

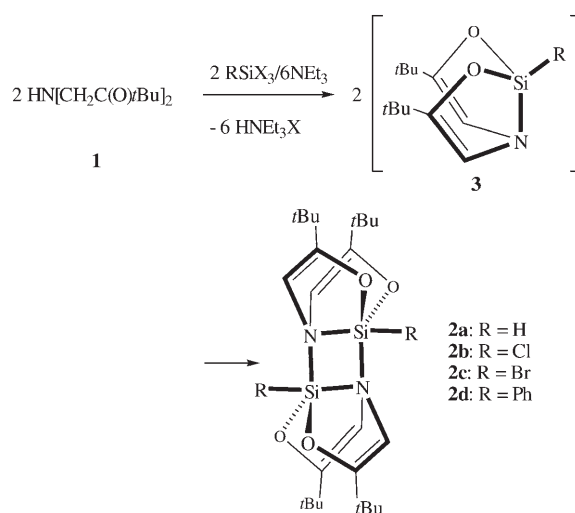
A Novel Type of Pentacoordinate Silicon Complexes and Unusual Ligand Coupling by Intramolecular Electron Transfer

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Dedicated to Professor Herbert Schumann
on the occasion of his 70th birthday

There are only a few reports on intramolecular electron-transfer (ET) reactions in coordination compounds of the main-group elements.^[1] Some years ago, Arduengo et al. reported on the intriguing coordination properties of the electron-rich trianionic amido-bis(enolate) ligand $[N\{CH=C(tBu)O\}_2]^{3-}$ (generated in situ from $HN[CH_2C(O)tBu]_2$ (**1**) and a base),^[2] which can serve both as a tridentate NO_2 ligand and intramolecular two-electron reducing agent toward heavier Group 15 elements (P, As, Sb, Bi) owing to ligand-to-element ET.^[3,4] Thus, reaction of PCl_3 with **1** in the presence of a base furnishes solely the corresponding nucleophilic phosphinidene with a planar λ^3 , T-shape-coordinated phosphorus atom with 10 valence electrons. Recently, we have shown that trilitiated **1** is a remarkable redox ligand even towards metal dihalides of the Group 14 elements Ge, Sn, and Pb, leading to novel nucleophilic carbene homologues.^[5] The fascinating coordination properties of **1** prompted us to explore whether the ligand is also capable of ET to a tetracoordinate Si^{4+} center. Here we describe the unexpected coordination behavior of **1** toward halosilanes, which affords two different types of unprecedented silicon complexes. Reaction of SiX_4 ($X = Cl, Br$) or $RSiCl_3$ ($R = H, Ph$) with **1** in the presence of NEt_3 as an auxiliary base furnishes deeply colored solutions from which the dimeric bis($N \rightarrow Si$) donor complexes **2a–d** can be isolated as the sole products (Scheme 1) in high yields. As expected, there is no reaction or color change if the halosilanes are added to solutions of **1** without the presence of a base. The final products **2a–d** are air-stable, moisture-sensitive, colorless solids that are well soluble in common aprotic organic solvents.

The composition and constitution of **2a–d** was confirmed by EI mass spectrometry, combustion analyses, and multinuclear NMR spectroscopy. The high-field ^{29}Si NMR chem-



Scheme 1. Synthesis of **2a–d** via the hypothetical monomers **3a–d**.

ical shifts in solution and in the solid state are diagnostic for λ^5 -coordinate silicon, and the similarity of respective solid state and solution values proves that the dimeric structure is retained in solution (see Table 1).^[6]

Table 1: ^{29}Si NMR chemical shift values for **2a–d**; CP-MAS solid-state values in parentheses.

Complex	2a	2b	2c	2d
δ [ppm]	−81.8 ^[a] (−87)	−85.9 (−93)	−106.7 (−112)	−38.3 (−45)

[a] $J_{Si,H} = 276.6$ Hz.

