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Reactivity of a Unique Si(I)–Si(I)-Based η²-Bis(silylene) Iron Complex

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ABSTRACT: In this paper, we report the synthesis of a unique silicon(I)-based metalla-disilirane and report on its reactivity toward TMS-azide and benzophenone. Metal complexes containing disilylenes ((bis)silylenes with a Si–Si bond) are known, but direct ligation of the Si(I) centers to transition metals always generated dinuclear species. To overcome this problem, we targeted the formation of a mononuclear iron(0)–silicon(I)-based disilylene complex via templated synthesis, starting with ligation of two Si(II) centers to iron(II), followed by a two-step reduction. The DFT structure of the resulting η²-disilylene-iron complex reveals metal-to-silicon π-back donation and a delocalized three-center–two-electron (3c–2e) aromatic system. The Si(I)–Si(I) bond displays unusual but well-defined reactivity. With TMS-azide, both the initial azide adduct and the follow-up four-membered nitrene complex could be isolated. Reaction with benzophenone led to selective 1,4-addition into the Si–Si bond. This work reveals that selective reactions of Si(I)–Si(I) bonds are made possible by metal ligation.

INTRODUCTION

Transition metal silylene complexes (Scheme 1a) have attracted significant interest as they have shown interesting (electronic) structures and reactivity, giving rise to synthetic and catalytic applications that differ significantly from transition metal carbene complexes.1 Several variants of transition metal silylene complexes have been reported, varying in the oxidation state of the silicon atom and the types of substituents, and among those variants, N-heterocyclic silylenes have been studied most extensively.2

Two types of the general class of bis(silylene) compounds have been reported: (1) “bis(silylenes) with a direct Si–Si bond”, wherein the two divalent silicon atoms are adjacent to each other and are connected by a central Si–Si bond (like others in the field,3 we term these “disilylenes”); (2) “spacer-separated bis(silylenes)”, with the two divalent silicon atoms separated by a spacer.4 Driess and co-workers recently reported a ferrocene-separated bis(silylene) acting as a bidentate ligand in catalytically active mono- and dicobalt complexes (Scheme 1b).4e

We consider “disilylenes” to be particularly interesting due to the potential reactivity associated with their Si–Si bond. Compound I, with each Si center bearing an amidinate ligand (Scheme 2), was synthesized by Roeskys and co-workers,5 while Jones et al. reported a bulkier derivative thereof.6 Additionally, “disilylenes” that are stabilized by an N-heterocyclic carbene (NHC) or an intramolecular phosphine are also reported.4a,7 Targeting the synthesis of η²-coordinated Si(I)-based “disilylene” complexes seems particularly useful because the altered electronic structure and the lability of the Si–Si bond induced

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of a Mononuclear Complex 3

Scheme 3. Synthetic Procedure for the Preparation of a Mononuclear \( \eta^2 \)-Disilylene Iron Complex (This Work)

a. Known Metal Complexes from Coordination to Si(II)-based disilylene

![Diagram of known metal complexes](image)

b. This work: \( \eta^2 \)-disilylene Complex Formation by Synthesis-at-the-metal.

![Diagram of synthetic procedure](image)

Si–Si bond acting as a \( \sigma \)-acceptor moiety, while the three-membered Fe–Si–Si ring shows \( \pi \)-aromaticity. It also displays selective Si–Si bond-centered reactivity toward azide activation and ketone addition, giving access to new "spacer-separated bis(silylenes)".

**RESULTS AND DISCUSSION**

**Synthesis of 3.** The amidinate-stabilized silylene iron-halide precursor \( \mathbf{I} \), synthesized from \( \text{Fe} \{\text{N(SiMe}_3\}_2 \} \) using a literature procedure, was characterized with zero-field \( ^{57}\text{Fe} \) Mössbauer spectroscopy (Figure 1). The isomer shift \( \delta \) (0.61 m/s) and the quadrupole splitting \( \Delta E_Q \) (2.81 mm/s) are in agreement with a four-coordinated Fe(II) center. 

