

This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Do, Dinh Cao Huan; Vasko, Petra; Fuentes, M. Ángeles; Hicks, Jamie; Aldridge, Simon

Title: Probing the non-innocent nature of an amino-functionalised β -diketiminate ligand in silylene/iminosilane systems

Year: 2020

Version: Accepted version (Final draft)

Copyright: © 2020 Royal Society of Chemistry

Rights: In Copyright

Rights url: http://rightsstatements.org/page/InC/1.0/?language=en

Please cite the original version:

Do, D. C. H., Vasko, P., Fuentes, M. Á., Hicks, J., & Aldridge, S. (2020). Probing the non-innocent nature of an amino-functionalised β -diketiminate ligand in silylene/iminosilane systems. Dalton Transactions, 49(25), 8701-8709. https://doi.org/10.1039/D0DT01447H

Dalton Transactions



Probing the non-innocent nature of an amino-functionalised β-diketiminate ligand in silylene/iminosilane systems

Journal:	Dalton Transactions
Manuscript ID	DT-ART-04-2020-001447.R1
Article Type:	Paper
Date Submitted by the Author:	08-Jun-2020
Complete List of Authors:	Do, Dinh Cao Huan; University of Oxford, Chemistry Vasko, Petra; University of Oxford, Chemistry; University of Jyväskylä, Department of Chemistry Fuentes, M. Angeles; University of Oxford, Chemistry Hicks, Jamie; University of Oxford, Chemistry Aldridge, Simon; University of Oxford, Chemistry

SCHOLARONE[™] Manuscripts

Dalton Transactions

ARTICLE

Probing the non-innocent nature of an amino-functionalised β -diketiminate ligand in silylene/iminosilane systems

Dinh Cao Huan Do,^a Petra Vasko,^{a,b} M. Ángeles Fuentes,^a Jamie Hicks,^a and Simon Aldridge^{*,a}

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Electron-rich β -diketiminate ligands, featuring amino groups at the backbone β positions ("N-nacnac" ligands) have been employed in the synthesis of a range of silylene (Si^{II}) complexes of the type (N-nacnac)SiX (where X = H, Cl, N(SiMe₃)₂, P(SiMe₃)₂ and Si(SiMe₃)₃). A combination of experimental and quantum chemical approaches reveals (i) that in all cases rearrangement to give an aza-butadienyl Si^{IV} imide featuring a contracted five-membered heterocycle is thermodynamically favourable (and experimentally viable); (ii) that the kinetic lability of systems of the type (Nnacnac)SiX varies markedly as a function of X, such that compounds of this type can be isolated under ambient

nacnac)SiX varies markedly as a function of X, such that compounds of this type can be isolated under ambient conditions for X = Cl and P(SiMe₃)₂, but not for X = H, N(SiMe₃)₂ and Si(SiMe₃)₃; and (iii) that the ring contraction process is most facile for systems bearing strongly electron-donating and sterically less encumbered X groups, since these allow most ready access to a transition state accessed via intramolecular nucleophilic attack by the Si^{II} centre at the β -carbon position of the N-nacnac ligand backbone.

REACTIVITY AT THE Y-CARBON

Introduction

The enduring popularity of the β -diketiminate ("Nacnac") ligand class, $[HC{(R)C(R')N}_2]$, in the coordination chemistry of metals from across the Periodic Table owes much to their versatility, tunability, and facile synthetic access.¹⁻⁴ These mono-anionic ligands benefit from having two strongly electron-donating nitrogen atoms, which, when coupled with the spatial protection from bulky Nbound groups, offer an effective blueprint for the stabilization of highly reactive coordinatively-unsaturated complexes of interest in small molecule activation. In addition, the relatively robust nature of the β -diketiminate framework means that they are typically regarded as "innocent" spectator ligands in much of this chemistry. Nonetheless, various chemical transformations have been reported involving modification of the backbone ligand sites - for example of reactive main group β -diketiminate complexes (Scheme 1).⁵ Examples of such behaviour include (i) addition to the γ -carbon (in conjunction with an electrophilic metal centre);⁶ (ii) substituent migration from the Main Group element centre to the $\beta\mbox{-}carbon$ position;⁸ and (iii) for the widely-used β -Me Nacnac ligand family, [HC{(Me)C(R')N}2], deprotonation of the backbone methyl group, which is often acidic enough to be attacked by strong bases.⁸

While these processes leave the six-membered chelate ring effectively intact, other studies have identified a transformation



1,3-MIGRATION



REACTIVITY AT THE β -METHYL POSITION



Scheme 1: Selected modes of reactivity of main group β -diketiminate complexes involving chemical modification of the ligand backbone (Dipp = 2,6-'Pr₂C₆H₂; counterions omitted for clarity).⁴⁻⁸

(primarily for low-valent metal complexes) which more severely reconfigures the coordination environment. This involves C–N bond cleavage to give an aza-butadienyl N,C-chelate, often with accompanying formation of a nitrogen-heteroelement multiple bond (Scheme 2).^{5,9,10}

^{a.} Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK. Simon.Aldridge@chem.ox.ac.uk

^b Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, Jyväskylä, Finland, Fl-40014

Electronic Supplementary Information (ESI) available: [NMR spectra of novel compounds, crystallographic details (CCDC refs 1995922-1995925), xyz coordinates associated with quantum chemical calculations]. See DOI: 10.1039/x0xx00000x

Page 2 of 8





In previous work we have been interested in developing the chemistry of a new class of electron-rich β -diketiminate ligands, featuring amino groups at the backbone β positions ("N-nacnac" ligands).^{11,12} During these studies we investigated the potential of the N-nacnac-stabilized chlorosilylene [HC{(Me₂N)C(Dipp)N}₂]SiCl, (**1-Dipp**)SiCl, as a synthetic intermediate for the formation of a range of silylene (Si^{II}) and sila-acyl (Si^{IV}) systems of the types (**1-Dipp**)SiX and (**1-Dipp**)Si(O)X. In probing the substitution chemistry of (**1-Dipp**)SiCl, we found that certain chloride metathesis processes (i.e. those associated with hydride or *tert*-butoxide) were accompanied by ring contraction of the N-nacnac backbone via C–N bond cleavage, leading to the generation of an imino-Si^{IV} product (Scheme 3).^{12c}



Scheme 3: Ring contraction of the N-nacnac ligand in conjunction with substitution of the ancillary chloride ligand in (**1-Dipp**)SiCl by hydride or *tert*-butoxide.^{12c}

Noting that – in our hands – this process seems to occur with strongly donating ancillary ligands,^{12c} and that previous studies on Nacnac-stabilised niobium systems had indicated that related rearrangements are usually associated with an electron-rich metal centre,^{5,10d} we sought to better understand the mechanism of ring contraction. With this in mind, we report here on our attempts to develop a systematic appraisal of scope/substituent effects, through experimental and quantum chemical studies of the reactivity of (**1-Dipp**)SiCl with amido-, phosphido-, and silyl-nucleophiles.

