rath, *J. Organomet. Chem.*, 1997, **533**, 61.

22(a) R. Becerra, J. P. Cannady and R. Walsh, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5530; (b) Z. Xu, J. Jin, H. Zhang, Z. Li, J. Jiang, G. Lai and M. Kira, *Organometallics*, 2011, **30**, 3311.

23(a) K. H. Pannell, M.-C. Brun, H. Sharma, K. Jones and S. Sharma, *Organometallics*, 1994, **13**, 1075; (b) K. H. Pannell, T. Kobayashi, F. Cervantes-Lee and Y. Zhang, *Organometallics*, 1999, **19**, 1.

24 B. Marciniec, S. Kostera, B. Wyrzykiewicz and P. Pawluc, *Dalton Trans.*, 2015, **44**, 782.

25 Q. Wang and J. Y. Corey, *Can. J. Chem.*, 2000, **78**, 1434.

26 I. I. Lapkin and A. S. Nivichkova, *Zhurnal Obshchei Khimii*, 1981, **51**, 393.

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Catalytic N–Si Coupling as a Vehicle for Silane Dehydrocoupling via α-Silylene Elimination

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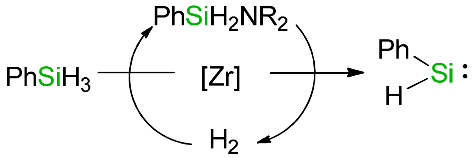

Zirconium compounds appear to promote the liberation of silylene fragments via and N–Si coupling event.