The \( ^1\text{H} \) NMR spectrum of diamagnetic \( \mathbf{2} \) in deuterated benzene exhibits a chemical shift for the \( \eta^1 \)-benzene fragment at \( \delta \) 5.15 ppm, which is similar to that seen for the previously reported zero-valent iron complex \( \left[ \text{SiFeSi} \right] \text{Fe-} \eta^1(C_{6}H_{5}) \) bearing a ferrocene-bridged bis(silylene) ligand \( \delta \) 5.16 ppm. The \( ^{29}\text{Si} \) NMR spectrum of \( \mathbf{2} \) exhibits two sharp singlets at \( \delta \) 45.12 and 42.45 ppm (suggesting chemically inequivalent Si centers), which are close to the reported chemical shift \( \delta \) 43.10 ppm for an \( \eta^1 \)-heterocyclic silylene iron(0) complex. Species \( \mathbf{2} \) was also examined using zero-field \( ^{59}\text{Fe} \) Mössbauer spectroscopy to confirm the oxidation state of Fe (Figure 1). Indeed, both the isomer shift \( \delta \) (0.38 m/s) and quadrupole splitting \( \Delta E_Q \) (1.53 mm/s) support reduction to Fe(0).

Single crystals of \( \mathbf{2} \) that were obtained from pentane at \( -30 \) °C proved suitable for crystallographic analysis by X-ray diffraction at room temperature; loss of crystallinity was observed at 150 K. The molecular structure (Figure 2) shows two different orientations for the Si–Cl bonds with respect to the Fe(\( \eta^1 \)-benzene) fragment (one “up” and one “down”), which explains the presence of two chemically inequivalent Si nuclei in the \( ^{29}\text{Si} \) NMR spectrum. The Si–Fe–Si angle is nearly \( 90^\circ \) (91.99°), and the intramolecular Si1···Si2 distance is 3.100(2) Å. The Si–Fe1 bond lengths are 2.162(2) Å (Si1) and 2.148(1) Å (Si2), which are significantly shorter than the corresponding bond lengths in precursor \( \mathbf{1} \) (2.445 Å) and slightly shorter than those found in the zero-valent iron silylene complex.
complexes ([((NHSi)Fe(dmpe))₂] (2.184(2) Å) and Fe(0)-[SiNSi] (2.164(15) and 2.170(13) Å)).

Further reduction of this zero-valent Fe species 2 by an excess of KC₈ at room temperature yielded the three-membered metallacyclic complex 3, featuring a direct Si−Si bond (Scheme 3). This reaction was also monitored using ¹H NMR spectroscopy, revealing quantitative conversion (see also Figure S26). The complex was characterized by multinuclear NMR spectroscopy ([H, ¹³C, and ²⁹Si]). The ¹H NMR signal of the Fe-coordinated η⁶-benzene shifts from δ 5.15 ppm in 2 to δ 5.34 ppm in 3. The ²⁹Si NMR spectrum of 3 contains only one singlet at δ 34.49 ppm, indicating formation of a symmetric molecule.

Dark red single crystals of 3 were collected after storing a pentane solution at −30 °C for 1 month. Compound 3 crystallizes in the monoclinic space group Cc, which is in line with the high degree of symmetry observed in the ¹H NMR spectrum. The Si(1)−Fe−Si(1) three-membered heterocycle forms an equilateral triangle with interatomic distances of 2.217(6) Å (Figure 3); for the Si−Si bond, this value falls in the range observed for Si−Si double bonds (2.120−2.250 Å). The isosceles Si−B−Si disilaborirane compound reported by Roesky and co-workers shows Si−Si bond length of 2.188(5) Å,⁵ while the equilateral triangular (di-t-butyl(methyl)silyl)bis(tri-t-butyldisilyl)cyclohexadienylum cation has an average Si−Si bond length of 2.217(3) Å.⁶

**Figure 3.** Molecular structure of 3 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1−Si1 and Si1−Fe1, 2.217(6); Si1−N1, 1.865(2); Si1−N2, 1.887(2); Si1−Fe1−Si1, 59.99; Fe1−Si1−Si1, 60.00.

