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From silicon(II)-based dioxygen activation to adducts of elusive dioxasiliranes and sila-ureas stable at room temperature

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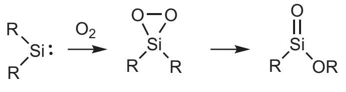
Dioxygen activation for the subsequent oxygenation of organic substrates that involves cheap and environmentally friendly chemical elements is at the cutting edge of chemical research. As silicon is a non-toxic and highly oxophilic element, the use of silylenes could be attractive for facile dioxygen activation to give dioxasiliranes with a SiO_2–peroxo ring as versatile oxo-transfer reagents. However, the latter are elusive species, and have been generated and studied only in argon matrices at −233 °C. Recently, it was demonstrated that unstable silicon species can be isolated by applying the concept of donor–acceptor stabilization. We now report the first synthesis and crystallographic characterization of dioxasiliranes stabilized by *N*-heterocyclic carbenes that feature a three-membered SiO_2-peroxide ring, isolable at room temperature. Unexpectedly, these can undergo internal oxygen transfer in toluene solution at ambient temperature to give a unique complex of cyclic sila-urea with $C{=}O \rightarrow Si{=}O$ interaction and the shortest $Si{=}O$ double-bond distance reported to date.

Activation of dioxygen is important in nature and in industrial chemistry, as shown by the key role of oxygenation in biochemistry and in the production of value-added compounds. Although nature employs metalloenzymes that contain redox-active metal sites for dioxygen activation[1], artificial chemical systems that involve electronically and coordinatively unsaturated centres[2–6] or metal nanoparticles[7] as mediators were developed in academia and industrial laboratories and are able to convert dioxygen into much more reactive superoxo (O_2^{-}) and peroxo (O_2^{2-}) compounds for direct oxygenation. Among non-metal peroxides, organic derivatives of H_2O_2 (for example, organohydroperoxides or cyclic organoperoxides) are well established as selective oxidants[8]. In line with this, dioxiranes with a cyclic CO_2–peroxo moiety represent powerful oxidants towards unsaturated organic substrates that have numerous applications[9,10]. The latter achievements prompted a great deal of interest in heavier main-group element analogues of dioxiranes with a three-membered EO_2 ring ($E = Si$, Ge, Sn and Pb) as potential oxygen-transfer reagents. However, exploration of such systems as reactive intermediates turned out to be rather difficult because of their intrinsic thermolability[11–13]. Accordingly, the silicon analogues of dioxiranes, that is, dioxasiliranes **I** (Fig. 1) have received particular attention because of their role as transient species in several photochemical and thermal transformations[14–18]. Dioxasiliranes **I** seem particular appealing as oxidants because they should be accessible easily by the direct addition of dioxygen onto silylenes, the silicon analogues of carbenes, owing to the enormous oxophilicity of silicon. In fact, a few derivatives of **I** have been synthesized by dioxygen activation with transient silylenes, which occurs even at very low temperatures (below −233 °C) in argon matrices[18–21]. However, their pronounced thermolability means they are elusive and could be characterized only by means of spectroscopy. In other words, because of its instability a dioxasilirane has not yet been isolated as a pure compound. Also, these species can undergo internal oxo transfer to give the corresponding silanoic esters **II** (Fig. 1) which, in turn, are also transient species because of the intrinsic high reactivity of the $Si{=}O$ double bond[19–21].

Recently, the concept of donor–acceptor stabilization has proved useful in the isolation of highly reactive main-group element compounds. Striking examples include the isolation of disilicon (:Si=Si:) stabilized by *N*-heterocyclic carbene (NHC)[22]. In this context, we synthesized an isolable silaformamide–borane complex[23], starting from a stable *N*-heterocyclic silylene[24]. Initially, we described the first isolation of a silanoic ester[25]. Very recently, we reported on NHC-stabilized silanones (sila-ureas) that resulted from the facile oxygenation of the NHC-activated silylenes **1a** and **1b** with N_2O (refs 26,27). The remarkably high oxophilicity of the silicon(II) atoms in **1** prompted us to probe whether they can activate dioxygen to give the isolable dioxasilirane adducts **2a** and **2b**. We now report for the first time the synthesis and crystallographic characterization of elusive dioxasiliranes stabilized in the form of the NHC complexes **2a** and **2b** and isolable at ambient temperature. Additionally, we show that **2a** undergoes a striking internal oxygen transfer in solution to give the unique cyclourea → sila-urea adduct **3**.