Results and Discussion

Substituent exchange reactions of (1-Dipp)SiCl with sources of (trimethylsilyl)amido-, phosphido- and silyl- anions

At the outset, a common synthetic methodology was utilised for the salt metathesis reactions of (1-Dipp)SiCl with Na[N(SiMe₃)₂], K[Si(SiMe₃)₃], and Li[P(SiMe₃)₂](dme) (dme = 1,2,-dimethoxy-ethane). The inorganic salt was added to the chlorosilylene at -78°C, and the reaction mixture slowly warmed to room temperature over a period of ca. 12 h. The identities of the products, isolated after recrystallization, reveal that (under these conditions) ring contraction leads to the formation of the aza-butadienyl Si^{IV} complexes (2-Dipp)Si(NDipp){N(SiMe₃)₂} and (2-Dipp)Si(NDipp)-{Si(SiMe₃)₃} in the cases of the amide and silyl reagents (Scheme 4), while a straightforward metathesis process with the phosphide reagent affords the phosphido-silylene (1-Dipp)Si{P(SiMe₃)₂}.



Scheme 4: Synthesis of the Si^{II} metathesis product (**1-Dipp**)Si{P(SiMe₃)₂} and the ringcontracted Si^V systems (**2-Dipp**)Si(NDipp){N(SiMe₃)₂} and (**2-Dipp**)Si(NDipp){Si(SiMe₃)₃} via reactions of (**1-Dipp**)SiCl with phosphide, amide or silyl nucleophiles.

In terms of diagnostic spectroscopic signals, the ²⁹Si{¹H} NMR resonances associated with the N,C-chelated Si^{IV} centres in (**2-Dipp**)Si(NDipp){N(SiMe₃)₂} and (**2-Dipp**)Si(NDipp){Si(SiMe₃)₃} ($\delta_{Si} = -81.1$ and -62.2 ppm, respectively), are located significantly upfield of that of Si^{II} precursor (**1-Dipp**)SiCl ($\delta_{Si} = 1.8$ ppm).^{12c} These shifts are comparable to those measured for the related compounds (**2-Dipp**)Si(NDipp)H and (**2-Dipp**)Si(NDipp)(O^tBu) ($\delta_{Si} = -74.2$ and -85.4 ppm), obtained from the reactions of (**1-Dipp**)SiCl with sources of hydride and *tert*-butoxide, respectively.^{12c} In addition, the ¹H NMR spectrum of (**2-Dipp**)Si(NDipp){Si(SiMe₃)₂}, for example, shares a similar pattern of resonances to the analogous hydrido and *tert*-butoxide systems (six Dipp methyl and three NMe₂ methyl signals).

By contrast, the ²⁹Si{¹H} NMR spectrum of (**1-Dipp**)Si{P(SiMe₃)₂} features a signal at a more downfield chemical shift ($\delta_{Si} = 18.6 \text{ ppm}$; ¹*J*_{SiP} = 213 Hz), consistent with the presence of a Si^{II} centre (*cf.* 1.8 ppm for (**1-Dipp**)SiCl). In a broader context, it can be compared to the ²⁹Si{¹H} signals for phosphido-silylenes stabilised by the amidinate ligand [PhC(N^tBu)₂]⁻ ($\delta_{Si} = 30$ to 60 ppm),^{13b-d} with the upfield shift for (**1-Dipp**)Si{P(SiMe₃)₂} hinting at the stronger donor capability of the N-nacnac ligand family. The ³¹P{¹H} resonance for

(**1-Dipp**)Si{P(SiMe₃)₂} at δ_P = -230.2 ppm features two satellite signals (¹J_{PSi} = 46 and 213 Hz) due to coupling to the silicon atoms in the SiMe₃ groups and the central Si^{II} centre, respectively. These data are closely comparable to those measured for {PhC(N^tBu)₂}Si-{P(SiMe₃)₂} (δ_P = -211.0 ppm, ¹J_{PSi} = 23, 194 Hz).^{13c}

The structures of all three compounds - the ring-contracted species $(2-Dipp)Si(NDipp){N(SiMe_3)_2}$ and $(2-Dipp)Si(NDipp){Si(SiMe_3)_3}$, and the simple metathesis product $(1-Dipp)Si{P(SiMe_3)_2}$ were confirmed by X-ray crystallography. For the five-membered ring systems, structural comparison with (2-Dipp)Si(NDipp)H illustrates the role of the pendant substituents on the geometry at the central silicon atom (Figure 1 and Table 1).



Figure 1: Molecular structures of the ring-contracted species (**2-Dipp**)Si(NDipp)-{N(SiMe₃)₂} and (**2-Dipp**)Si(NDipp){Si(SiMe₃)₃} in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths and angles can be found in Table 1.

Table 1: Selected bond lengths (Å) and angles (°) for ring-contracted species of the type $(2-Dipp)Si(NDipp)X (X = Si(SiMe_3)_3, N(SiMe_3)_2, H, P(SiMe_3)_2).$

Parameter ^a	Si(SiMe ₃) ₃	$N(SiMe_3)_2$	н	P(SiMe ₃) ₂
d(Si—N1)	1.869(1)	1.848(2)	1.818(1)	1.836(2)
d(Si—N2)	1.613(1)	1.590(2)	1.576(1)	1.587(2)
d(Si—C3)	1.935(1)	1.926(2)	1.901(2)	1.922(2)
d(C2—C3)	1.384(2)	1.382(3)	1.380(2)	1.373(3)
d(C1—C2)	1.415(2)	1.424(3)	1.431(2)	1.422(3)
d(C1-N1)	1.366(2)	1.372(3)	1.360(2)	1.342(3)
∠(N1—Si—C3)	86.63(5)	88.54(8)	88.79(6)	88.1(1)
∠(Si−N2−C _{ipso})	153.0(1)	173.5(2)	172.4(1)	156.1(2)
Reference	This work	This work	12c	This work

^{*a*} See Figure 2 for numbering scheme.



