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Novel silicon bisalkoxy complexes with a pseudo-atrane structure. Synthesis and molecular structures of 2,6-di(2-hydroxy(2-adamantyl))ethylpyridine and 2,6-di(2-oxy(2-adamantylidine))ethylpyridine dimethylsilicon

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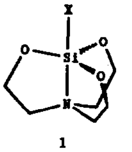
Abstract

Reaction of 2,6-lutidine with 2 equivalents of ^{n}BuLi followed by addition of 2-adamantanone affords the doubly functionalized 2,6-di-(2-oxy(2-adamantylidine))ethylpyridine (**2a**). Reaction of **2a** with Me_2SiCl_2 gives the pseudo-pentacoordinate 2,6-di-(2-oxy(2-adamantylidine))-ethylpyridinedimethylsilicon (**4**). The structures of **2a** and **4** have been determined by an X-ray diffraction study.

Key words: Silicon; Pyridine

1. Introduction

Oligo- and poly-alcohols are known to form strong complexes with silicon [1] and so are of interest for the preparation of oligo- and polysiloxanes. The silyl derivatives of triethanolamine (TEA) constitute a special case of silicon alkoxides, since in a number of cases they contain hypercoordinate silicon [2–5]. These so-called silatranes **1** possess a characteristic five-coordinate trigonal bipyramidal (TBP) structure in which the basic nitrogen atom of the triethanolamine ligand is usually axially coordinated to silicon (Fig. 1).



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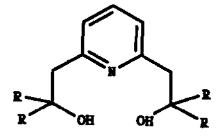

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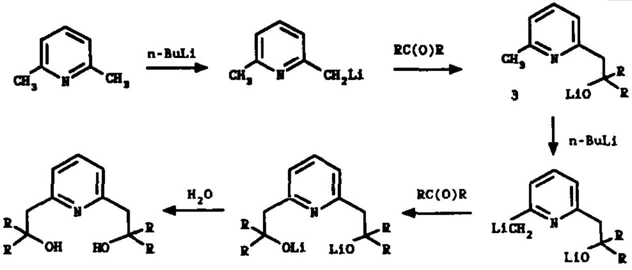
Fig. 1.

In extension of our research concerning the chemistry of bishydroxyethyl functionalized pyridines **2** as model systems for zinc alcohol dehydrogenase [6a], carboxypeptidase [6b] and specific ligand systems for the preparation of new classes of transition-metal alkoxo complexes [8–11], we thought that compounds **2** [6,7] might be suitable systems for the preparation of interesting new types of silicon alkoxides [12*].



Scheme 1.

2. Results and discussion

The synthesis of ligand **2a** was carried out analogously to that used for other members of this family

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* Reference number with asterisk indicates a note in the list of references.

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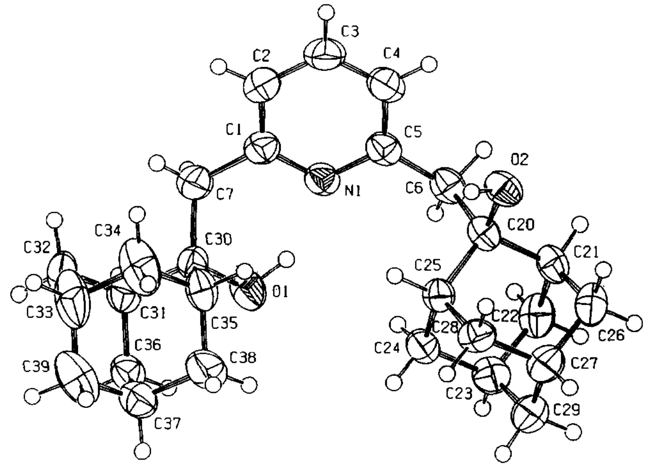
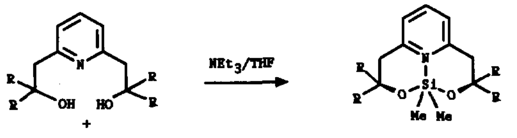


Fig. 2. Thermal motion ellipsoid (50% probability) plot of **2a**. Selected bond distances (Å) and angles (°) H(1)...N(1) = 1.79(2), O(1)–H(1) = 0.95(2), O(1) ··· H(2) = 2.02(2), O(1) ··· H(1) ··· N(1) = 153(2), O(2)–H(2) ··· O(1) = 155(2).