**Electronic Structure of 3.** Given the unprecedented nature of the ferracyclic motif found in this species, the bonding of the Si(1)−Si(1) fragment to iron(0) was theoretically investigated at the T22P/OPBE level of theory using energy decomposition analysis (EDA). The lowest energy structure with C₂ᵥ symmetry is analogous to that derived from X-ray diffraction. To facilitate the EDA analysis (for symmetry reasons), the bonding of the disilene moiety to iron has been analyzed using a C₂ᵥ optimized structure, which is only 4.4 kcal·mol⁻¹ higher in energy. This small energy difference is consistent with the dynamic behavior observed in solution-state NMR spectroscopy, resulting in a single signal for the Bu substituents at nitrogen.

The Fe(η⁶-benzene) fragment has been computed in the singlet state (Fe(0)-d⁰). It has a two-electron occupied dₓz orbital (perpendicular to the Si−Fe−Si plane) and an empty dₓ²−y² orbital. The electronic structure of the Si(1)−Si(1) fragment is best described as having a Si−Si single bond with a lone pair on each silicon atom and an empty π-orbital perpendicular to that plane (Figure S31). The symmetry-adapted linear combinations of the two lone pairs on silicon donate electron density toward the Fe(η⁶-benzene) fragment, forming two (delocalized) σ-bonds of −30.3 kcal·mol⁻¹ (A1) and −74.4 kcal·mol⁻¹ (B1). The iron itself donates electron density back from the occupied dₓz orbital into an empty π-orbital formed by the two Si π orbitals (B2: −67.8 kcal·mol⁻¹), giving rise to considerable π-backbonding (Figure 4).

Figure 4. Graphical representation of the Fe-to-(Si−Si) π-back donation in 3.

To probe the resulting orbital (which is delocalized over the Si−Fe−Si three-membered ring) for aromaticity, we employed the nucleus-independent chemical shift (NICS(0/1)) approach at the B3LYP/6-11+G(d,p) level (negative value of the isotropic magnetic shielding at the center of the Fe−Si−Si three-membered ring and 1 Å perpendicularly above and below, respectively). These are found to be −47.8 and −21.4 ppm, respectively, corroborating the magnetic aromaticity. For comparison, the NICS(0/1) values at the center of the benzene ring in 3 are calculated to be −42.8 and −18.4 ppm. Similar values have been reported for other metallacycles. A more refined method by Stanger following the out-of-plane component to the shielding tensor along a trajectory orthogonal to the plane of the ring (NICSzz) has been used by Roesky et al. to assign 2π-aromaticity to their disilaborirane species. However, instead of showing the typical off-center minimum for 2π-aromatic systems, the NICS scan of 3 shows a steady and continuous increase to less negative NICSzz values over a value of 3 Å (see Figure S33), which may be caused by anisotropy of the metal center at the ring and/or by π-aromaticity.

Therefore, we resorted to the canonical molecular orbital (CMO) analysis of the NICS(0), which separates the total shieldings into contributions from canonical molecular orbitals. Indeed, there is a sizable contribution of −13.8 ppm from the Fe dₓz orbital (HOMO−5, see Figure S32), which is part of the π-framework. More importantly, the major contribution of −16.6 ppm originates from the delocalized π-orbital shown in Figure 4, substantiating the 2π-aromaticity of the Si−Fe three-membered ring in complex 3.