The shielding of the ^{29}Si nucleus is influenced by the nature of the substituents, thus the least shielding in the case of the phenyl-substituted complex **2d** is in accordance with values for related pentacoordinate silicon complexes with $N \rightarrow Si$ donor bonds (e.g., intramolecular amine $\rightarrow Si(Ph)$ donor-acceptor adducts).^[7] Remarkably, there was no indication for a dissociation up to 100 °C in toluene solutions, as shown by variable-temperature ^{29}Si NMR experiments. The dimeric structure of **2c** was additionally confirmed by a single-crystal X-ray diffraction analysis.^[8] Compound **2c** crystallizes in the triclinic space group $P\bar{1}$, and the molecular structure consists of a planar four-membered Si_2N_2 ring as the central structural motif (Figure 1). The latter results from a head-to-tail dimerization through $N \rightarrow Si$ donor-acceptor bonds of two hypothetical monomeric amido-bis(enolate) silicon bromide units. This leads to a slightly distorted trigonal-bipyramidal coordination of silicon with the Br1 and N1 atoms in axial and the O1, O2, and N1A atoms in equatorial positions. The axial Si1–N1 distance is about 20 pm longer than the equatorial Si1–N1A value (180.4(14) pm) but similar to $N \rightarrow Si$ distances observed in related Si_2N_2 dimers and silatranes.^[9] The Si1–O1 distance (166.2(13) pm) is slightly longer than the Si1–O2 value (163.8(13) pm) but similar to Si–O distances observed for hypercoordinate silicon in silatranes with a N_2O_3 coordination.^[9] Both the

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Si–O single and the endocyclic C6–C7 and C11–C14 double-bond lengths of the ligand skeleton confirm that each silicon atom in **2c** is coordinated by a trianionic amido-bis(enolate) chelate ligand.

Since similarly substituted amido-di-alkoxyhalosilanes such as $\text{XSi}(\text{OR})_2(\text{NR}')_2$ ($\text{X} = \text{Cl}$, $\text{R} = \text{Me}$, $\text{R}' = \text{alkyl}$, SiMe_3)^[10] are reluctant to dimerize, the formation of the thermally resistant dimers **2a–d** is amazing. To understand the facile dimerization of the hypothetical monomers **3** (see Scheme 1), we performed DFT calculations (B3LYP/6-311G** level of theory)^[11] of the three possible monomeric valence isomers **3A–3C**. The resulting energy profile for **3A–3C** is depicted in Figure 2. The calculations revealed that the amido-bis(enolate)-chloro silicon complex **3A**, which has a puckered, bicyclic $\text{C}_4\text{O}_2\text{NSi}$ skeleton, is most favored, whereas the silylene-like species **3C**, which implies a two-electron transfer from the ligand to silicon, is disfavored by $34.4 \text{ kcal mol}^{-1}$ and the least stable one. This is in marked contrast to the Ge and Sn analogues, which clearly prefer the formation of nucleophilic germynes and stannynes,^[4,5] reflecting that Si^{4+} is more electropositive than Ge^{4+} and Sn^{4+} . Interestingly, the optimized structure of **3B** with a planar-tetra-coordinate silicon atom represents the transition state (one imaginary frequency) for the ring inversion of **3A**, being only $12.3 \text{ kcal mol}^{-1}$ higher in energy (Figure 2). The latter process is reminiscent of related theoretical results on the hypothetical bis(*o*-catecholate)silicon complex with a much higher inversion barrier of $32.9 \text{ kcal mol}^{-1}$.^[12] In accordance to previous predictions,^[12] the significant lowering of the barrier in **3** indicates that the tridentate amido-bis(enolate) chelate is a more efficient π -donor- σ -acceptor than the