Figure 2: Atom numbering scheme used in Table 1.

The more sterically encumbered groups $(Si(SiMe_3)_3 > N(SiMe_3)_2 >> H)$ are associated with (i) longer endocyclic Si–N and Si–C bonds, and (ii) a longer exocyclic Si=N bond, and a narrower $(Si-N2-C_{ipso})$ angle within the SiNDipp moiety. In addition, at the aza-butadienyl backbone, the torsion angles between the pendant NMe₂ groups and the mean (NC₃Si) plane are wider for larger X groups. With regards to the exocyclic Si–X bonds themselves, the Si–N(SiMe₃)₂ distance (1.7441(18) Å) falls in the middle of the range of reported

bond lengths between four-coordinate silicon and three-coordinate nitrogen (1.65 – 1.85 Å), while the Si–Si(SiMe₃)₃ distance (2.4055(5) Å) is towards the longer end of structurally-characterised Si-Si single bonds (2.30 – 2.45 Å).¹⁴

(1-Dipp)Si{P(SiMe₃)₂} represents one of the few examples of structurally characterized phosphidosilylenes reported to date (Figure 3).¹³ Compared to (1-Dipp)SiCl, the greater steric bulk of P(SiMe₃)₂ substituent gives rise to a lower symmetry structure in the solid state: a pronounced steric clash between the P(SiMe₃)₂ moiety and one of the Dipp groups in (1-Dipp)Si{P(SiMe₃)₂} forces the latter to rotate out from the least-squares mean NC₃N plane. This in turn is manifested by disparate C–N distances within the N-nacnac ligand chelate (1.3422(15) and 1.3782(15) Å) and by differences in the associated Si–N bond lengths (1.9014(10) and 1.8313(10) Å). The silylene Si–P distance of 2.3674(4) Å in (1-Dipp)Si{P(SiMe₃)₂} is longer than the corresponding value in the amidinate-based system {PhC(N^tBu)₂Si{P(SiMe₃)₂} (2.2838(12) Å),^{13c} consistent with the more sterically hindered nature of the divalent silicon centre in the N-nacnac-ligated complex.



Figure 3: Molecular structure of (1-Dipp)Si{P(SiMe₃)₂} in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°): Si—P 2.3674(4); Si—N 1.9014(10), 1.8313(10); C—N 1.3422(15), 1.3782(15); N—Si—N 93.1(1); N—Si—P 91.9(1), 106.0(1).

Quantum chemical studies of the thermodynamics and kinetics of ring contraction

DFT calculations have been carried out in order to identify factors which influence the propensity for N-nacnac ligated silylene complexes to undergo ring contraction. At the outset, analyses of the frontier orbitals of the (isolable) silylene species (**1-Dipp**)SiX (X = Cl, P(SiMe₃)₂) were carried out. These reveal (i) that a major contribution to the HOMO comes (intuitively) from the lone pair at the silicon centre; and (ii) that the LUMO is best described as an anti-bonding π^* -orbital based on the N-nacnac ligand framework (Figure 4).



Figure 4: DFT-calculated HOMO (left) and LUMO (right) of (1-Dipp)SiCl (iso-surface = 0.04).

ARTICLE

These frontier orbital characteristics are also common to the (non-isolable) silylene complexes (**1-Dipp**)SiX (where X = H and Si(SiMe₃)₃), the geometries of which have been optimised with no restraints. Comparing all four calculated systems (Figure 5), it is evident that the energy of the LUMO is relatively unperturbed by changes in the silicon-bound X substituent, falling in the energy range -79.3 to -101.6 kJ mol⁻¹. On the other hand, variation in the X group is found to significantly affect the energy of the HOMO, which ranges from -508.3 to -432.8 kJ mol⁻¹. This is not unexpected given the covalent bond linking X to the silicon centre - the lone pair of which contributes substantially to the HOMO. Thus, the HOMO with the highest energy (-432.8 kJ mol⁻¹) is associated with the strongly σ -donating Si(SiMe₃)₃ function, while the σ -withdrawing effect of Cl presumably explains the much lower HOMO energy in (**1-Dipp**)SiCl (-508.3 kJ mol⁻¹).



Figure 5: Energies of the frontier orbitals (HOMO and LUMO), associated with the optimised structures of systems of the type (1-Dipp)SiX (where X = Cl, H, P(SiMe₃)₂ and Si(SiMe₃)₃).

Heterocyclic ring contraction mechanisms have been proposed for Nacnac-ligated titanium and niobium complexes, initiated by nucleophilic attack on the β -carbon of the ligand by the electron rich metal centre.^{9f,10} From an elementary molecular orbital point of view, the frontier orbital picture for the (1-Dipp)SiX systems appears to be consistent with a similar mechanistic postulate, involving interaction between the HOMO (effectively the Si-centred lone pair) and the LUMO, which has imine π^* character polarized towards the β -carbon atom. Based on these observations, a mechanistic pathway has been calculated for the conversion of the six-membered heterocyclic Si^{II} species (1-Dipp)SiX to their ringcontracted Si^{IV} counterparts (**2-Dipp**)Si(NDipp)X for X = CI, H, P(SiMe₃)₂ and Si(SiMe₃)₃ (Scheme 5 and Table 2). In each case this transformation proceeds via a single transition state, involving the formation of a bond between the Si centre and the β -carbon of the N-nacnac ligand, with accompanying C-N bond cleavage. The overall process is always exergonic ($\Delta G_r = -81.4$ to -118.4 kJ mol⁻¹), reflecting established trends in the thermodynamic stability of the Si^{II}/Si^{IV} oxidation states. That said, the associated activation energy varies markedly. Of the systems investigated, this barrier is highest in the case of X = Cl (+193.4 kJ mol⁻¹), consistent with the experimentally observed robustness of (1-Dipp)SiCl, and the

hypothesis that this is kinetic in its origin. In a broader sense, this relative inertness correlates with **(1-Dipp)**SiCl having the largest HOMO-LUMO gap (412.2 kJ mol⁻¹; Figure 5). Consistently, access to the transition state in the case of the hypothetical silyl-silylene **(1-Dipp)**Si{Si(SiMe₃)₃} - which has the smallest HOMO-LUMO gap (331.2 kJ mol⁻¹) - is significantly more facile, with an activation energy of only 60.3 kJ mol⁻¹.



