Abstract: Air- and moisture-stable heterobimetallic tetrahedral clusters [Cp(CO)2MSil]2 (M = Mo or W; R = SitBu3) were isolated from the reaction of N-heterocyclic carbene (NHC) stabilized silylsilylidyne (M) metal complexes [Cp(CO)2M=Si(SitBu3)NHC] with a mild Lewis acid (BPh3). Alternatively, treatment of the NHC-stabilized silylidene complex [Cp(CO)2W=Si(SitBu3)NHC] with stronger Lewis acids such as AlCl3 or B(C6F5)3 resulted in the reversible coordination of the Lewis acid to one of the carbonyl ligands. Computational investigations revealed that the dimerization of the intermediate metal silylidene (M=Si) complex to a tetrahedral cluster instead of a planar four-membered ring is due to steric bulk.

Introduction

Tetrahedral clusters that consist of main-group elements are attractive synthetic targets because of their high ring strain and reactivity. Even white phosphorus (P4), which has been known for centuries, has recently been the subject of intense research (Figure 1)[1,2]. The heavier homologue, As4, is challenging to handle because of its thermal and photochemical instability. Nevertheless, Cummins and co-workers even managed to isolate As2P, the first example of a heteroatomic tetrahedrane.[3] The archetypical organic tetrahedrane (rBuC)2 (II) was isolated by Maier and co-workers in 1978,[4] whereas Wiberg et al. reported the heavier analogue, tetrasilatetrahedrane (rBuSiSi)2 (III), in 1993.[5] One decade later, Sekiguchi and co-workers isolated a further tetrasilatetrahedrane (R3SiR = SiMe(CH2SiMe3)3) while trying to isolate a disilane with a Si2Si triple bond.[6] Very recently, another neutral tetrahedron that contains two different heteroatoms, (rBuCP)2 (IV), was reported to form upon dimerization of phosphaalkynes (R=SiP).[7] In addition to neutral tetrahedral complexes, anionic tetrahedral [E4]4− (E = Si, Ge, Sn) species, so-called Zintl-type polyanions, are known.[8] Whilst binary combinations in Zintl tetrahedral clusters [E2Mn4] have been reported,[9] there are no examples of neutral heterobimetallic tetrahedral clusters with heavier main-group elements and transition metals.

Numerous examples are known of M2Si2-type bimetallic complexes (V) with bridging acetylene or acetylene derivatives that exhibit tetrahedral structures.[10] Such complexes find application in the Pauson–Khand synthesis of cyclopentanone derivatives and are catalysts in hydroboration reactions,[11,12] yet heavier congeners have remained unexplored to the best of our knowledge. Among heavier analogues of Group 14 element compounds M2E2 (E = Si, Ge, Sn), particular interest has been devoted to silicon as bimetallic clusters with bridging silicon atoms are indeed alleged key intermediates in various transition-metal-catalyzed transformations.[13] Since the 1990s, various M2Si2 binuclear transition-metal complexes have been reported and their catalytic activities have been exploited in the dehydrocoupling of hydrosilanes and the metathesis of olefins.[14] Thus far, however, all of these complexes feature a planar, diamond-shaped, or butterfly-type M2Si2 core, whereas tetrahedral structures remain elusive.[13,14] Generally, monoatomic tetrahedral derivatives RE4 can be generated photochemically from the corresponding planar linear compounds by elimination or photoisomerization as reported for II.[15] Accordingly, tetrahedranes can form by dimerization of disilanes or nickel-mediated dimerization of phosphaalkynes.[7,16]

Herein, we report the first isolable heterobimetallic M2Si2 cluster with a tetrahedral structure. Inspired by the previous reports from the groups of Wiberg and Sekiguchi, we based our synthetic strategy on the elimination of an N-heterocyclic carbene (NHC) from a silylidene complex (Si=Si) to generate...
a silyldiyne complex (Si≡M), which was hypothesized to dimerize subsequently to a tetrahedral M₂Si₃ cage cluster (Scheme 1).

![Scheme 1. Synthetic strategy to isolate a neutral M₂Si₃ tetradehdre upon dimerization of a transient silyldiyne complex (Si≡M).](image)

The chemistry of transition-metal silyldiyne complexes has a short, yet spectacular history. The arguably first silyldiyne complex \([\text{Cp}^*(\text{dmpe})(\text{H})\text{MoSiMes}]\) (dmpe = PMe₂CH₂CH₂PMe₂) was reported by Tilley and Morok in 2003.[17] Shortly after, when the role of the NHC in stabilizing low-valent silicon(II) species had been recognized, a genuine Mo=Si triple-bonded complex was isolated by the group of Filippou using this elegant synthetic approach.[18] Following this achievement, a handful of transition-metal silyldiyne complexes and their reactivities were reported by further research groups.[17–19] Characteristically, all room-temperature isoalbe transition-metal silyldiyne complexes bear very bulky ligands either on the silicon center (e.g., Ar²p, Eind) or on the metal center (e.g., Cp*, Tbb). We concluded that a M=Si complex with comparably reduced bulk on both the silicon atom and the transition-metal center should be an excellent choice for the targeted tetrahedral cluster.