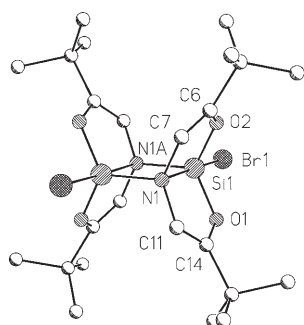


Figure 1. Molecular structure of **2c**; hydrogen atoms are omitted for clarity. Selected distances [pm] and angles [°]: Si1–Br1 227.5(6), Si1–O1 166.2(13), Si1–O2 163.8(13), Si1–N1 200.6(13), Si1–N1A 180.4(14), O1–C14 139(2), O2–C6 143(2), C7–N1 146(2), C11–N1 145(2), C6–C7 129(2), C11–C14 131(2); O1–Si1–O2 124.1(6), O2–Si1–N1A 115.8(6), O1–Si1–N1 85.1(6), N1–Si1–N1A 79.4(6), Br1–Si1–N1 177.4(4).

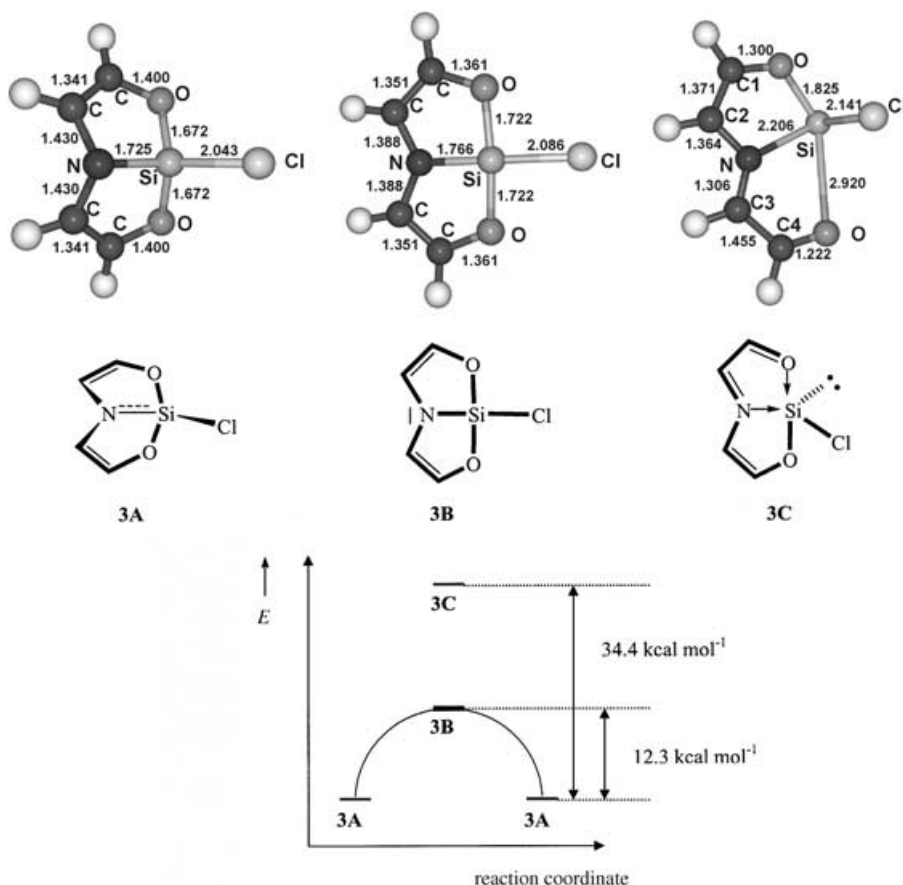


Figure 2. Top: DFT-(B3LYP/6-311G**)-optimized structures of **3A–3C**; distances are given in Å. Bottom: Energy profile for the isomerization of **3A** to **3B** and **3C**. The valence isomer **3B** is the transition state (one imaginary frequency) for ring-inversion of **3A**.

bidentate *o*-catecholate ligand. What is the driving force for the facile dimerization of **3A**? According to the calculation of the natural atomic charges in **3A**, the Si and the N atoms bear partial charges (Si +2.14, N –0.88) in accordance with the presence of a masked (ylide-like) Si–N π bond, reminiscent of iminosilane adducts with λ^4 -coordinate silicon and λ^3 -coordinate nitrogen atoms.^[13]