Scheme 5: DFT-calculated free energy profiles for the ring contraction of (1-Dipp)SiX to (2-Dipp)Si(NDipp)X (energies given in each case relative to the (1-Dipp)-ligated starting complex).

Table 2: Free energy changes and activation energies associated with the ring contraction process outlined in Scheme 5 as a function of X substituent.

	ΔG_r / kJ mol ⁻¹	ΔG^{\dagger} / kJ mol ⁻¹
Cl	-81.4	193.4
P(SiMe ₃) ₂	-96.8	126.2
H	-118.4	98.7
Si(SiMe ₃) ₃	-95.6	60.3

Interestingly, the calculated activation energy in the case of X = H (98.7 kJ mol⁻¹) is lower than that determined for the P(SiMe₃)₂ substituted system (126.2 kJ mol⁻¹), despite the hypothetical hydridosilylene species (**1-Dipp**)SiH having a wider HOMO-LUMO gap (382.8 vs. 341.9 kJ mol⁻¹; Figure 5). This implies that steric factors are also important in accessing the transition state, with the bulkier phosphide function inducing greater steric repulsion with the NDipp group.

In general, the DFT-calculated free energy profiles for the ring contraction mechanism (Scheme 5 and Table 2) are in good agreement with the experimental findings, insofar as the systems with the lowest calculated activation energies (X = H and Si(SiMe₃)₃) are isolated as the ring-contracted species at room temperature, while those with higher barriers (X = P(SiMe₃)₂ and Cl) require significant heating in order to effect the corresponding isomerization process (*vide infra*).

Isomerization of (1-Dipp)SiCl and (1-Dipp)Si{P(SiMe₃)₂}

The DFT calculations outlined above suggest that the aza-butadienyl systems (**2-Dipp**)Si(NDipp)X are thermodynamically more stable

than the corresponding silylenes, (1-Dipp)SiX, even in the cases of X = Cl and P(SiMe₃)₂. As such, it was envisaged that isomerization might be effected at elevated temperatures to form the respective five-membered ring species, (2-Dipp)Si(NDipp){P(SiMe₃)₂} and (2-Dipp)Si(NDipp)Cl. To probe this hypothesis, a C₆D₆ solution of (1-Dipp)Si{P(SiMe₃)₂} was heated at 100 °C in a J. Young's NMR tube, and conversion monitored in situ by ³¹P{¹H} NMR spectroscopy (see ESI). These measurements revealed the emergence of a new resonance at δ_P = -246 ppm after 1 day, which grows in intensity at the expense of the signal due to $(1-Dipp)Si\{P(SiMe_3)_2\}$ ($\delta_P = -230.2$ ppm). Complete consumption of the phosphido-silylene is evident after 3 days, at which point the ³¹P{¹H} NMR spectrum features only one signal at -246.3 ppm. The identity of the product associated with this resonance was unambiguously confirmed by X-ray crystallography as the aza-butadienyl complex (2-Dipp)Si(NDipp)- $\{P(SiMe_3)_2\}$ (Figure 6) thereby confirming that the expected ring contraction process has indeed occurred under forcing conditions.



Figure 6: Molecular structure of $(2-Dipp)Si(NDipp){P(SiMe_3)_2}$ in the solid state as determined by X-ray crystallography. Hydrogen atoms and benzene solvate molecule omitted and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths and angles can be found in Table 1.

With the exception of the metrics associated with the siliconbound P(SiMe₃)₂ group, the geometry of (**2-Dipp**)Si(NDipp)-{P(SiMe₃)₂} closely resembles that of the related amido system (**2-Dipp**)Si(NDipp){N(SiMe₃)₂} (Table 1). On the other hand, the Si–P(SiMe₃)₂ distance (2.2456(10) Å) is markedly shorter than the corresponding value in (**1-Dipp**)Si{P(SiMe₃)₂} (2.3674(4) Å), reflecting the smaller covalent radius of Si^{IV} compared to that of Si^{II.15} Spectroscopically, (**2-Dipp**)Si(NDipp){P(SiMe₃)₂} displays a diagnostic doublet signal in its ²⁹Si{¹H} NMR spectrum for the central silicon atom at -75.8 ppm, in the range characteristic of the other (**2-Dipp**)Si(NDipp)X systems (δ_{Si} = -60 to -90 ppm). Additionally, the associated coupling constant (${}^{1}J_{SiP}$ = 25 Hz) is as expected for a Si^{IV}—P^{III} bond; those reported for Si^{II}—P^{III} bonds, by contrast, are typically in excess of 150 Hz.¹³

Having established a protocol for the thermally-induced ring contraction of $(1-Dipp)SiP{(SiMe_3)_2}$, the corresponding process for the chloride analogue was also investigated, acknowledging that the DFT-calculated activation barrier is significantly higher for the chloro derivative. Thus, a sample of (1-Dipp)SiCl in C_6D_6 was heated at 100 °C and monitored *in situ* by ¹H NMR spectroscopy. After 36 days at this temperature > 90% of the starting material had been consumed (see ESI). The pattern of new ¹H NMR resonances features six Dipp-methyl signals (in integrated ratio 1:1:1:1:2:2) and three NMe₂-methyl signals (1:1:2), and is characteristic of the (2-Dipp)Si(NDipp)X family of compounds. Furthermore, a new singlet

appears at δ_{Si} = -90.0 ppm in the ²⁹Si{¹H} NMR spectrum, which is significantly upfield compared to that of (**1-Dipp**)SiCl (δ_{Si} = 1.8 ppm), and similar to those observed for other (**2-Dipp**)Si(NDipp)X systems (e.g. δ_{Si} = -81.1 ppm for (**2-Dipp**)Si(NDipp){N(SiMe_3)_2}). Although single crystals of this product could not be obtained to verify its structure in the solid state, the spectroscopic evidence strongly suggests that it is the aza-butadienyl complex (**2-Dipp**)Si(NDipp)Cl.

Experimentally, the temporal profile for the six-to-fivemembered ring contraction is (given the timeframe) most conveniently monitored by *in situ* NMR for the Cl-substituted system. A logarithmic plot yields a straight line, consistent with the expected first-order rate law, from which the rate constant k_{obs} is calculated to be 6.93 (±0.03) × 10⁻⁷ s⁻¹, corresponding to a half-life of ca. 12 days (see ESI).