**Results and Discussion**

Very recently, we reported the synthesis of the first silyl-substituted chlorosilylene (1) and studied the reactivity associated with its lone pair and chloride substituent.[20] Compound 1 is prone to salt metathesis reactions because of the presence of the chloride atom. In fact, heating an orange toluene solution of chlorosilylene 1 with \([\text{Cp}(\text{CO})_2(\text{PMe}_2)_2]\)MLi (M = Mo, W) at 75 °C smoothly gave the IE₃Me₂, (1,3-diethyl-4,5-dimethyl-imidazolin-2-ylidene) stabilized transition-metal silyldiene complexes 2 and 3 as air- and moisture-sensitive, dark-green solids (2, M = Mo, 82%; 3, M = W, 78%; Scheme 2).

The \(^{29}\)Si NMR spectra of 2 and 3 show characteristic resonances, which are shifted strongly downfield to 278.8 ppm and 229.7 ppm (\(J_{Si,W} = 261\) Hz), respectively, in reference to those of 1 (\(\delta = 18.3\) ppm). Similar chemical shifts were observed for the previously reported transition-metal silyldiene complexes[18,19a,21] The silicon-bonded NHC carbene atoms resonate at 168.3 ppm (2) and 172.6 ppm (3) in the \(^{13}\)C NMR spectroscopic analysis, which is similar to the chemical shift found for 1 (\(\delta = 169.7\) ppm).

The IR spectra of 2 and 3 each show two ν(CO) absorption bands at 1782 and 1864 cm⁻¹ (2), and at 1770 and 1849 cm⁻¹ (3). The positions of these bands agree well with previously reported metal arsilenyiidene complexes and our predictions by density functional theory (DFT) calculations (3: 1837 and 1892 cm⁻¹).[18,19] Single crystals of 2 and 3 were obtained from a toluene/pentane (1:3) mixture at ambient temperature, and the structure in the solid state was determined by X-ray diffraction analysis (Figure 2). Complex 2 features a Mo=Si double bond (2.3499(10) Å), which is shorter than that found for the donor-free molybdenum silyldiene complex \([\text{Cp}^*(\text{CO})_2(\text{SiMe}_3)_2]\)Mo=Si(Mes)₂ (2.3872(7) Å) and lies in the range of previously reported molybdenum silyldiene complexes \(d(\text{Mo}–\text{Si}) = 2.288(2)–2.3872(7)\) Å.[22] Similarly, 3 exhibits a W=Si (2.346(2) Å) bond that is considerably shorter than in \([\text{Cp}^*\text{W}(\text{CO})_2]=(\text{SiMe}_3)_2(\text{SiMe}_3)]\) (2.3850(12) Å) in the neutral alkyl(sily-
liden) tungsten complex, [(η⁵-C₅Me₅(Me)Et)(CO)₂(W=Si(C₅H₆Me)₃)] (2.370(11) Å), but slightly longer than that of the anionic complex [Cp⁵⁺(CO)₂W(SiH(C₅H₆Me)₃)] [HMe₄PPr] (2.336(17) Å).²¹,²² UV/Vis analysis (Figure S6) revealed a characteristic absorption band at \( \lambda_{\text{max}} = 418 \) nm for the Mo=Si complex 2. For the W=Si complex 3, a band at \( \lambda_{\text{max}} = 418 \) nm and a very broad and weak band ranging from approximately \( \lambda = 500 \) to 700 nm were found (Figure S12). Time-dependent DFT (TD-DFT) calculations reproduced these values very well (Figure S63). In addition, the Löwdin population analysis indicates that 3 has a d⁴ electron configuration with considerable negative partial charge at the tungsten atom, which is consistent with an oxidation state of +II. Both complexes 2 and 3 feature trigonal-planar-coordinated silicon centers, with the sum of bond angles at the silicon center being 360°.