Results and discussion

In spite of the sterically encumbered environment around silicon, the NHC-activated, highly nucleophilic silicon(II) atoms in precursors **1a** and **1b** reacted smoothly with dioxygen, even at low temperatures, to afford the first dioxasilirane adducts **2a** and **2b**,



I

II

Figure 1 | Transient dioxasiliranes I and their rearrangement to silanoic esters II. **I** was generated by side-on addition of dioxygen onto a silylene precursor. **II** resulted from internal oxygen transfer (oxygen insertion) of diorgano-substituted dioxasiliranes **I** into a Si–C bond ($R = $ organo or halogen).

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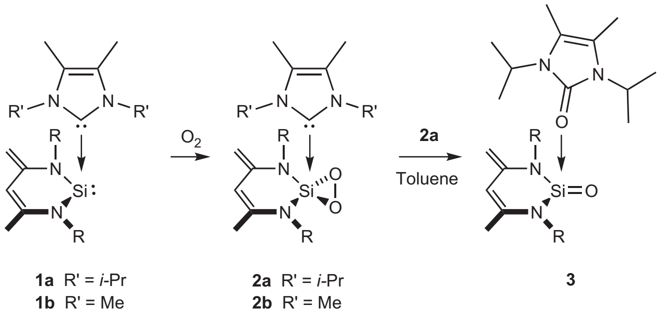


Figure 2 | Synthesis of 2a, 2b and 3. Compounds **2a** and **2b** were obtained from dioxygen activation by NHC-supported silylene precursor **1a** and **1b**, respectively. Compound **3** was obtained by internal oxygen transfer of **2a** into the C → Si dative bond. R = 2,6-i-$Pr_2C_6H_3$.

respectively (Fig. 2). The conversion of the precursors was evident by gradual decolouration of the yellow solutions at −60 °C. Subsequent concentration of the reaction solution and cooling at −20 °C furnished colourless crystals of the desired NHC-stabilized dioxasiliranes **2a** and **2b** in 79% and 69% yield, respectively, and both were stable at room temperature.

Their compositions were corroborated by mass spectrometry and elemental analyses, and the constitutions are consistent with the ^1H and ^{29}Si NMR data and infrared spectroscopy (see Supplementary Information). As a result of the pentacoordination of the silicon atom, the $^{29}Si\{^1H\}$ NMR spectra show high-field singlets at $\delta = -131.9$ (**2a**) and −133.3 ppm (**2b**). Single-crystal X-ray diffraction (XRD) analyses proved that **2a** and **2b** are isostructural (Fig. 3). The O_2 ligand is 'side-on' coordinated to the tetravalent silicon atom and lies almost within the plane of the C_3N_2Si ring. Additionally, the Si atom binds to the respective NHC ligand and achieves an unexpected square-pyramidal coordination. The Si1–C30 (NHC) distance of 1.963(3) Å in **2a** is about 0.1 Å shorter than that in the precursor **1a** and indicates dative bonding from the NHC ligand. The Si1–N1 and Si1–N2 distances (1.767(2) and 1.799(2) Å, respectively) in **2a** are a little shorter than those in **1a** (1.794(2) and 1.820(2) Å, respectively). The O–O distances of 1.547(3) Å in **2a** and 1.510(3) Å in **2b**, respectively, are a little longer than that in dimesityldioxirane (1.50 Å) (ref. 28) and than those observed for related 'side-on' metal peroxo complexes (1.4–1.5 Å) (ref. 29), but shorter than those calculated for 'donor-free' dioxasiliranes (1.57–1.81 Å) (refs 11,12,18). Similarly, the Si–O distances in **2a** (1.682(2) and 1.693(2) Å) and **2b** (1.667(2) and 1.692(2) Å) are slightly longer than those calculated for dioxasiliranes with tetracoordinate silicon atoms (1.632–1.678 Å) (ref. 11). Obviously, these differences originate from the higher coordination number at silicon. In addition, we carried out quantum-chemical calculations (using density functional theory; see the Supplementary Information for computational details) on different model compounds. The computed energy of the fragmentation of **2** into dioxasilirane and NHC fragments was 25 kJ mol^{-1} (B3LYP/TZVPP//RI-BP86/TZVP), which underlines the dative character of this C → Si bond.