(Scheme 1) [13]. Reaction of 2,6-lutidine with ^{n}BuLi in ether proceeded smoothly with formation of the monolithium salt [6a]. Quenching of this Li-salt with adamantanone gave, we assume, the corresponding Li-alkoxo complex **3a** and treatment *in situ* of the reaction mixture with ^{n}BuLi and subsequent reaction with the same ketone gave **2a** in 51% yield after aqueous work-up.

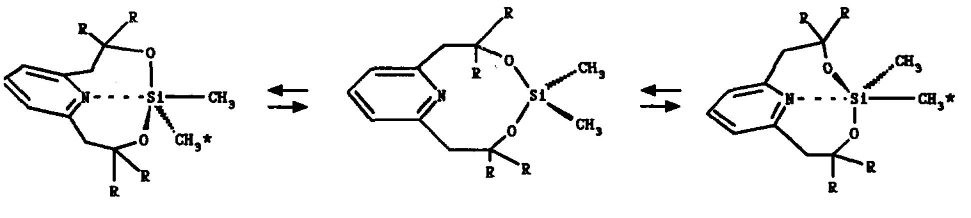
The molecular structure of **2a** was determined by X-ray diffraction methods and is illustrated in Fig. 2. The molecule possesses an open conformation in the solid state, as a result of extensive intramolecular hydrogen bonding of the hydroxyl group with the pyridine N-atom and intermolecular hydrogen bonding between two neighbouring –OH moieties (H(1) ··· N(1) = 1.79(2), O(1) ··· H(2) = 2.02(2), O(1)–H(1) ··· N(1) = 153(1), O(2) ··· H(2) ··· O(1) = 155(1)°). Because of this combination of interactions, a linear polymeric arrangement is attained running in the crystallographic *a*-direction. However, this polymeric arrangement is a feature of the solid state and is not found in solution, as was shown by ^{1}H NMR spectroscopy in $CDCl_3$. Analogous intramolecular hydrogen bonding has been found also in the acetone and chiral *l*-menthone derivative **2b** [6c].

Reaction of **2a** with Cl_2SiMe_2 in THF in presence of NEt_3 led to the quantitative formation of the bis alkoxo silicon derivative **4**, which to the best of our knowledge, is the first example of a silatrane-type complex with a pyridine-based skeleton. The identity of **4** was established from analytical and spectral data. At ambient temperature, the ^{1}H NMR signals of the two methyl groups of the $-SiMe_2$ unit are equivalent (0.209 ppm) suggesting at first sight that there is symmetric coordination of the silicon atom in the complex. Moreover, over the temperature range −20 to 25°C, no splitting of the methyl signals was observed.



However, upon cooling to −30°C the signals from both the lutidyl methylene groups and the two silane methyl moieties become broader, and eventually at −55°C split into two discrete singlets for the $Si-CH_3$ fragment (0.026 and 0.335 ppm) and a set of two doublets (2.806, 2.852 and 3.336, 3.380 ppm) due to geminal coupling (${}^{2}J(H_aH_b) = 13.2$ Hz) for the two non-equivalent methylene protons of the 2,6-lutidyl fragment. These observations can be explained by postulating either an asymmetrically substituted, probably pentacoordinated, silicon that undergoes a flipping-like process at elevated temperatures or a distorted tetrahedrally coordinated Si-complex, possibly with a weak N–Si interaction due to the close proximity of the Si-atom. This proximity may be imposed by the geometrical constraints of the ligand system which force the nitrogen atom over towards the silicon atom. In eqn. (2), the fluxional behavior (ring flip of the pyridine moiety) of the molecule is schematically illustrated.