**Reactivity of 3.** The unligated Si(1)-based disilylene species I shows stoichiometry-dependent reactivity toward trimethylsilyl azide, forming either a silaazatriene or a silaimine
product, Roesky and co-workers described ring opening of their disilaborirane species VI with TMSN₃, forming a 1-aza-2,3-disila-4-boretidine derivative (Scheme 4).⁴⁷ We observed selective conversion of 3 with 1 equiv of TMSN₃ to give the unique azide adduct 4 after 1 h at 40 °C in benzene solution. This species was obtained as a single crystalline material by recrystallization from pentane at −30 °C. The molecular structure, as determined by X-ray diffraction, is displayed in Figure 5. It contains a planar four-membered Si₁=N₅ heterocycle resulting from the insertion of trimethylsilylnitrene in the Si−Si bond. The two Si−Fe distances are nearly identical, Si₁−Fe₁ (2.174(2) and 2.177(2) Å), and so are the Si₁−N₅ (1.770(5) and 1.767(4) Å) bond lengths. The Si−Fe σ-bonds are on average 0.2547 Å longer than the Si−B distance, while the Si−N₅ bond length is similar. The intramolecular Si−Si distance (2.412(2) Å) in 5 is shortened relative to that in 4. Apart from the X-ray crystallographic analysis, reaction monitoring and product identification have also been achieved using NMR spectroscopy. The ¹H NMR signal of the Fe-bound η⁶-benzene fragment shifts from δ 5.34 ppm (3) to δ 5.26 ppm (4) and 5.12 ppm (5), and the trimethylsilyl group in azide adduct 4 appears at δ 0.47 ppm (for 5, δ 0.39 ppm) compared to −0.08 ppm for TMSN₃. In ²⁹Si NMR, the NSiN signals for both 4 and 5 are strongly upfield-shifted (∆δ ~ 27 ppm) with respect to 3 (δ: 7.05 ppm; 5: δ 7.42 ppm), in line with the rupture of the Si−Si bond, which also disrupts the 2π-aromaticacy and leads to loss of ring current. The Si(CH₃)₃ signal appears at δ 15.41 ppm for 4 and at ~20.71 ppm for 5.

To understand the observed two-step reaction between 3 and trimethylsilylazide, we used DFT calculations to explore the reaction mechanism. The initial step involves the nucleophilic attack of the azide onto one of the Si centers, which results in induced nucleophilic character at the second Si center that subsequently attacks back onto the azide in TS₁ (Figure 6). As a result, this insertion can be considered to involve induced FLP reactivity. The energy barrier to afford Int₁ (15.4 kcal mol⁻¹) is consistent with the experimentally determined barrier (15.1 kcal mol⁻¹) for formation of 4 (Arrhenius plot, Figure 5). After forming this symmetric azide adduct, the energy barrier for the subsequent dinitrogen release (29.4 kcal mol⁻¹) is high enough to rationalize the successful isolation of 4. Finally, a Staudinger pathway, involving four-membered ring transition state TS₃, releases dinitrogen from 4 to afford product 5 (~110 kcal mol⁻¹).

The ambivalent reactivity of the Si(I) centers in the Si−Si bond of 3, able to act either as nucleophile or electrophile, was also apparent during the conversion of species 3 conversion with benzophenone. Disilylene I was previously reported to react with benzophenone to furnish selective C−O cleavage with formation of a cyclodisiloxane (Scheme 5).⁴⁸ Strikingly...
different reactivity was observed when complex 3, featuring a “protected” Si–Si bond, was exposed to benzophenone for 1 h at 80 °C. Selective formation of seven-membered ring product 6 was obtained via a formal 1,4-addition of benzophenone, displaying strongly attenuated and controlled reactivity of the Si–Si fragment in complex 3. Complex 6 was characterized in the solid state using single-crystal X-ray diffraction (Figure 7). The structure consists of a nonplanar seven-membered O–Si–Fe–Si–C–C–C ring (angle between the planes O1–C37–C44–C49 and O1–Si1–Fe1–Si2 is 7.20°). The C37–C44 bond length (1.348(5) Å) lies in between that of a typical single carbon bond and a double carbon bond (1.510–1.317 Å). The Si–Fe–Si angle (∠88.21(4)°) is larger than in species 4 and 5 because of increased steric hindrance. One of the phenyl rings has undergone ortho-silylation, concomitant with ring de-aromatization and formation of an enolate-type fragment bound via the oxygen to the second Si center. As a result, overall 1,4-addition of benzophenone has occurred, with no sign of the 1,2-C,O addition product. The 1H NMR signal for the η6-benzene fragment shifts from δ 5.34 ppm (3) to δ 5.07 ppm (6). The C–H hydrogen at the ortho-silylated position resonates at around δ 6.99 ppm according to 2D-COSY NMR spectroscopy, while the other four hydrogens of the de-aromatized ring appear in the range of 4.90–6.20 ppm. The 29Si NMR spectrum of 6 exhibits two sharp singlets at δ