Conclusions

Investigation of a range of N-nacnac ligated silylene (Si") complexes of the type [HC{(Me₂N)C(Dipp)N}₂]SiX ((1-Dipp)SiX, where X = H, Cl, N(SiMe₃)₂, P(SiMe₃)₂, Si(SiMe₃)₃) by a combination of experimental and quantum chemical approaches has revealed that (i) in all cases rearrangement to give an aza-butadienyl Si^{IV} imide featuring a contracted fivemembered heterocycle is thermodynamically favourable (and experimentally viable); (ii) the kinetic lability of systems of the type (1-Dipp)SiX varies markedly as a function of X, such that compounds of this type can be isolated for X = CI and $P(SiMe_3)_2$, but not for X = H, $N(SiMe_3)_2$ and $Si(SiMe_3)_3$; and (iii) the ring contraction process is most facile for systems bearing strongly electron donating and sterically less encumbered X groups, since these allow most ready access to a transition state accessed via intramolecular nucleophilic attack by the Si^{II} centre at the $\beta\mbox{-}carbon$ position of the N-nacnac ligand backbone.

Experimental

General Methods

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in C₆D₆, which had been dried over potassium metal, distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under an inert atmosphere in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^1H,\ ^{13}C\{^1H\},\ ^{29}Si\{^1H\},\ and\ ^{31}P\{^1H\}\ NMR\ spectra$ were measured on a Bruker Avance III HD nanobay 400 MHz, Bruker Avance III 500 MHz or Bruker AVII 500 MHz spectrometer at ambient temperature. ¹H and ¹³C{¹H} NMR spectra are referenced internally to residual protio-solvent/solvent signals; ²⁹Si{¹H} and ³¹P{¹H} NMR spectra are referenced externally to tetramethylsilane and 85% H_3PO_4 , respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. Starting materials (1- $K[Si(SiMe_3)_3]^{16}$ and $Li[P(SiMe_3)]_2(dme)^{17}$ were **Dipp**)SiCl,^{12c}

 $((Me_3Si)_3Si),$

Journal Name

ARTICLE

synthesized according to literature methods. $Na[N(SiMe_3)_2]$ was used as received.

Syntheses of novel compounds

Generic method for metathesis reactions with (1-Dipp)SiCI. A solution of (**1-Dipp**)SiCI (100 mg, 0.19 mmol) in toluene was treated with the reagent of choice at -78 °C, and the solution slowly warmed to ambient temperature overnight. Subsequent filtration, followed by removal of solvent *in vacuo* yielded the crude residue, which was then recrystallized to give the pure product (unless otherwise stated).

(2-Dipp)Si(NDipp){N(SiMe₃)₂} was synthesized via the above method using Na[N(SiMe₃)₂] (37 mg, 1.1 equiv.). Storage of a concentrated solution in toluene/hexane (1:4) at -26 °C for several days yielded single crystals suitable for X-ray crystallography. Isolated yield of crystalline material: 39 mg, 29 %. ¹H NMR (C₆D₆, 400 MHz): δ_{H} 0.33 (s, 9H, (CH₃)₃Si), 0.51 (d, ³J_{HH} = 7.1 Hz, 3H, (CH₃)₂CH), 0.53 (s, 9H, (CH₃)₃Si), 0.58 (d, ³J_{HH} = 6.6 Hz, 3H, (CH₃)₂CH), 0.77 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 3H, (CH₃)₂CH), 1.24 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 3H, $(CH_3)_2$ CH), 1.27 (d, ${}^{3}J_{HH}$ = 6.6 Hz, 3H, (CH₃)₂CH), 1.34 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 3H, (CH₃)₂CH), 1.40 (d, ³J_{HH} = 7.1 Hz, 3H, (CH₃)₂CH), 1.59 (d, ³J_{HH} = 6.8 Hz, 3H, (CH₃)₂CH), 1.72 (s, 3H, (CH₃)₂N), 2.09 (s, 3H, (CH₃)₂N), 2.38 (s, 3H, (CH₃)₂N), 2.76 (sept, ³J_{HH} = 6.6 Hz, 1H, (CH₃)₂CH), 3.28 (s, 3H, $(CH_3)_2N$, 3.63 (overlapping sept, ${}^{3}J_{HH}$ = 6.9 Hz, 2H, (CH₃)₂CH), 3.96 (br sept, ${}^{3}J_{HH} = 6.9$ Hz, 1H, (CH₃)₂CH), 4.63 (s, 1H, methine H), 6.84-7.20 (6H, aromatic protons). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 125 MHz): δ_{C} 5.3, 7.2 $((CH_3)_3Si)$, 23.8, 24.1, 24.9, 25.4, 26.3, 26.5, 26,6, 26.7 ((CH₃)₂CH), 27.3, 27.8, 28.5 ((CH₃)₂CH), 38.8, 39.7, 40.5, 45.1 ((CH₃)₂N), 90.4 (methine C), 113.7, 122.6, 123.2, 125.1, 125.7, 127.1, 137.6, 139.9, 140.1, 145.8, 147.6, 147.9 (aromatic C), 170.2, 176.5 (imine C and silyl-dimethylamino C). ²⁹Si¹H NMR (C₆D₆, 99 MHz): δ_{si} -81.1 (*Si*=NDipp), -1.6, 2.4 (Me₃*Si*). EI/MS (*m*/*z*, %): 663.4, 8, [M]⁺; 620.4, 67, [M - NMe₂]⁺; accurate mass: calc. for C₃₇H₆₅N₅Si₃ ([M]⁺) 663.4548, found 663.4523. Elemental microanalysis: calc. for C37H65N5Si3: C 66.91 %, H 9.86 %, N 10.54 %; meas. C 66.85 %, H 9.98 %, N 10.42 %.