A square-pyramidal configuration is rare for pentacoordinate silicon compounds, so we wanted to learn whether the unusual coordination geometry of silicon in **2** is caused by steric substituent effects. Thus, the structure of the parent system in which all substituents were replaced by hydrogen atoms was also optimized fully. Although the orientations of the NHC and dioxygen ligands change somewhat, the overall coordination around silicon remains square pyramidal to a large extent. This indicates that the origin of the structural preference is electronic rather than steric, as is the case for related pentacoordinated spirobicyclic silicates with silicon bonded to one carbon and four oxygen atoms[30,31]. Allowing the hypothetical free dioxasilirane to relax to a tetrahedral SiO_2N_2-type structure after removal of the NHC donor from **2** provided a computed relaxation energy of 230 kJ mol^{-1} (see Supplementary Fig. S7). This indicates a large influence of the NHC ligand on the overall silicon-coordination environment. Solutions of **2a** in toluene can be stored for several days at −20 °C without significant change. At room temperature, however, the compound underwent internal oxygen transfer to give the unique adduct **3** (Fig. 2), in which one of the oxygen atoms in the SiO_2–peroxo moiety in **2a** was transferred internally into the Si1–C30 (NHC) bond. The conversion occurred almost quantitatively for **2a** in benzene at ambient temperature. Similarly, **2b** is thermolabile in solution at room temperature, but it gave a mixture of as yet unidentified products.

Compound **3**, in the form of colourless crystals, precipitated readily from the reaction solution at room temperature and was isolated in 72% yield. Its composition was proved by elemental analysis, and the constitution is consistent with the ^1H, ^{13}C and ^{29}Si NMR and infrared spectroscopic data (see Supplementary Information). The $^{29}Si\{^1H\}$ NMR spectrum of **3** displayed a singlet at $\delta = -77.1$ ppm, which is comparable to that observed for the related NHC-stabilized silanones (cyclic sila-urea derivatives)[26,27]. A single-crystal XRD analysis revealed that **3** represents a unique cycloureа → sila-urea adduct, in which the oxygen atom of the cyclourea coordinates to the silicon centre of the sila-urea moiety (Fig. 4).

The silicon centre in **3** adopts a strongly distorted tetrahedral coordination, reminiscent of the situation in the related NHC-stabilized cyclic sila-ureas[26,27]. Thus, the sum of the bond angles for the X_3Si subunit (X = O1, N1 and N2) of 339.4° is slightly larger than the corresponding values of NHC-stabilized sila-ureas and the C30–O2–Si1 angle is 145.4(2)°. The Si1–O1 distance of 1.532(2) Å in **3** is most notable, as it is the shortest Si–O distance in a molecular Si=O compound hitherto reported[23,25–27]. The relatively long Si1–O2 (1.727(2) Å) bond and the short O2–C30 distance (1.294(3) Å) are in accordance with a dative interaction between the cyclourea and the cyclic sila-urea moieties. This is supported well by quantum-chemical calculations of the model

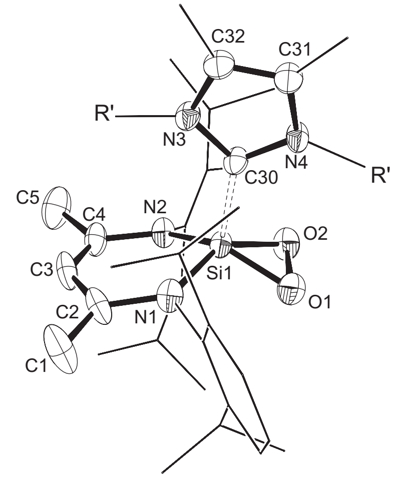


Figure 3 | Oak Ridge Thermal-Ellipsoid Plot (ORTEP) of the isostructural molecules 2a (R′ = *i*-Pr) and 2b (R′ = Me) in the crystal. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected distances (Å) and angles (°) of **2a**: Si1–O1, 1.682(2); Si1–O2, 1.693(2); Si1–N2, 1.767(2); Si1–N1, 1.799(2); Si1–C30, 1.963(3); O1–O2, 1.547(3); O1–Si1–O2, 54.6(1); N2–Si1–N1, 98.5(1); O1–Si1–C30, 103.9(1); O2–Si1–C30, 101.2(1). Selected distances (Å) and angles (°) of **2b**: Si1–O1, 1.667(2); Si1–O2, 1.692(2); Si1–N2, 1.781(2); Si1–N1, 1.777(2); Si1–C30, 1.933(3); O1–O2, 1.510(3); O1–Si1–O2, 53.4(1); N2–Si1–N1, 98.8(1); O1–Si1–C30, 104.1(1); O2–Si1–C30, 99.1(1).