Figure 6. Computed free energy profile for nitrene formation from trimethylsilyl azide and complex 3 (B3LYP-TZVP and def2-TZVP). Transient bonds in transition states are drawn as dashed lines. The inset shows the Arrhenius plot for the consumption of 3 (for details, see the Supporting Information).

Scheme 5. Synthetic Scheme for the Preparation of 6

Previous work: C–O cleavage of benzophenone by dilithylene I.

This work: 1,4-dipolar cycloaddition of benzophenone.

Figure 7. X-ray crystal structure of 6 with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of 6: Si1–Si2, 3.101(1); Si1–Fe1, 2.146(9); Si2–Fe1, 2.179(9); Si1–O1, 1.688(2); O1–C37, 1.384(3); C37–C44, 1.348(5); C44–C49, 1.503(5); C49–Si2, 1.983(4); Si1–Fe1–Si1, 88.21(4).
65.57 and δ 33.66 ppm, in accordance with the two different bonding features.

**CONCLUSIONS**

In summary, we have developed an efficient method to synthesize the first example of a mononuclear transition metal complex bearing a ligated Si(I)–Si(I) disilylene fragment, ferracyclic η₂-disilylene complex 3. The electronic structure of this species shows that the Si–Si fragment acts as a four-electron σ-donor to iron, while significant π-back donation from the iron(0) center to the silicon atoms of the disilylene moiety leads to further stabilization of the overall structure. Complex 3 shows well-defined nucleophile-induced FLP reactivity toward TMS-azole and benzophenone, leading to Si–Si bond cleavage by addition of the reagents to the Si₂ fragment, generating unexpected four- and seven-membered ring structures. Expanding this unique reactivity to other small molecules is currently being explored within our groups.

**EXPERIMENTAL SECTION**

**Materials and Methods.** Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques on a Vigor glovebox maintained at or below 1 ppm of O₂ and H₂O. All new metal complexes were prepared and handled in the glovebox under a N₂ atmosphere. Anhydrous FeCl₃ (98%) was purchased from Strem Chemicals. PhC(N′Bu)₂SiHCl₂,²⁸ LiN(SiMe₃)₃(µ-Et)_₂,²⁸ Fe(N(SiMe₃)₃)_₂,²⁹ and complex 1 (FeCl₂[PhC(N′Bu)₂SiCl₂])₃⁰ were synthesized according to reported procedures. Other reagents were purchased from J&K Chemical and SCRCl. Glassware was dried at 150 °C overnight. Celite and molecular sieves were dried at 200 °C under vacuum. Benzene, pentane, hexanes, and diethyl ether were degassed with nitrogen, dried over activated molecular sieves, and kept over 4 Å molecular sieves in a N₂ atmosphere. Anhydrous FeCl₃ (98%) was purchased from Sigma-Aldrich and a small (m4) grid of quartz crystals was used for X-ray quality crystals. A solution of Fe(N(SiMe₃)₃)_2 (110 mg, 0.153 mmol) in benzene (5 mL) was added dropwise to a solution of KC₆ (53.7 mg, 0.398 mmol) in THF (5 mL) in a vial while stirring. The color of the reaction mixture turned from yellow to dark-red-brown. After stirring for 12 h, volatile materials were removed under vacuum and compound 2 was extracted with pentane solution. The solid was crystallized in pentane solution in a −30 °C freezer for 2 days, and only crystalline material was used for subsequent reactions (yield: 40 mg, 40%).¹¹ "H NMR (500 MHz, benzene-d₆, ppm) δ 8.04 (m, 1H, Ar-H), 7.26 (d, 1H, Ar-H), 7.09 (d, 1H, Ar-H), 7.00−6.9 (m, 6H, Ar-H), 6.86 (t, 1H, Ar-H), 5.15 (s, 6H, benzene-H), 1.52 (s, 18H, N′Bu-H), 1.31 (s, 18H, N′Bu-H).¹¹ "C NMR (126 MHz, benzene-d₆, ppm) δ 173.84 (NCN), 132.55, 132.44, 129.80, 129.70, 129.47, 129.24, 129.02, 128.84, 125.73, 125.63, 123.36 (132.55−127.36: Ph), 80.23 (Fe-C benzene), 54.24 (CMe₃), 53.64 (CMe₃), 31.86 (CH₃), 31.39 (CH₃).²¹ "Ni NMR (99 MHz, benzene-d₆, ppm) δ 45.12, 42.45. UV−Vis (THF, λ (nm) (ε, M⁻¹·cm⁻¹)): 410 (1604). IR-ATR (cm⁻¹): 3059 (VW), 2970 (w), 2928 (VW), 2868 (VW), 1640 (VW), 1577 (VW), 1519 (VW), 1472 (m), 1443 (m), 1415.63 (S), 1389 (S), 1361 (S), 1272 (m), 1203 (S), 1085 (m), 1022 (S), 972 (VW), 926 (W), 882 (W), 789 (W), 753 (S), 726 (W), 708 (S), 636 (m), 617 (S). Anal. calc. for C₃₆H₃₆Fe₂N₂Si₆: C, 59.74; H, 7.24; N, 7.74. Found: C, 57.43; H, 7.29; N, 7.77. Note: Due to the formation of silicon carbide, the carbon values in the elemental analyses were consistently too low for all the disilylene Fe compounds reported in this paper. 