(2-Dipp)Si(NDipp){Si(SiMe₃)₃} was synthesized via the above method using K[Si(SiMe₃)₃] (58 mg, 1.1 equiv.). Recrystallization on a bulk scale exploited slow-evaporation of a concentrated toluene solution at ambient temperature. Yield 71 mg, 51 %. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in hexane stored at 4 °C for several days. ¹H NMR (C₆D₆, 400 MHz): δ_{H} 0.37 (s, 27H, (CH₃)₃Si), 0.81 (d, ³J_{HH} = 6.8 Hz, 3H, $(CH_3)_2CH)$, 0.88 (d, ${}^{3}J_{HH}$ = 6.6 Hz, 3H, $(CH_3)_2CH)$, 1.22-1.25 (overlapping doublets, 9H, (CH₃)₂CH), 1.30 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 6H, $(CH_3)_2CH)$, 1.33 (d, ${}^{3}J_{HH}$ = 6.7 Hz, 3H, $(CH_3)_2CH)$, 2.01 (br s, 6H, $(CH_3)_2N$, 2.31 (s, 3H, $(CH_3)_2N$), 2.80 (sept, ${}^{3}J_{HH}$ = 6.6 Hz, 1H, (CH₃)₂CH), 3.40 (s, 3H, (CH₃)₂N), 3.55 (sept, ³J_{HH} = 6.6 Hz, 1H, (CH₃)₂CH), 3.89 (sept, ³J_{HH} = 6.6 Hz, 2H, (CH₃)₂CH), 4.74 (s, 1H, methine H), 6.99 - 7.30 (m, 4H, aromatic protons), 7.29 (d, 2H, aromatic protons). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 100 MHz): δ_{C} 5.4 ((CH₃)₃Si), 25.1, 25.3, 25.5, 25.8, 26.5 ((CH₃)₂CH), 27.5 ((CH₃)₂CH), 28.3 $((CH_3)_2CH)$, 28.9, 29.2 $((CH_3)_2CH)$, 38.4, 40.7, 46.3 $((CH_3)_2N)$, 90.0 (methine C), 115.1, 122.7, 125.9, 126.7, 126.9, 128.1, 128.2, 128.3, 140.2, 140.9, 143.9, 146.9, 149.3 (aromatic C), 170.8, 176.1 (imine C and silyl-dimethylamino C). ²⁹Si{¹H} NMR (C₆D₆, 80 MHz): -127.6 -62.2 (*Si*=NDipp), -10.2 (Me₃*Si*). Elemental

microanalysis for this compound was repeatedly low in carbon.

(1-Dipp)Si{P(SiMe₃)₂} was synthesized via the above method using Li[P(SiMe₃)₂](dme) (56 mg, 1.1 equiv.). Storage of a concentrated toluene solution at -26 °C for several days yielded the product as a dark-red precipitate. Yield 75 mg, 55 %. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a toluene solution at ambient temperature. ¹H NMR (C₆D₆, 400 MHz): $\delta_{\rm H}$ 0.47 (d, ${}^{3}J_{\rm PH}$ = 3.8 Hz, 9H, (CH₃)₃Si), 0.48 (d, ${}^{3}J_{\rm PH}$ = 4.2 Hz, 9H, $(CH_3)_2CH)$, 1.03 (d, ${}^{3}J_{HH}$ = 6.7 Hz, 6H, ($CH_3)_2CH$), 1.25 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 6H, (CH₃)₂CH), 1.27 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 6H, (CH₃)₂CH), 1.70 (d, ${}^{3}J_{HH}$ = 6.5 Hz, 6H, $(CH_3)_2$ CH), 2.24 (s, 12H, $(CH_3)_2$ N), 3.20 (sept, ${}^{3}J_{HH} = 6.7$ Hz, 2H, (CH₃)₂CH), 3.67 (sept, ${}^{3}J_{HH} = 6.6$ Hz, 2H, (CH₃)₂CH), 4.58 (s, 1H, methine H), 7.03-7.20 (m, 6H, aromatic protons). $^{13}C{^{1}H}$ NMR (C₆D₆, 101 MHz): δ_{C} 5.4 (d, ${}^{2}J_{CP}$ = 8.8 Hz, (CH₃)₃Si), 5.9 (d, ${}^{2}J_{CP}$ = 10.7 Hz, $(CH_3)_3Si$, 24.6 (d, through-space coupling with P, J_{CP} = 3.7 Hz, (CH₃)₂CH), 26.1 ((CH₃)₂CH), 28.2, 28.3 (overlapping multiplets, $(CH_3)_2$ CH and $(CH_3)_2$ CH), 29.8 (d, through-space coupling with P, J_{CP} = 4.7 Hz, (CH₃)₂CH), 40.7 ((CH₃)₂N), 79.6 (methine C), 124.8, 125.4, 126.3 (aromatic carbons), 142.2 (d, through-space coupling with P, J_{CP} = 3.2 Hz, *ipso*-C of Dipp), 144.7, 146.2 (*o*-C of Dipp), 166.1 (d, through-space coupling with P, J_{CP} = 7.1 Hz, imine C). ²⁹Si{¹H} NMR $(C_6D_6, 80 \text{ MHz}): \delta_{Si} 18.6 \text{ (d, } {}^1J_{SiP} = 213 \text{ Hz}, \text{ NSiN})$ (the resonances corresponding to Me₃Si- moieties were determined via 2D-NMR techniques at -1.3 and 2.6 ppm). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 162 MHz): δ_{P} -230.2 (s, ${}^{1}J_{siP}$ = 46 and 213 Hz). Elemental microanalysis: calc. for C37H65N4PSi3: C 65.24 %, H 9.62 %, N 8.23 %; meas. C 65.16 %, H 9.74 %, N 8.08%.

