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A Stable, Highly Fluorescent Vinylogous *β*-Diketonate Silicon Complex

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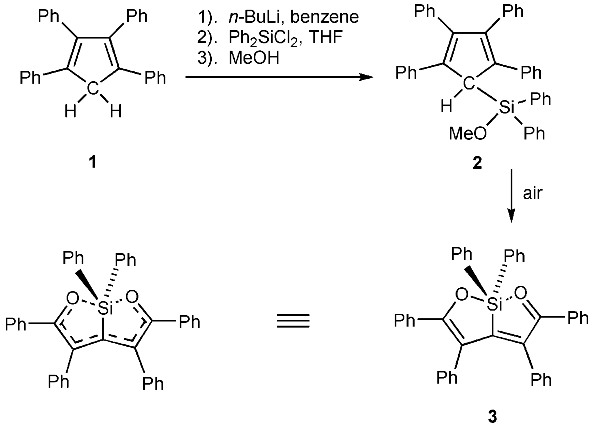
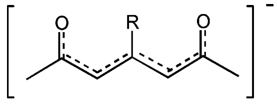
Summary: We report the synthesis of a novel, highly fluorescent pentacoordinate silicon compound which is apparently the first example of a vinylogous β-diketonate complex. The compound was generated by slow, solid-state oxidation of a methoxysilane derivative of tetraphenylcyclopentadiene.

We report the synthesis of a novel pentacoordinate silicon compound, **3**, which is apparently the first example of a vinylogous *β*-diketonate complex. This compound was generated by slow solid-state oxidation from the methoxysilane **2**, obtained from tetraphenylcyclopentadiene (**1**) (Scheme 1).[1,2] In **3** the OC=CC=CC=O moiety serves as a tridentate ligand. The corresponding unbridged anions **4** are known as their sodium salts,[3] but no chelate complexes of anions of this type have been reported. However, Arduengo and co-workers have prepared several 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-triene complexes containing a diketoamine ligand isoelectronic with the vinylogous *β*-diketonate ligand in **3**.[4] Bridging from the central carbon atom in **3** to the silicon atom is evidently necessary, to transform what would otherwise be an unstable eight-membered chelate ring into two five-membered rings.

Scheme 1. Solid-State Transformation of the Methoxysilane Derivative 2 to a Pentacoordinate Silicon Complex





4, R = CH_3, OCH_3

Compound **3** forms pink crystals stable both in air and moisture and exhibits a bright orange fluorescence under white light.[2] The X-ray crystal structure of **3** is shown in Figure 1.[5] The structure is remarkably analogous to those of typical *β*-diketonate complexes.

The molecule is bilaterally symmetrical, consistent with electron delocalization over the eight-membered ring. The ring C−C distances (1.414, 1.394 Å) are within the range of typical *β*-diketonates of both transition and main-group metals; however, the C−O distances (1.309 Å) are relatively elongated.[6] This can be attributed to the greater strength of Si−O bonds over typical metal oxide bonds, which results in the oxygen atoms being pulled closer to the silicon center. The ligands are disposed about silicon in a slightly distorted trigonal pyramidal arrangement. On the basis of the dihedral angle method,[7] the trigonal-pyramidal distortion of **3** is 16.0% along the Berry pseudorotation pathway toward the square pyramid.[8]

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[2] Synthesis of **3**: a solution of **2** (1.0 g, 1.72 mmol) in $CHCl_3$ (5 mL) was added to a 1000 mL Erlenmeyer flask, and the solvent was allowed to evaporate slowly. A film of **2** was formed on the glass wall. Slow oxidation of a colorless film of **2** in the air after 2 months yielded a pink film containing 8% of **3** and 90% unreacted **2**. When the film of **2** was first pretreated with dilute aqueous NaOH and then dilute aqueous HCl, the yield of **3** was 20% after exposure to air for 1 month. The film was dissolved in toluene (50 mL). After separation by preparative GPC (toluene elution), pink crystals of **3** were obtained in 15% yield. Anal. Calcd for $C_{41}H_{30}SiO_2$: C, 84.54; H, 5.15. Found: C, 84.12; H, 5.40. ^1H NMR (300.133 MHz, $CDCl_3$): δ 8.06−8.02 (m, 4H), 7.51 (d, 4H), 7.39−7.31 (m, 8H), 7.19 (t, 4H), 6.95 (t, 2H), 6.82 (t, 4H), 6.64 (d, 4H). ^{13}C NMR (125.710 MHz, $CDCl_3$): δ 184.43, 176.71, 136.88, 136.23, 136.03, 134.89, 131.41, 131.02, 130.33, 129.105, 128.15, 127.68, 127.64, 127.36, 125.92. ^{29}Si NMR (99.314 MHz, $CDCl_3$): δ −70.521. UV−Vis (hexane): 526 nm ($\epsilon = 2.162 \times 10^4$). IR (film; cm^{-1}): 3056.6 (m), 3020.9 (w), 2958.2 (w), 2927.4 (w), 2853.1 (w), 1959.3 (w), 1895.6 (w), 1813.2 (w), 1598.7 (m), 1543.7 (m), 1475.2 (m), 1377.8 (m), 1207.2 (s), 1177.3 (s), 1105.9 (m), 1066.4 (m), 1025 (m), 754.9 (m), 697.1 (s), 581.4 (w), 508.1 (m). MS (MALDI, anthracene/C_{60} matrix; *m/z*): 582.2 (M^+). Mp: 197−199 °C.