We investigated the replacement of the NHC moiety and treated the bulky IMe₃Me₃ compound with more nucleophilic IMe₄.²⁴ Indeed, treatment of 3 with excess IMe₄ resulted in quick conversion (60% in 30 min) and eventually, after 12 h, quantitative exchange of IMe₃Me₃ by IMe₄ (3′; Scheme 3). As expected, only minor shifts in reference to the starting material were observed in all \(^{1}H, ^{13}C, ^{29}Si\) NMR experiments. Single crystals of 3′ were obtained at ambient temperature from a C₆D₆/pentane (1:1) mixture, and the molecular structure was also confirmed by X-ray diffraction analysis (Figure 2). The W=Si bond is slightly elongated for 3′ (2.3534(12) Å) in comparison to that of the anionic silylidene complex. 3′ isomerized in solution and eventually, after 12 h, quantitative exchange of IMe₃Me₃ by IMe₄ (3′; Scheme 3).

The ligand exchange ability of 3 encouraged us to abstract the NHC by treatment with Lewis acids. Indeed, treatment of 3 with the strong Lewis acid B(C₆F₅)₃, or more oxophilic AlCl₃, resulted in an immediate color change from dark green to dark red in toluene (Scheme 3). Significant downfield shifts of the \(^{29}Si\) NMR resonances for 4a (\( \delta = 322.0 \) ppm) and 4b (\( \delta = 323.2 \) ppm) compared to that of 3 (\( \delta = 229.7 \) ppm) were observed, whereas the \(^{13}C\) NMR spectra of 4a and 4b displayed only a very small change in shift (166.9 ppm for 4a and 167.3 ppm for 4b) from 3 (\(^{13}C\) \( \delta = 172.6 \) ppm). This suggests that the NHC remains coordinated to a silyldiene unit. Intriguingly, the addition of coordinating THF to the red solutions of 4a or 4b resulted in the regeneration of the dark-green color, and the \(^{1}H\) NMR spectroscopic analysis confirmed the regeneration of the initial starting material 3. This reaction corroborated the formation of a peculiar Lewis acid–carbonyl adduct, and was likewise confirmed by X-ray crystal structure analysis of 4a (Figure 3). A comparable terminal carbonyl ligand activation was observed by Cummins and co-workers during preparation of a terminal molybdenum carbide upon acylation of a MoIV carbonyl complex with pivaloyl chloride.²⁵

**Figure 3.** Ellipsoid plot (set at 30% probability) of the molecular structure of compound 4a. Hydrogen atoms are omitted for clarity, and tert-butyl groups are depicted in wireframe for simplicity.²⁶

Selected bond lengths [Å] and angles [°]: S1–W1 2.3630(18), S1–Si 2.437(2), S1–C1 1.940(10), Al1–O2 1.777(8), W1–C27 1.975(7), W1–C28 1.840(7); C1–S1–Si 106.4(9), W1–C11 114.6(6), W1–S1–Si 138.89(9).

The W–Si bond in 4a (2.3630(18) Å) is elongated in reference to 3 (2.346(2) Å) because of the reduced back-donation from tungsten to silicon and in line with the downfield-shifted resonance in the \(^{29}Si\) spectrum (\( \delta = 322.0 \) ppm). The W–C bond length for the AlCl₃-coordinated CO ligand (1.840(7) Å) is significantly shortened in comparison with that of the terminal carbonyl ligand (1.975(7) Å) and even in the range of tungsten carbyne complexes (1.82–1.87 Å).²⁶ The Al–O bond length in 4a (1.777(8) Å) is comparable with previously reported AlCl₃ coordinated to the oxygen atom of a carbonyl ligand without bond rupture (1.812(2) Å).²⁷ Compound 4a has a similar absorption band at 400 nm in the UV/Vis spectrum in toluene. Unfortunately, 4b could only be isolated as a sticky solid and not in crystalline form. The IR spectrum of 4a in the solid state shows two ν(CO) bands that appear as broad bands at 1813 cm⁻¹ for AlCl₃-coordinated CO and at 1901 cm⁻¹ for the terminal CO. Two peculiar carbonyl stretching frequencies are observed because of enhanced π-back-donation from tungsten to the carbonyl ligand and simultaneous weakening of the C–O bond (C27–O1 1.158(8) Å, C28–O2 1.255(9) Å) that is coordinated to AlCl₃. Similarly, 4b also shows two ν(CO) bands at 1906 cm⁻¹ and 1873 cm⁻¹. The latter can be assigned to CO–B(C₆F₅)₃, which appears at a higher wavenumber than in [Cp⁵⁺(CO)–(C₅H₆Me)₂B–OC]W=Si(H)₃Si[HMe₄PPr] (ν(CO–BCF) = 1535 cm⁻¹).²⁸ This observation indicates weaker coordination of the borane to the carbonyl group in comparison to that of the anionic silyldiene complex. In order to abstract the NHC from the silyldiene complexes, we hence used a milder Lewis acid, namely triphenylboron (BPh₃, Scheme 4). Indeed, heating toluene...
solutions of 2 and 3 with one equivalent of BPh$_3$ for 30 min to 90°C afforded the desired tetrahedral clusters 5 and 6 in 40% and 52% yield, respectively. These heterobimetallic compounds are well soluble in aromatic as well as aliphatic organic solvents. Surprisingly, the heterobimetallic tetrahedral Si$_3$M$_2$ clusters 5 and 6 are perfectly stable in moist air, as has been also reported for tetrasilatetrahedrane (tBu$_2$SiSiM$_3$) (III). It is interesting to note that these complexes did not even react with methanol when heated to 70°C for 24 h.