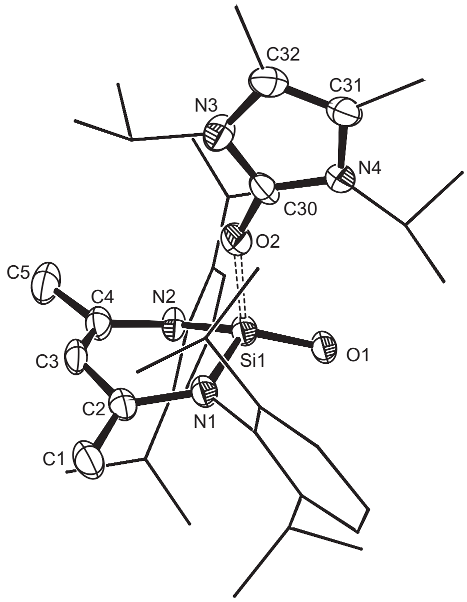
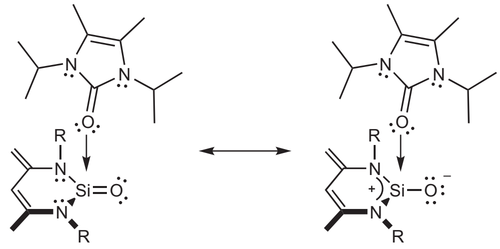


Figure 4 | ORTEP of the molecular structure of 3 in the crystal. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected distances (Å) and angles (°): Si1–O1, 1.532(2); Si1–O2, 1.727(2); Si1–N2, 1.732(2); Si1–N1, 1.744(2); O2–C30, 1.294(3); N1–C2, 1.413(3); N2–C4, 1.410(3); C2–C3, 1.460(4); C3–C4, 1.341(4); C31–C32, 1.346(4); O1–Si1–O2, 112.20(9); N2–Si1–N1, 102.7(1); C30–O2–Si1, 145.4(2).

compound $L'(NHC{=}O)Si{=}O$ (**3′**), in which the 2,6-*i*-$Pr_2C_6H_3$ groups at nitrogen in the C_3N_2 ligand are replaced by methyl substituents and the organic groups in the cycloурea moiety by hydrogen atoms (see Supplementary Information). The bonding characteristics of **3′** were analysed as for the model systems $L'Si{=}O$ (**4**), $(H_2N)_2Si{=}O$ (**5**) and $H_2Si{=}O$ (**6**) within the framework of natural resonance theory (NRT; see Supplementary Information). Compared to the simplest Si=O reference model **6**, delocalization reduces the covalent Si–O bond order in the sequence **5**, **4**, **3′**, as confirmed by the NRT bond orders (see Supplementary Table S5). At the same time, the ionic contribution increases, which overall leads to relatively similar bond orders. The simpler Wiberg bond indices (see Supplementary Table S4) decrease, in agreement with the reduced covalency. In all cases, a partial multiple-bonding character remains present for the Si=O1 bond.

Furthermore, the NRT bond orders, the Wiberg bond indices and plots of the electron localization function (ELF) (see Fig. 6 and Supplementary Figs S5 and S6) support the coordinative nature of the C=O2 → Si interaction and thus the general bonding picture of **3** as a complex between a cyclic sila-urea and a cycloурea donor, as depicted in the resonance structure **3A** in Fig. 5.



3A **3B**

Figure 5 | Resonance structures 3A and 3B. These represent two of the leading mesomeric forms in accordance with results from density functional theory calculations and NRT. Structure **3A** shows the dative C=O → Si=O interaction and **3B** depicts that the Si=O moiety in **3** bears significant ylide character. ($R = 2{,}6\text{-}i\text{-}Pr_2C_6H_3$).