The non-symmetrical (frozen) coordination suggested by the low temperature ^{1}H NMR data is reinforced by an X-ray diffraction study of **4** (Fig. 3). The solid state structure shows one of the conformers that may be present in solution at ambient temperature. The molecule possesses only one symmetry element. A mirror plane intersects C(3)–N ··· Si. The Si-atom is principally four-coordinate, while the direct coordina-



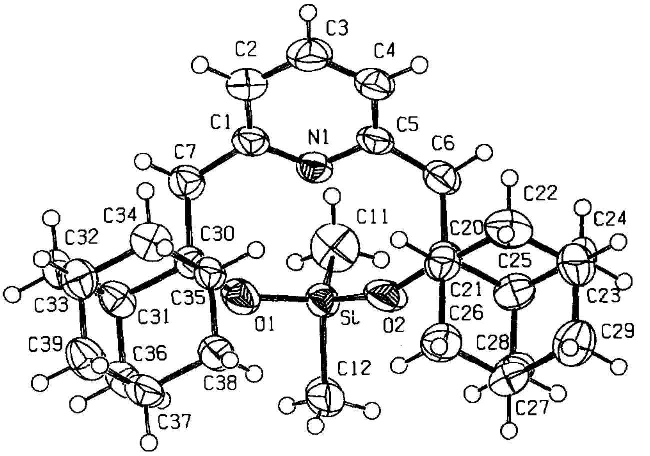


Fig. 3. Thermal motion ellipsoid (50% probability) plot of **4**. Selected bond distances (Å) and angles (°) Si–O(1) = 1.623(2), Si–O(2) = 1.610(2), Si ··· N = 2.727(2), O(2)–Si–O(1) = 116.15(12), O(1)–Si–C(11) = 112.76(15), C(12)–Si–C(11) = 106.50(16), O(2)–Si–C(11) = 116.56(17).

tion sphere is formed by two methyl ligands and two alkoxomoieties (O(2)–Si–O(1) = 116.15(12), O(1)–Si–C(11) = 112.76(15), C(12)–Si–C(11) = 106.50(16), O(2)–Si–C(11) = 116.56(17)°). At a longer distance of 2.727(2) Å, the pyridine nitrogen atom approaches the $(RO)_2Si(CH_3)_2$ fragment with an angle N(1)...Si–C12 = 172.08(12)°. The silicon atom is not perfectly coplanar with the pyridine moiety, lying 0.769(12) Å below the plane defined by the pyridine ring.

The distortion from the idealized tetrahedral coordination geometry may arise either from the presence of a (weak) N → Si interaction or from steric effects. The latter may also account for the small differences in $Si{-}CH_3$ bond lengths (Si–C(11) = 1.854(3), Si–C(12) = 1.871(3)A).

The results of ^{27}Si NMR studies in $CDCl_3$, however, suggest the existence of a definite interaction. The effect of the pyridine ring on the chemical shift of the Si-atom seems to be quite strong, causing an upfield shift of roughly 20 ppm. The symmetrically substituted $(RO)_2Si(CH_3)_2$ exhibits a chemical shift of Si of −21.9 ppm relative to $Si(CH_3)_4$, whereas in the parent system, the Si-signal is found at −41.6 ppm.

Although long Si–N bonds are known for these systems [1–5] (up to 3.19 Å [4e]) the distance in the parent case does not unambiguously justify the possibility that there is a real bond, as in ordinary silatranes [1,4a,b], which usually possess Si–N bond distances of approximately 1.7–2.2 Å. Therefore, if any interaction is present in this case, it must be considered to be weak.

Further work on the coordination chemistry of ligand **2a** and other members of this family is in progress.

3. Experimental section

All reactions were carried out under nitrogen. Solvents were dried and distilled according to standard procedures prior to use. Adamantanone, ^nBuLi (solution in hexanes) and 2,6-lutidine were purchased from Aldrich and used as received. ^1H NMR (300 MHz) and ^{13}C NMR (75.43 MHz) spectra were recorded on a Varian spectrometer. Infrared data were obtained from a Perkin-Elmer 781 spectrometer. Mass spectra were obtained on an AEI-MS9 mass spectrometer at 70 eV.