(2-Dipp)Si(NDipp){P(SiMe3)2}. A J. Young NMR tube, containing (1-**Dipp**){P(SiMe₃)₂} (25 mg, 37 mmol) in benzene-d₆ (0.5 mL) was heated at 100 °C for 84 h, and the reaction monitored in situ by ¹H and ³¹P{¹H} NMR spectroscopy. Subsequently, slow-evaporation of solvent from the sample at ambient temperature yielded the product as dark-orange crystals suitable for X-ray crystallography (18 mg, 72 %). ¹H NMR (C_6D_6 , 400 MHz): $\delta_H 0.28$ (d, ³ $J_{PH} = 4.4$ Hz, 9H, $(CH_3)_3$ Si), 0.41 (d, ${}^{3}J_{PH}$ = 5.0 Hz, 9H, (CH₃)₂CH), 0.61 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 3H, $(CH_3)_2$ CH), 0.83 (d, ${}^{3}J_{HH}$ = 6.6 Hz, 3H, $(CH_3)_2$ CH), 0.84 (d, ${}^{3}J_{HH}$ = 6.3 Hz, 3H, (CH₃)₂CH), 1.25 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 3H, (CH₃)₂CH), 1.36 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 3H, (CH₃)₂CH), 1.40 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 3H, (CH₃)₂CH), 1.44 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 3H, (CH₃)₂CH), 1.76 (d, ${}^{3}J_{HH}$ = 6.6 Hz, 3H, (CH₃)₂CH), 2.10 (br, 6H, (CH₃)₂N), 2.37 (s, 3H, (CH₃)₂N), 3.05 (sept, ³J_{HH} = 6.7 Hz, 1H, (CH₃)₂CH), 3.14 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 1H, (CH₃)₂CH), 3.49 (s, 3H, $(CH_3)_2N$, 3.94 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 1H, $(CH_3)_2CH$), 4.31 (d of sept, ${}^{3}J_{HH}$ = 6.9 Hz, through-space coupling with P, J_{HP} = 2.1 Hz, 1H, (CH₃)₂CH), 4.61 (s, 1H, methine H), 6.83-7.21 (m, 6H, aromatic protons). ¹³C{¹H} NMR (C₆D₆, 101 MHz): δ_{C} 3.6 (d, ²J_{CP} = 11.6 Hz, (CH₃)₃Si), 4.8 (d, ²J_{CP}) = 12.9 Hz, (CH₃)₃Si), 24.2, 24.3, 24.6, 25.3, 25.5, 26.2 ((CH₃)₂CH), 27.5, 27.6 ((CH₃)₂CH), 27.9 (d, through-space coupling with P, J_{CP} = 11.5 Hz, (CH₃)₂CH)), 28.3 (d, through-space coupling with P, J_{CP} = 12.5 Hz, (CH₃)₂CH), 29.1 ((CH₃)₂CH), 38.9, 40.4, 45.4 ((CH₃)₂N), 87.1 (methine C), 114.5, 122.2, 122.8, 125.2, 125.8, 138.1, 138.4, 140.0, 147.2, 147.5, 148.3 (aromatic carbons), 168.5 (d, through-space coupling with P, J_{CP} = 3.4 Hz, imine C), 174.3 (d, through-space coupling with P, J_{CP} = 13.5 Hz, silvl-dimethylamino C). ²⁹Si{¹H} NMR $(C_6D_6, 80 \text{ MHz})$: δ_{Si} -75.8 (d, ${}^{1}J_{SiP}$ = 25 Hz, *Si*=NDipp), -0.3 (d, Me₃*Si*, ${}^{1}J_{SiP}$ = 29 Hz), 3.3 (d, Me₃Si, ${}^{1}J_{SiP}$ = 17 Hz). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 162

MHz): δ_P -246 (s). Elemental microanalysis: calc. for $C_{37}H_{65}N_4PSi_3$: C 65.24 %, H 9.62 %, N 8.23 %; meas. C 65.16 %, H 9.78 %, N 8.03 %.

Crystallography

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device.¹⁸ Data were collected at 150 K (except in the case of (**1-Dipp**)Si{P(SiMe₃)₂} (115 K)) using mirror monochromated Cu K_α radiation ($\lambda = 1.5418$ Å) or Mo K_α radiation ($\lambda = 0.71073$ Å). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).¹⁹ Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using SheIXT 2014 and refined on F² using the SheIXL 2014 package and the graphical interface Olex2 or XSeed.²⁰

Quantum chemical calculations

DFT calculations were performed using Gaussian09 (Revision D.01) programme package.²¹ Geometry optimisations were performed with the PBE1PBE hybrid exchange-correlation functional,²² and the Def2-TZVP basis set,²³ with an ultrafine integration grid. Structural optimisations were carried out for the full ligand systems, and were reported as Gibbs free energies in the gas phase. Full frequency calculations were performed for optimized geometries to confirm the nature of the stationary points found (minimum or saddle point). Graphics were created with the GaussView programme.²⁴

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Jardine-Oxford Scholarship (DDCH), the Academy of Finland (PV, grant number 314794), the Leverhulme Trust (JH, RP-2018-246) and the EPSRC (MÁF, EP/K014714/1) We also thank the Oxford Advanced Research (ARC) facilities for computing resources.

Notes and references

- For early references, see: a) W. Bradley and I. Wright, J. Chem. Soc., 1956, 640-648; b) J. E. Parks and R. H. Holm, Inorg. Chem., 1968, 7, 1408–1416; c) S. G. McGeachin, Can. J. Chem., 1968, 46, 1903–1912; d) C. L. Honeybourne and G. A. Webb, Chem. Commun. (London), 1968, 739-740; e) R. Bonnett, D. C. Bradley and K. J. Fisher, Chem. Commun., 1968, 886-887.
- 2 L. Bourget-Merle, M. F. Lappert and J. R. Severn, Chem. Rev., 2002, 102, 3031-3066.
- 3 For landmark examples from the s-, p- and d-block elements, see, for example: a) M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Science*, 2006, **311**, 1904-1907; b) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754-

1757; c) M. M. Rodriguez, E. Bill, W. W. Brenessel and P. L Holland, *Science*, 2011, **334**, 780-783.