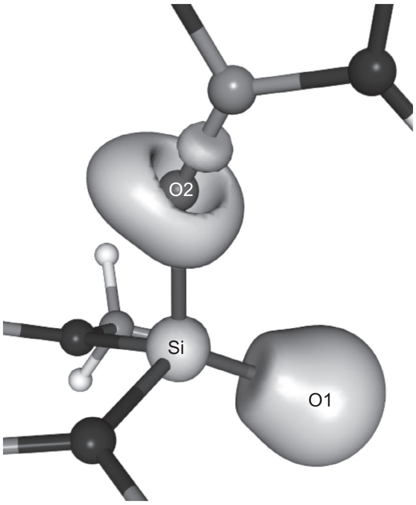


Figure 6 | ELF representation (ELF surface = 0.80 isosurface) of the Si–O1 versus C–O2 and C–O2 → Si bonding of the model compound 3′ (B3YLP/TZVPP//RI-BP86/TZVP). The polar Si–O1 bond and the even more polar dative C–O2 → Si bond may be contrasted to the more covalent C–O2 bond. ELF areas outside the O1-Si-O3 moiety are removed for clarity.

Additionally, the large ionicity of the Si=O bond in **3** and in model compounds is clearly apparent from ELF plots (Fig. 6 and Supplementary Information), and supports the role of the second main resonance form **3B**, as shown in Fig. 5. ELF is a real-space function closely related to electron pairing and allows us also to visualize successfully the bonding in strongly delocalized cases (see Supplementary Information references). Essentially, the ELF domain for Si–O1 bonding is merged with the large O1 lone-pair type domain, consistent with a very polar bond. The ELF surface for the C=O2 → Si donor interaction exhibits an even larger polarization towards the O2 atom (Fig. 6; note, in comparison, the ELF domain for the more covalent C=O2 bond), consistent with the general dative-bonding picture developed above. Single-point calculations (B3LYP/TZVPP//RI-BP86/TZVP) on **3′** provide a binding energy of 56 kJ mol^{-1} between the cycloурea and the sila-urea, again in agreement with a largely dative character of the C=O → Si=O interaction.

In conclusion, the first isolable adducts **2a** and **2b** of transient dioxasiliranes stable at ambient temperature were prepared through facile oxygen activation with the nucleophilic NHC-activated silylenes **1a** and **1b**. Strikingly, the five-coordinate silicon atoms in **2a** and **2b** adopt a square-pyramidal geometry, seldom observed for pentacoordinated silicon compounds, and feature a ‘side-on’ coordinated peroxo ligand. Remarkably, **2a** undergoes internal oxygen transfer in toluene solution at ambient temperature to afford solely the first cycloурea → cyclic sila-urea adduct **3** with a unique C=O → Si=O dative interaction and the shortest Si=O distance reported to date. These results highlight the importance of donor–acceptor stabilization for the isolation of elusive silicon–oxygen species isolable even at room temperature. The facile access to ‘bottleable’ dioxasiliranes **2** could pave the way to novel, mild and aprotic oxygenation reagents in organic synthesis. Respective investigations are in progress.

Methods

General considerations. All experiments and manipulations were carried out under dry nitrogen using standard Schlenk techniques or in an MBraun drybox that contained an inert atmosphere of purified nitrogen. Solvents were deoxygenated and dried by standard methods, saturated with purified nitrogen and freshly distilled prior to use. The precursor complexes **1a** (ref. 27) and **1b** (ref. 26) were prepared according to literature procedures. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker ARX200 and AV 400 spectrometers. High-resolution electrospray ionization mass spectra (ESI-MS) were measured on a Thermo Scientific LTQ orbitrap XL. ESI-MS analyses were carried out with a Finnigan-MAT 955 instrument. The infrared spectra were taken on a Nicolet Magna 750 spectrometer with nitrogen-gas purge. Elemental analyses were performed on a FlashEA 1112 CHNS Analyser.

Single-crystal X-ray structure determinations. Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold nitrogen flow. The data for compounds **2a**, **2b** and **3** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 (ref. 32) software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. In **2b** the toluene solvent molecule was disordered and refined with restraints for the anisotropic displacement parameters. In **3** one of the isopropyl groups was disordered and refined with restraints for the anisotropic displacement parameters. CCDC 731581 (**2a**), 750427 (**2b**) and 731579 (**3**) contain the supplementary crystallographic data for this paper.