3.1. Preparation of ***2a***

To a cold (−50°C), stirred solution of 5.0 g (47 mmol) of 2,6-lutidine in 150 ml of THF was added 50 mmol of a ^nBuLi solution in hexane (1.6 N). The mixture was allowed to warm to room temperature then cooled to −80°C, and 2-adamantanone (7.07 g, 47 mmol) was added slowly dropwise. The mixture was stirred for 1 h at −80°C then allowed to warm to room temperature. Stirring was continued for 1.5 h, after which the mixture was cooled to −40°C and a second equivalent of ^nBuLi was added. The mixture was warmed and stirred for 1.5 h then the second portion of 2-adamantanone was introduced. The mixture was warmed gradually to room temperature then stirred for 20 h. Aqueous NH_4Cl (50 ml, 1.3 M) solution was added slowly, the THF was evaporated off *in vacuo*, and the residual aqueous layer was extracted with several portions of CH_2Cl_2. The organic extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent left an off-white residue, which was washed with Et_2O (2 × 25 ml), then recrystallized from boiling EtOH (150 ml); yield 8.25 g (51%) of white crystals; m.p. 199–200°C. Anal. Found: C, 79.26; H, 8.97; N, 3.37. $C_{27}H_{37}NO_2$ calc.: C, 79.56; H, 9.15; N, 3.44%. ^1H NMR ($CDCl_3$): 1.40–2.22 (adamantyl, 9H); 3.12 (s, 4H); 4.21 (s, 2H); 7.08 (d, $^3J(HH)$ = 14.5 Hz, 2H); 7.56 (t, $^3J(HH)$ = 14.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): 158.23 (s); 136.81 (d); 122.46 (d); 75.35 (t); 38.31 (t); 37.14 (d); 34.57 (t); 32.71 (t); 27.30 (d); 27.24 (d). IR (KBr): 3449s, 2902s, 1610m, 1453s cm^{-1}. Mass spectrum: (m/e^+) 257, 239, 238, 108. HRMS: (m/e^+) 407.282 (calcd. 407.282 for $C_{27}H_{37}NO_2$).

3.2. Preparation of ***4***

To a cold (0°C) stirred solution of **2a** (4.1 g, 10 mmol) in 150 ml of CH_2Cl_2 was added a mixture of Cl_2SiMe_2 (2.96 g, 15 mmol) and NEt_3 (4.9 ml, 3.5 g, 35 mmol). The mixture was allowed to warm to room temperature and the stirring continued for 1.5 h, and then refluxed for 20 h. The mixture was then cooled to room temperature, the solvent was removed *in vacuo*, and the residue was washed with saturated aqueous

TABLE 1. Crystal data and structural analysis results

	2a	**4**
Formula	$C_{27}H_{37}NO_2$	$C_{29}H_{41}NO_2Si$
MW	407.60	463.74
Space group	$P2_1/c$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
Z	4	4
a (A)	6.6646(3)	11.4088(6)
b (A)	23.929(1)	12.7546(6)
c (A)	13.8615(5)	20.3610(9)
β (°)	92.382(1)	121.991(4)
V (A^3)	2206.8(2)	2512.9(2)
$D_{calc.}$ (g cm^{-3})	1.227	1.226
μ (cm^{-1})	0.7	1.1
Radiation (Mo Kα, A)	0.71073	0.71073
T (K)	295	295
R_f	0.048	0.060
R_w	0.048	0.050

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

bicarbonate. The solid was redissolved in $CHCl_3$ and the solution dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel with CH_2Cl_2 as eluent. Evaporation of the eluate left a colorless solid which was recrystallized from boiling hexane to yield 63% of plate-like crystals, m.p. 225–226°C. Anal. Found: C, 75.22; H, 9.01; N, 3.13. $C_{29}H_{41}NO_2Si$ calc.: C, 75.11; H, 8.91; N, 3.02% ^{1}H NMR ($CDCl_3$): 0.209 (s, 6H); 1.37 (s); 1.63 (s); 1.72 (s); 1.85 (m); 2.32 (d, adamantyl signals); 3.08 (s, 4H); 6.92 (d, ^3J(HH) = 15.3 Hz, 2H); 7.46 (t, ^3J(HH) = 15.3 Hz, 1H). ^{13}C NMR ($CDCl_3$); 156.78 (s); 135.81 (s); 120.66 (s); 80.18 (t); 41.52 (t); 38.77 (t); 37.96 (d); 34.54 (t); 33.27 (t); 27.11 (d); 4.828 (q). ^{27}Si NMR ($CDCl_3$): −41.9 (s). IR (KBr): 3434m, 2899s, 1088s, 1450s cm^{-1}. Mass spectrum: (m/e^+) 449, 448, 313, 314. HRMS: (m/e^+) 463.292 (calcd. 463.291 for $C_{29}H_{41}NO_2Si$).