[3] Assad, F. M.; Becher, J. *Synthesis* **1983**, 1025−1027.

[4] Arduengo, A. J., III; Steward, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 627−647.

[5] Crystal structure analysis of **3**: Brüker Smart CCD-1000 diffractometer, $T = 173(2)$ K, Mo Kα radiation ($\lambda = 0.710\,73$ Å), ω scans, $C_{41}H_{30}O_2Si$, $M_r = 582.74$, monoclinic, space group $C2/c$, $a = 23.5233(15)$ Å, $b = 11.0132(8)$ Å, $c = 15.5384(10)$ Å, $\beta = 130.891(1)°$, $V = 3043.1(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.272$ g/cm^{-3}, $\mu = 0.114$ mm^{-1}, $F(000) = 1224$, θ range 2.18−25.00°, 7417 reflections collected, 2549 (R(int) = 0.0261) unique, maximum/minimum transmission 0.9667/0.9559, no. of data/restraints/parameters 2549/0/201, R1 = 0.0421, wR2 = 0.128 87. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-167495. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

[6] See for example: Bancroft, G. M.; Davies, B. W.; Payne, N. C.; Sham, T. K. *Dalton Trans.: Inorg. Chem.* **1975**, *11*, 973−8 and Campo, J. A.; Cano, M.; Heras, J. V.; Lagunas, M. C.; Perles, J.; Pinilla, E.; Torres, M. R. *Helv. Chem. Acta* **2001**, *84*, 2316−2329.

[7] Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326.

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10.1021/om061163k CCC: $37.00

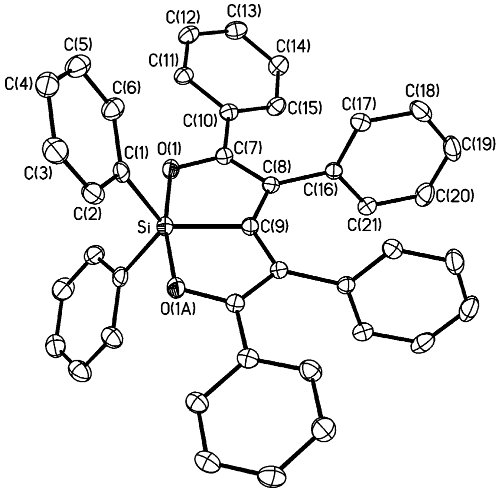
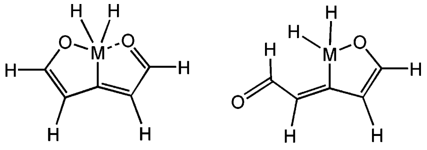


Figure 1. Thermal ellipsoid (40%) diagram of structure **3**. Selected bond lengths (Å) and angles (deg): Si−O(1) = 1.8661(13), Si−C(9) = 1.882(3), Si−C(1) = 1.898(2), O(1)−C(7) = 1.309(2), C(7)−C(8) = 1.414(3), C(7)−C(10) = 1.475(3), C(8)−C(9) = 1.394(2), C(8)−C(16) = 1.492(3); O(1)−Si−O(1A) = 168.78(9), O(1)−Si−C(9) = 84.39(4), O(1)−Si−C(1) = 93.20(7), C(9)−Si−C(1) = 120.76(6), C(1A)−Si−C(1) = 118.48(1), C(7)−O(1)−Si = 113.79(12), O(1)−C(7)−C(8) = 117.46(17), C(9)−C(8)−C(7) = 110.84(18), C(8)−C(9)−C(8A) = 133.1(2), C(8)−C(9)−Si = 113.43(12).



5 **6**

M = B$^-$, Al$^-$, C, Si

Figure 2. Related pentacoordinate and tetracoordinate structures.