Computational methods. For our calculations different models of compounds **2** and **3** were used. Crystal structure data were taken as a starting point for full-structure optimizations of **2** and **3** without restrictions. For models **2′** and **3′** all residues of the NHC fragment were replaced by hydrogen atoms and the aryl groups of the dioxasilirane or cyclic sila-urea moiety, respectively, were substituted by methyl groups (see Supplementary Fig. S4). Only the substituted groups and all hydrogen atoms were optimized subsequently, with all other coordinates fixed at the crystal structure data. To be able to compare the specific bonding characteristics of **2** and **3** with related species of the sila-urea type, the parent sila-urea fragment **4** (and model **4′**, in which the 2,6-i-$Pr_2C_6H_3$ substituents at nitrogen were replaced by methyl groups) and the much simpler model systems silaformaldehyde $H_2Si{=}O$ (**6**) (studied recently by Gusel'nikov and co-workers[33]) and sila-urea $(H_2N)_2Si{=}O$ (**5**) (also studied extensively by Epping *et al.*[34]) were taken into account as reference structures. These were optimized fully. For all optimizations, we used the BP86 functional in conjunction with the resolution-of-identity and a TZVP basis set. Further information on subsequent single-point calculations for energetics and wave-function analyses is given in the Supplementary Information.

See also the Supplementary Information for detailed experimental conditions and procedures, and analytical data for the novel compounds **2a**, **2b** and **3**.