3.3. X-Ray data collection and refinement

All calculations were performed on a DEC-5000 system. Scattering factors were taken from Cromer and Mann [14] and data were corrected for anomalous dispersion [15]. Illustrations were drawn by use of PLATON [16]. Details of the data collection and refinement are listed in Table 1.

X-Ray data for **2a**. $C_{27}H_{37}NO_2$ were collected on an Enraf-Nonius CAD 4T/Rotating Anode (Mo Kα, monochromator) for a transparent colorless crystal. Unit cell dimensions were derived from the SET4 setting angles of 25 reflections in the range $10 < \theta < 14$°. A total of 10,785 reflections were scanned and averaged in a unique set of 3293 reflections with ($I > 2.5\sigma(I)$). No decay was observed during data collection. The structure was solved with DIRDIF92/ORIENT [17] and refined on F by full-matrix least-squares techniques (SHELX76) [18] to a final $R = 0.048$. Hydrogen atoms were located from a difference Fourier map and their positional and individual isotropic parameters refined. Final atomic coordinates for the non-hydrogen atoms are listed in Table 2.

X-Ray data for **4**. $C_{29}H_{41}NO_2Si$ were collected on an Enraf-Nonius CAD 4T/Rotating Anode (Mo Kα, monochromator) for a transparent colorless crystal cut from a plate. Unit cell dimensions were derived from the SET4 setting angles of 25 reflections in the range $14 < \theta < 18$°. A total of 12,086 reflections were scanned and averaged in a unique set of 3502 reflections with ($I > 2.5\sigma(I)$). No decay was observed during data collection. The structure was solved by direct methods (SHELXS-86/TREF) [19] and refined on F by full-matrix least-squares techniques (SHELX76) [18] to a final $R = 0.060$. H-atoms were taken into account at calculated positions (C–H = 0.98 Å) with three common isotropic

TABLE 2. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **2a**

Atom	x	y	z	U_{eq} (Å^2) [a]
O(1)	0.8230(2)	0.34791(5)	0.11216(10)	0.0543(5)
O(2)	0.01812(18)	0.45203(6)	0.14145(9)	0.0491(4)
N(1)	0.5115(2)	0.39840(6)	0.01968(10)	0.0452(5)
C(1)	0.5275(3)	0.36216(8)	−0.05378(13)	0.0496(6)
C(2)	0.3835(3)	0.35985(10)	−0.12943(15)	0.0621(8)
C(3)	0.2244(3)	0.39634(10)	−0.13104(15)	0.0623(8)
C(4)	0.2097(3)	0.43379(9)	−0.05708(14)	0.0534(7)
C(5)	0.3550(3)	0.43365(7)	0.01875(12)	0.0430(5)
C(6)	0.3521(3)	0.47392(8)	0.10144(14)	0.0468(6)
C(7)	0.7161(3)	0.32681(11)	−0.05065(15)	0.0612(8)
C(20)	0.2196(2)	0.45674(7)	0.18383(12)	0.0389(5)
C(21)	0.2162(3)	0.50256(7)	0.26131(14)	0.0464(6)
C(22)	0.4235(3)	0.50932(8)	0.31400(17)	0.0540(7)
C(23)	0.4845(3)	0.45409(8)	0.36329(15)	0.0537(7)
C(24)	0.4922(3)	0.40854(9)	0.28694(15)	0.0501(7)
C(25)	0.2851(3)	0.40189(7)	0.23426(12)	0.0398(5)
C(26)	0.0635(3)	0.48733(9)	0.33482(16)	0.0542(7)
C(27)	0.1247(3)	0.43246(8)	0.38404(14)	0.0526(7)
C(28)	0.1331(3)	0.38626(8)	0.30853(14)	0.0482(6)
C(29)	0.3317(3)	0.43875(10)	0.43615(16)	0.0594(8)
C(30)	0.7811(2)	0.30194(7)	0.04807(12)	0.0395(5)
C(31)	0.9762(3)	0.26811(8)	0.04534(14)	0.0495(6)
C(32)	0.9439(4)	0.21570(12)	−0.01655(18)	0.0760(10)
C(33)	0.7842(4)	0.17932(11)	0.0254(2)	0.0862(10)
C(34)	0.5876(4)	0.21232(11)	0.0265(3)	0.0833(12)
C(35)	0.6218(3)	0.26427(7)	0.08905(15)	0.0475(6)
C(36)	1.0463(3)	0.25013(9)	0.14705(15)	0.0539(7)
C(37)	0.8885(3)	0.21366(9)	0.18882(17)	0.0636(8)
C(38)	0.6922(4)	0.24703(11)	0.19180(17)	0.0674(9)
C(39)	0.8537(4)	0.16190(10)	0.1274(2)	0.0864(12)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalized U.