The infrared spectrum of **3** also resembles that of diketonate complexes. Two strong bands are found at 1599 and 1544 cm^{-1} and two medium bands at 1475 and 1388 cm^{-1}. The same pattern is observed for many metal β-diketonates.[9]

Although pentacoordinate pentalene-like structures such as **3** were previously unknown, in 1999 Minyaev and Starikov carried out MO calculations on these potential molecules with boron, carbon, aluminum, and silicon atoms at the central positions (Figure 2) using ab initio RHF/6-31G** and MP2-(full)/6-31** methods.[10] The calculated results predicted that silicon should form the most stable pentacoordinated structure among all four elements. Moreover, the pentacoordinated structure **5** (M = Si) was predicted to be 8.2 (RHF) and 13.5 kcal/mol (MP2) more favorable energetically than the corresponding tetracoordinated structure **6**.

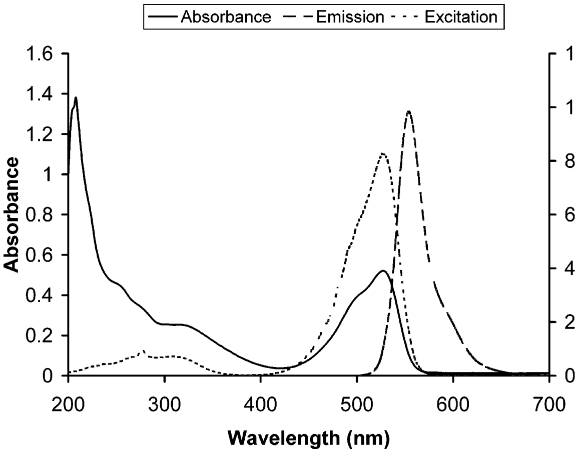


Figure 3. Absorption, excitation, and emission spectra of **3**.

The ^{29}Si NMR resonance of **3**, at −70.5 ppm, is greatly shielded compared to that of the precursor **2**, −9.7 ppm. Such upfield shifts are common in many pentacoordinate silicon complexes. The large chemical shift difference of 60.8 ppm between **3** and **2** is consistent with strong O−Si coordination.[11] With an increase in temperature from −40 to 60 °C, the ^{29}Si chemical shift of **3** in toluene-d_8 moves downfield from −68.76 to −66.73 ppm ($\Delta\delta = +2.1$ ppm); concomitantly, the ^{29}Si chemical shift of TMS decreases from 0.00 to −0.43 ppm, indicating the relative chemical shift change $\Delta\delta = +2.5$ ppm for **3**. Thus, the geometry and the degree of coordination in **3** are not strongly affected by temperature variation.[11] The ^{13}C NMR resonances for the carbonyl carbons of **3** are somewhat shielded, at δ 184.4. Electron delocalization into the five-membered rings may cause this upfield shift.[12]

Absorption, excitation, and emission spectra of **3** in hexane are shown in Figure 3. The electronic spectrum of **3** in hexane solution has an intense absorption band at 526 nm (ϵ_{max} 2.16 × 10^4), which is responsible for the pink color. Preliminary calculations using TD/B3LYP/6-311+G(d,p)//B3LYP/6-31G* show that this absorption results from a $\pi \rightarrow \pi^*$ transition of the conjugated OC=CC=CC=O moiety in **3**, with little contribution from the Si atom. Compound **3** exhibits a bright orange fluorescence. The emission spectrum displays a peak at 554 nm, with a fluorescence quantum yield of 0.13.[13,14] The Si atom in **3** serves as a bridge to fix the conjugated OC=CC=CC=O chain into two planar fused rings and thus may enhance the luminescence of the chromophore.[15]

3 is unreactive toward both HCl(aq) and NaOH(aq). The fluorescence and color of **3** faded slowly over weeks in dilute acetone solution. The chemical properties of **3**, and the remarkable rearrangement leading to its formation, are still under investigation. We have also observed the appearance of a similar bright orange fluorescence from the solid-state oxidation of germanium analogues of **2** and are looking into this further as well.

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Note Added after ASAP Publication. In the version of this paper published on the Web on February 10, 2007, the list of author names was incomplete. This list of names that now appears is complete.

Supporting Information Available: A table of dihedral angles for **3** and a CIF file for the crystal structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The quantum yield for emission was measured in dilute hexane solution in which the UV absorbance was between 0.05 and 0.01, using Rhodamine B as a standard with excitation at 366 nm, and was calculated using $\Phi_s = \Phi_r(A_rF_s/A_sF_r)(n_{s2}/n_{r2})$.

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