The single-crystal structure of 6 revealed the formation of a tetrahedral, bimetallic transition-metal silicon cluster (Figure 4). The W–Si (2.5507(15)–2.6913(15) Å) bonds in 6 are significantly longer than those in 3 (2.346(2) Å) and reported W–Si double bonds (2.34–2.47 Å), and fall in the range of W–Si single bonds (2.47–2.71 Å). The structural parameters of complex 6 are akin to the planar complexes W-Si-W-Si (W–W 3.183(1) Å, W–Si 2.586(5)–2.703(4) Å) and W-Si-W-H (W–Si 2.489(2)–2.487(2) Å). The Si–Si bond (2.2221–19 Å) is significantly shorter than those in previously reported SiSiSiM butterfly-shaped clusters (d(Si–Si) = 2.85–2.98 Å) and also those of tetrasilatetrahedrane, where the Si–Si bond lengths range from 2.315(2) to 2.3830–(19) Å.[5, 6, 14, 31] The short Si–Si separation is attributed to the partial multiple bond character (Figure 4, right) and reduced $\sigma$-donation from the silyl substituents due to the elongation of the exocyclic Si–Si bonds (Si1–Si2 = 2.437(2) Å, Si2–Si4 = 2.430(2) Å). The formation of bimetallic clusters for 5 and 6 was also confirmed by mass-spectrometric analysis (Figures S36–S46), which suggested that 5 is isostructural with 6. The tetrahedral M$_3$Si$_4$ clusters melt below 70°C (m.p. 64–65°C for 5; 67–69°C for 6), yet we did not observe any changes in the 'H NMR spectra upon heating xylene solutions to 120°C. This observation corroborates the high thermal stability and the absence of an equilibrium between the monomer (Cp(CO)$_3$M=Si(SiBu$_3$)$_2$) and the dimeric forms of 5 and 6, and is consistent with diffusion NMR experiments (DOSY; Figures S28 and S40). The $^{29}$Si NMR signals of skeletal silicon atoms shifted strongly to higher fields ( $\delta$ = 3.65 ppm for 5, GIAO = 5 ppm; $\delta$ = −63.04 ppm ($J_{\text{Si,W}}$ = 52 Hz) for 6; GIAO = −48 ppm), which corroborates strong silyl character due to a change in hybridization from $sp^3$ to $sp^2$.[19, 32] In addition, such an upfield shift is also typically observed for ring C atoms of tetrahedrane.$^{[1, 4, 13c, 33]}$ The small $J_{\text{Si-W}}$ coupling constant of 52 Hz indicates a high degree of p-character at the Si atom and a relatively small contribution from the silicon’s s-orbital. A significant low-field shift was observed for the supersilyl ligand ($\delta$ = 48.32 ppm for 5; 43.99 ppm for 6). Similar shifts for tBu$_2$Si were also reported for Wiberg’s tetrasilatetrahedrane (tBu$_2$SiSiM$_3$) ($^{29}$Si, $\delta$ = 53.07 ppm; III, Figure 1).[5] The IR spectra of 5 and 6 showed two ν(CO) bands at higher wavenumbers than for the NHC-TM-silylidenes 2-4a,b (1844 and 1918 cm$^{-1}$ for 5; 1860 and 1914 cm$^{-1}$ for 6; DFT: 1904 and 1916 cm$^{-1}$).[36] This hypsochromic shift is due to reduced π-back-donation from the transition metal to the CO ligand. The UV/Vis spectra of 5 and 6 in toluene showed absorption bands at 543 nm and 530 nm, respectively. In excellent agreement, TD-DFT calculations for 6 predict the HOMO–LUMO transition to lie at 501 nm.