TABLE 3. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **4**

Atom	x	y	z	U_{eq} ($Å^2$) [a]
Si	0.12806(7)	0.29510(6)	0.29030(4)	0.0422(2)
O(1)	0.07880(17)	0.31210(16)	0.35112(10)	0.0568(7)
O(2)	0.23971(18)	0.20360(14)	0.31119(13)	0.0702(8)
N(1)	0.3644(2)	0.35586(15)	0.42272(13)	0.0428(7)
C(1)	0.3599(3)	0.39058(18)	0.48340(16)	0.0431(9)
C(2)	0.4763(3)	0.3934(2)	0.55693(17)	0.0550(11)
C(3)	0.5992(3)	0.3574(2)	0.5685(19)	0.0649(11)
C(4)	0.6028(3)	0.3180(2)	0.50664(18)	0.0600(10)
C(5)	0.4833(3)	0.31834(19)	0.43420(16)	0.0459(9)
C(6)	0.4720(3)	0.2737(2)	0.36302(17)	0.0502(10)
C(7)	0.2173(3)	0.41754(19)	0.46463(16)	0.0456(9)
C(11)	0.1575(4)	0.4204(2)	0.2551(2)	0.0737(12)
C(12)	−0.0343(3)	0.2378(3)	0.20748(17)	0.0649(10)
C(20)	0.3765(2)	0.1765(2)	0.33131(15)	0.0440(9)
C(21)	0.4238(3)	0.0870(2)	0.39017(16)	0.0490(10)
C(22)	0.5652(3)	0.0454(2)	0.41007(18)	0.0626(11)
C(23)	0.5550(3)	0.0046(2)	0.3373(2)	0.0651(11)
C(24)	0.5093(3)	0.0914(3)	0.27845(19)	0.0640(12)
C(25)	0.3691(3)	0.1332(2)	0.25912(16)	0.0532(10)
C(26)	0.3199(3)	−0.0031(2)	0.35668(18)	0.0605(11)
C(27)	0.3093(3)	−0.0443(2)	0.28337(18)	0.0590(11)
C(28)	0.2648(3)	0.0440(2)	0.22458(17)	0.0626(11)
C(29)	0.4508(3)	−0.0850(2)	0.3041(2)	0.0740(14)
C(30)	0.1173(2)	0.32317(19)	0.42939(14)	0.0374(8)
C(31)	−0.0180(3)	0.3444(2)	0.42685(16)	0.0459(9)
C(32)	0.0076(3)	0.3531(2)	0.50828(18)	0.0553(10)
C(33)	0.0712(3)	0.2525(2)	0.55218(17)	0.0544(11)
C(34)	0.2059(3)	0.2315(2)	0.55594(16)	0.0507(10)
C(35)	0.1780(2)	0.22057(17)	0.47398(15)	0.0406(9)
C(36)	−0.1196(3)	0.2547(2)	0.38479(17)	0.0544(10)
C(37)	−0.0584(3)	0.1524(2)	0.42882(18)	0.0545(10)
C(38)	0.0772(3)	0.1305(2)	0.43291(18)	0.0522(10)
C(39)	−0.0289(3)	0.1624(2)	0.51111(18)	0.0623(11)

[a] $U_{eq} = 1/3$ of the trace of the orthogonalized U.

temperature parameters. Final atomic coordinates of the non-hydrogen atoms are listed in Table 3.

4. Supplementary material available

Tables of crystal structure data, atomic positional parameters, anisotropic parameters, and complete bond distances for **2a** and **4** (86 pages) have been deposited with the Cambridge Crystallographic Data Centre. Lists of structure factors are available from the authors.

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