- For selected recent reviews of Nacnac chemistry, see: a) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354-396; b) S. P. Sarish, S. Nembenna, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2011, **44**, 157–170; c) Y. Tsai, *Coord. Chem. Rev.*, 2012, **256**, 722-758; d) C. Chen, S. M. Bellows and P. L. Holland, *Dalton Trans.*, 2015, **44**, 16654-16670; e) R. L. Webster, *Dalton Trans.*, 2017, **46**, 4483–4498.
- 5 C. Camp and J. Arnold, *Dalton Trans.*, 2016, **45**, 14462-14498.
- a) C. E. Radzewich, M. P. Coles and R. F. Jordan, J. Am. Chem. Soc., 1998, 120, 9384–9385; b) A. Ariafard, Z. Lin and R. F. Jordan, Organometallics, 2005, 24, 5140–5146; c) A. J. Boutland, I. Pernik, A. Stasch and C. Jones, Chem.-Eur. J. 2015, 21, 15749–15758.
- 7 a) B. Qian, S. W. Baek and M. R. Smith, *Polyhedron*, 1999, 18, 2405–2414; b) W. D. Woodul, E. Carter, R. Müller, A. F. Richards, A. Stasch, M. Kaupp, D. M. Murphy, M. Driess and C. Jones, *J. Am. Chem. Soc.*, 2011, 133, 10074–10077.
- See, for example: a) H. Zhu, J. Chai, A. Stasch, H. W. Roesky, T. Blunck, D. Vidovic, J. Magull, H. G. Schmidt and M. Noltemeyer, *Eur. J. Inorg. Chem.*, 2004, 4046–4051; b) M. Driess, S. Yao, M. Brym, C. van Wüllen and D. Lentz, *J. Am. Chem. Soc.*, 2006, **128**, 9628–9629; c) S. P. Sarish, B. Nekoueishahraki, A. Jana, H. W. Roesky, T. Schulz and D. Stalke, *Chem.-Eur. J.*, 2011, **17**, 890–894; d) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767; e) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin and S. Aldridge, *Angew. Chem. Int. Ed.*, 2015, **54**, 5098–5102.
- 9 See, for example: a) X. Li, X. Cheng, H. Song and C. Cui, Organometallics, 2007, 26, 1039–1043; b) W. Wang, S. Yao, C. Van Wüllen and M. Driess, J. Am. Chem. Soc., 2008, 130, 9640–9641; c) W. D. Woodul, A. F. Richards, A. Stasch, M. Driess and C. Jones, Organometallics, 2010, 29, 3655–3660; d) S. L. Choong, C. Schenk, A. Stasch, D. Dange and C. Jones, Chem. Commun., 2012, 48, 2504–2506; e) J. Li, X. Li, W. Huang, H. Hu, J. Zhang and C. Cui, Chem.-Eur. J., 2012, 18, 15263–15266; f) L. Xie, J. Zhang, H. Hu and C. Cui, Organometallics, 2013, 32, 6875–6878.
- 10 For related examples in early transition metal chemistry see, for example: a) F. Basuli, U. J. Kilgore, D. Brown, J. C. Huffman and D. J. Mindiola, *Organometallics*, 2004, 23, 6166–6175; b) G. Bai, P. Wei and D. W. Stephan, *Organometallics*, 2006, 25, 2649–2655; c) H. Hamaki, N. Takeda and N. Tokitoh, *Organometallics*, 2006, 25, 2457–2464; d) N. C. Tomson, J. Arnold and R. G. Bergman, *Organometallics*, 2010, 29, 5010–5025.
- 11 a) P. T. K. Lee, Masters Thesis, St. Mary's University, Halifax, Canada, 2009; b) Z. Janousek and H. G. Viehe, *Angew. Chem. Int. Ed. Engl.*, 1971, **10**, 574-575; c) S. Brenner and H. G. Viehe, *Tetrahedron Lett.*, 1976, **17**, 1617-1620; d) A. Albers, T. Bayer, S. Demeshko, S. Dechert and F. Meyer, *Chem.-Eur. J.*, 2013, **19**, 10101-10106; e) V. Regnier, Y. Planet, C. E. Moore, J. Pecaut, C. Philouze and D. Martin, *Angew. Chem. Int. Ed.*, 2017, **56**, 1031-1035.
- 12 a) D. C. H. Do, A. Keyser, A. V. Protchenko, B. Maitland, I. Pernik, H. Niu, E. L. Kolychev, A. Rit, D. Vidovic, A. Stasch, C. Jones and S. Aldridge, *Chem.-Eur. J.*, 2017, 23, 5830-5841; b) D. C. H. Do, A. V. Protchenko, P. Vasko, J. Campos, E. L. Kolychev and S. Aldridge, *Z. Anorg. Allg. Chem.*, 2018, 644, 1238-1242; c) D. C. H. Do, A. V. Protchenko, M. Á. Fuentes, J. Hicks, E. Kolychev, P. Vasko and S. Aldridge, *Angew. Chem. Int. Ed.*, 2018, 57, 13907-13911; d) D. C. H. Do, A. V. Protchenko, M. Á. Fuentes, M. Á. Fuentes, J. Hicks, P. Vasko and S. Aldridge, *Chem. Commun.*, 2020, in press (DOI: 10.1039/D0CC00875C).
- 13 a) H. H. Karsch, U. Keller, S. Gamper and G. Müller, Angew. Chem. Int. Ed., 1990, 29, 295–296; b) C. W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones

ARTICLE

and S. Blaurock, J. Am. Chem. Soc., 2007, **129**, 12049–12054; c) S. Inoue, W. Wang, C. Präsang, M. Asay, E. Irran and M. Driess, J. Am. Chem. Soc., 2011, **133**, 2868–2871; d) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf and D. Stalke, Organometallics, 2012, **31**, 4588–4592; e) K. Hansen, T. Szilvási, B. Blom, E. Irran and M. Driess, Chem.-Eur. J., 2015, **21**, 18930–18933; f) H. Cui, J. Zhang, Y. Tao and C. Cui, Inorg. Chem., 2016, **55**, 46–50.

- 14 M. Kaftory, M. Kapon and M. Botoshansky in *The Chemistry* of Organic Silicon Compounds, Vol.2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, 1998, pp. 181-265.
- 15 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832-2838.
- 16 a) C. Marschner, *Eur. J. Inorg. Chem.*, 1998, 221-226; b) C. Kayser, R. Fischer, J. Baumgartner and C. Marschner, *Organometallics*, 2002, **21**, 1023–1030.
- 17 a) G. Fritz and W. Hölderich, Z. Anorg. Allg. Chem., 1976, 422, 104–114; b) F. Uhlig, S. Gremler, M. Dargatz, M. Scheer and E. Herrmann, Z. Anorg. Allg. Chem., 1991, 606, 105–108.
- 18 J. Cosier and A. M. Glazer, J. Appl. Crystallogr., 1986, 19, 105-107.
- 19 CrysAlisPro v.1.171.35.8 (Agilent Technologies, 2011).
- 20 a) G. M. Sheldrick, SHELX-2014 (2014); b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341; c) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Crystallogr., 2011, 44, 1281–1284.
- 21 Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT 2009.
- 22 a) M. Ernzerhof and G. E. Scuseria, J. Chem. Phys., 1999, 110, 5029–5036; b) C. Adamo and V.Barone, J. Chem. Phys., 1999, 110, 6158-6170; c) J. P. Perdew, K.Burke and M. Ernzerhof, Phys. Rev. Lett., 1997, 78, 1396; d) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868; e) J. P. Perdew, M.Ernzerhof and K. Burke, J. Chem. Phys., 1996, 105, 9982-9985.
- 23 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
- 24 R. D. Dennington, T. A. Keith and J. M. Millam, *GaussView* 5.0.8, Gaussian, 2008.

Figure for table of contents



SILYLENE-TO-IMINOSILANE RING CONTRACTION