We performed detailed DFT calculations at the PBE0-D3BJ(SMD)/ZORA-def2-TZVPP//PBE0-D3BJ/def2-SVP level of theory in order to understand the electronic structures of 6 and 3 (Figures S57–S62). Indeed, Löwdin population analysis of the DFT-optimized structure of 6 also indicated a Si–Si bond order of 1.1, indicative of very small multiple bond character (Figure 4, right), which is in line with the short Si–Si bond length in 6. Interestingly, the calculations suggest a higher Si–Si multiple bond character of 1.3 for the molybdenenum complex 5 (Figure S61), which is in line with the relative $^{29}$Si NMR shifts of 5 and 6 (see above). Plotting the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) corroborates delocalization of both orbitals over the whole cluster (Figure S58). The intrinsic bond orbitals (IBOs)$^{[36]}$ show two different, yet quite covalent, $\pi$-interactions between Si1 and W1 or W2, respectively (Figure 5, top). The Si–W1 $\sigma$-bond is polarized towards Si1, whereas the longer Si1–W2 $\sigma$-bond features additionally a $\pi$-back-bonding interaction with the CO $\pi^*$ orbitals. Besides, we found a Si1–Si2 $\sigma$-bond as well as considerable bonding interactions between the W1 and W2 atoms (Fig-
ure 5, bottom). Overall, the calculations confirmed a tetrahe-
dral structure with strong and covalent interactions between
all silicon and tungsten atoms.

Furthermore, the reaction mechanism for the formation of 6
was modeled in order to understand the peculiar Si–Si
dimerization (Figure 6).[37] The restricted DFT calculations
suggest that the formation of the intermediate silylidyne
complex 7 proceeds essentially in isoergic fashion (ΔG =
+1.7 kcal mol⁻¹). The subsequent dimerization (ΔG =
-43.1 kcal mol⁻¹) features a barrier of ΔG* = 26.6 kcal
mol⁻¹, which agrees well with a reaction occurring at elevated
temperatures. The transition state (Figure 6) shows a very
large separation of the two tungsten atoms (5.05 Å) and hence
is indicative of only weak interactions between these two
atoms. Nevertheless, a very small orbital overlap in HOMO-3
substantiates a very asynchronous, yet still concerted forma-
tion of the Si–Si and W–W bonds.[38]

Figure 5. Intrinsic bond orbitals (IBOs) associated with the Si1−W1
(top, left), Si1−W2 (top, right), Si1−Si2 (bottom, left) and W1−W2
(bottom, right) bonds (tBu groups and hydrogen atoms are omitted
for clarity, but were included in the calculations).

Figure 6. Proposed reaction profile for the formation of W₂Si₂ tetrahe-
dral cluster 6.

Most importantly, the transition state reveals that the
steric bulk associated with the supersilyl groups and the Cp
substituents allows only for a perpendicular arrangement of
the two silylidyne groups. This orientation consequently
determines the formation of the tetrahedral cluster instead
of four-membered rings as would be expected by simplifying
polarity considerations. Indeed, attempts to geometry-opti-
fize four-membered rings with either Si–Si/W–W or alter-
nating Si–W bonds led to isomeric tetrahedra (ΔG =
-34.0 kcal mol⁻¹; Figure S70), three-membered rings (ΔG =
-15.8 kcal mol⁻¹; Figure S70), or quadrangles of much higher
energy (Si-W-Si-W quadrangle: ΔG = -10.2 kcal mol⁻¹).
Attempts to model dimeric compounds with decooordination
of only one NHC also did not meet with success. We conclude
that the steric bulk in 6 prevents the formation of quadrangles
or triangles and allows only for the formation of a tetrahedral
cluster subsequent to abstraction of the NHC ligand.

Conclusion

We have reported the isolation of the heteroatomic,
bimetallic M₂Si₂ tetrahedral clusters 5 and 6. These com-
ponds form after NHC abstraction from the respective
NHC-stabilized silylidene complexes 2 and 3 by dimerization
of transient transition-metal silylidyne complexes. These
tetrahedral clusters are air- and moisture-stable unlike many
other main-group organometallic compounds. Furthermore,
we have shown that the NHC (IEt₂Me₂) in complex 3 can be
exchanged for a more nucleophilic NHC (IME₄). Contrarily,
the addition of stronger Lewis acids such as AlCl₃ or B(CF₆)₃,
resulted in reversible activation of the carbonyl ligands
(4a, b). Calculations confirm the covalent bonding in the
cluster and indicate that steric bulk is crucial for the formation
of the tetrahedron-type structure.

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Conflict of interest

The authors declare no conflict of interest.

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FOID analysis and CASSCF(12,12) calculations suggest small multireference character for the transition state. For details, see the Supporting Information.

CCDC 1970332 (2), 1970333 (3), 1970334 (3'), 1970335 (4a), and 1970336 (6) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.