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References

1. Nam, W. Special issue on dioxygen activation by metalloenzymes and models. *Acc. Chem. Res.* **40,** 465–634 (2007).
2. Meunier, B. *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations* (Springer, 2000).
3. Costas, M., Mehn, M. P., Jensen, M. P. & Que, L. Jr Dioxygen activation at mononuclear nonheme iron active sites: enzymes, models and intermediates. *Chem. Rev.* **104,** 939–986 (2004).
4. Lewis, E. A. & Tolman, W. B. Reactivity of dioxygen–copper systems. *Chem. Rev.* **104,** 1047–1076 (2004).
5. Cho, J. *et al.* Geometric and electronic structure and reactivity of a mononuclear 'side-on' nickel(III)–peroxo complex. *Nature Chem.* **1,** 568–572 (2009).
6. Yao, S. *et al.* O–O bond activation in heterobimetallic peroxides: synthesis of the peroxide $[LNi(\mu,\eta^2{:}\eta^2\text{-}O_2)K]$ and its conversion into a bis(μ-hydroxo) nickel zinc complex. *Angew. Chem. Int. Ed.* **48,** 8107–8110 (2009).
7. Edwards, J. K. *et al.* Switching off the hydrogen peroxide hydrogenation in the direct synthesis process. *Science* **323,** 1037–1041 (2009).
8. Adam, W. *Peroxide Chemistry* (Wiley, 2000).
9. Greer, A. A view of unusual peroxides. *Science*, **302,** 235–236 (2003).
10. Curci, R., D'Accolti, L. & Fusco, C. A novel approach to the efficient oxygenation of hydrocarbons under mild conditions. Superior oxo transfer selectivity using dioxiranes. *Acc. Chem. Res.* **39,** 1–9 (2006).
11. Sawwan, N. & Greer, A. Rather exotic types of cyclic peroxides: heteroatom dioxiranes. *Chem. Rev.* **107,** 3247–3285 (2007).
12. Ishiguro, K. & Sawaki, Y. Structure and reactivity of amphoteric oxygen species. *Bull. Chem. Soc. Jpn* **73,** 535–552 (2000).
13. Clennan, E. L. & Pace, A. Advances in singlet oxygen chemistry. *Tetrahedron* **61,** 6665–66691 (2005).
14. Gasper, P. P., Holten, D., Konieczny, S. & Corey, J. Y. Laser photolysis of silylene precursors. *Acc. Chem. Res.* **20,** 329–336 (1987).
15. Sabdhu, V., Jodhan, A., Safarik, I. & Strausz, O. P. Dichlorosilylene: rate constant for reaction with oxygen. *Chem. Phys. Lett.* **135,** 260–262 (1987).
16. Permenov, D. G. & Radzig, V. A. Mechanisms of heterogeneous processes in the system SiO_2+CH_4. *Kinet. Catal.* **45,** 273–278 (2004).
17. Murakami, Y., Koshi, M., Matsui, H., Kamiya, K. & Umeyama, H. Kinetics of the SiH_3+O_2 reaction: a new transition state for SiO production. *J. Phys. Chem.* **100,** 17501–17506 (1996).
18. Becerra, R. *et al.* Time-resolved gas-phase kinetic and quantum chemical studies of the reaction of silylene with oxygen. *Phys. Chem. Chem. Phys.* **7,** 2900–2908 (2005).
19. Patyk, A., Sander, W., Gauss, J. & Cremer, D. Dimethyldioxasilirane. *Angew. Chem. Int. Ed. Engl.* **28,** 898–900 (1989).
20. Sander, W. & Kirschfeld, A. in *Matrix-Isolation of Strained Three-Membered Ring Systems* Vol. 4 (ed. Halton, B.) Ch. 2, 1–80 (JAI Press, 1995).
21. Bornemann, H. & Sander, W. Oxidation of methyl(phenyl)silylene – synthesis of a dioxasilirane. *J. Am. Chem. Soc.* **122,** 6727–6734 (2000).
22. Wang, Y. *et al.* A stable silicon(0) compound with a Si=Si double bond. *Science* **321,** 1069–1071 (2008).
23. Yao, S., Brym, M., van Wüllen, C. & Driess, M. From a stable silylene to a mixed-valent disiloxane and an isolable silaformamide–borane complex with considerable silicon–oxygen double-bond character. *Angew. Chem. Int. Ed.* **46,** 4159–4162 (2007).
24. Driess, M., Yao, S., Brym, M., van Wüllen, C. & Lentz, D. A new type of N-heterocyclic silylene with ambivalent reactivity. *J. Am. Chem. Soc.* **128,** 9628–9629 (2006).
25. Yao, S., Xiong, Y., Brym, M. & Driess, M. An isolable silanoic ester by oxygenation of a stable silylene. *J. Am. Chem. Soc.* **129,** 7268–7269 (2007).
26. Xiong, Y., Yao, S. & Driess, M. An isolable NHC-supported silanone. *J. Am. Chem. Soc.* **131,** 7562–7563 (2009).
27. Yao, S., Xiong, Y. & Driess, M. N-heterocyclic carbine (NHC)-stabilised silanechalcogenones, $NHC{\rightarrow}Si(R_2){=}E$ (E=O, S, Se, Te). *Chem. Eur. J.* **16,** 436–439 (2010).
28. Sander, W. *et al.* Dimesityldioxirane, *J. Am. Chem. Soc.* **119,** 7265–7270 (1997).
29. Gubelmann, M. H. & Williams, A. F. *Struct. Bond.*, **55,** 1–65 (1983).
30. Holmes, R. R., Day, R. O., Harland, J. J. & Holmes, J. M. Synthesis and molecular structure of hydrogen-bonded cyclic anionic silicates isoelectronic with phosphoranes. Structural principles of five-coordinated silicon. *Organometallics* **3,** 347–353 (1984).
31. Pülm, M., Willeke, R. & Tacke, R. in *Organosilicon Chemistry IV – From Molecules to Materials* (eds Auner, N. & Weis, J.) 478–488 (Wiley-VCH, 2000).
32. Sheldrick, G. M. SHELX-97 Program for crystal structure determination (Universität Göttingen, 1997).
33. Avakyan, V. G., Sidorkin, V. F., Belogolova, E. F., Guselnikov, S. L. & Gusel'nikov, L. E. AIM and ELF electronic structure/G2 and G3 π-bond energy relationship for doubly bonded silicon species, $H_2Si{=}X$ ($X{=}E^{14}H_2$, $E^{15}H$, E^{16}). *Organometallics* **25,** 6007–6013 (2006).
34. Epping, J. D., Yao, S., Karni, M., Apeloig, Y. & Driess, M. Si=X Multiple bonding with four coordinate silicon? Insights into the nature of the Si=O and Si=S double bonds in stable silanoic esters and thioesters: a combined NMR spectroscopic and computational study. *J. Am. Chem. Soc.* **132,** 5443–5455 (2010).

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Author contributions

M.D. conceived and designed the concepts and experiments. Y.X. and S.Y. carried out the experiments. S.Y. collected and solved the XRD data. R.M. and M.K. designed and carried out the quantum-chemical work. M.D. and M.K. co-wrote the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/. Correspondence and requests for materials should be addressed to M.D.