**X-ray Crystallography.** Crystals were coated with Paratone-N oil and mounted on a Bruker D8 Venture diffractometer equipped with an APEX-II CCD diffractometer. The crystal was kept at 150 K during data collection. Using Olex2, an APEX-II CCD diffractometer. The crystal was kept at 150 K during and mounted on a Bruker D8 Venture diffractometer equipped with a 300K X-ray generator. Elemental analysis was performed by the Analytical Laboratory of the Thermo Scientific Nicolet iS5 FTIR, and signal strength is given relative to the iron metal at ambient temperature. The UV−Vis spectrum was recorded using a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by optical fiber using 1 cm matched quartz cuvettes at room temperature. Elemental analysis was performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry (CAS).

Crystallization and data collection. Crystals were soaked in a 10% aqueous solution of MeOH for 15 min and then slowly cooled to 150 K. X-ray quality crystals were obtained within 2−3 days.

**Computational Details.** Geometries were fully optimized as minima or transition states using the Turbomole program package.¹³

11730

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benzene), 3.68 (CMe), 32.04 (CH₃), −0.08 (Si(CH₃)₃), −1.23 (N,Si(CH₃)₃). ²⁰Si NMR (99 MHz, benzene-d₆, ppm) δ 15.41, 7.05. UV–Vis (THF, λ (nm) (ε, M⁻¹·cm⁻¹)): 485 (2343). IR-ATR (cm⁻¹): 3048 (VW), 2962 (W), 2033 (W), 1523 (VW), 1472 (W), 1422 (S), 1391 (W), 1358 (W), 1274 (W), 1237 (W), 1207 (S), 1148 (m), 1078 (W), 1021 (W), 989 (m), 966 (W), 923 (W), 832 (S), 789 (W), 751 (S), 724 (W), 704 (S), 641 (W), 609 (W). Elemental analysis of this species did not yield satisfactory results, which is attributed to the demonstrated thermal instability of this complex, leading to “decomposition” to form species 5.

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CCDC 2157512–2157516 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01369.

General information; synthetic procedures of new compounds, including NMR, IR, and UV–Vis spectra; reaction of 3 with TMS-azide followed by NMR; EDA and DFT calculations; single-crystal X-ray data diffrac tion (PDF)
Computational details (ZIP)

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Z.H. and L.L. contributed equally to this work. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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