In fact, the HOMO exhibits an unsymmetrical π -charge distribution around the nitrogen and silicon atom and two symmetrical C–C π bonds (Figure 3). The calculated energy of the head-to-tail Si=N dimerization of **3A** to the corresponding dimer **2A** is $-21 \text{ kcal mol}^{-1}$, and the geometrical

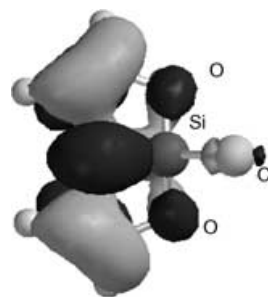
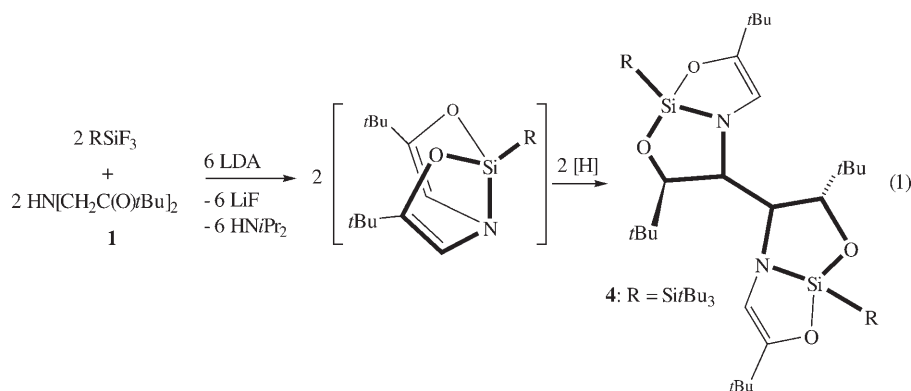


Figure 3. HOMO of **3A** with an ylidic Si–N π bond.

parameters of the latter are in good agreement with the respective experimental data of **2c**. Thus, the remarkably exothermic process prevents the observation of the monomeric units in **2a–d**. To protect the Si=N moiety against dimerization, we used the highly substituted trifluoro(silyl)silane $t\text{Bu}_3\text{SiSiF}_3$ as starting material.^[14] The latter readily reacts with trilitiated **1** in THF at -78°C but leads to the unusual dimer **4** in the form of pale yellow crystals in moderate yield (29%) as the only isolable product [Eq. (1); LDA = lithium diisopropylamide].



The composition and constitution of **4** was confirmed by NMR spectroscopy, EI mass spectrometry, and an X-ray diffraction analysis (Figure 4).^[8] The latter reveals that **4** crystallizes as a racemic mixture in the triclinic space group $P\bar{1}$.

In contrast to the dimeric complexes **2a–d**, the dinuclear compound **4** possesses only tetracoordinate silicon atoms. Its formation involves a remarkably mild C–C bond coupling of two amido-bis(enolate) frameworks of **1** and the concomitant

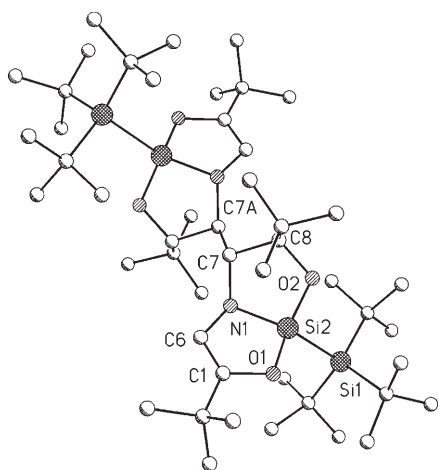


Figure 4. Molecular structure of **4**; hydrogen atoms are omitted for clarity. Selected distances [pm] and angles $^\circ$: Si1–Si2 236.8(10), Si2–O1 168.6(5), Si2–O2 164.7(6), Si2–N1 174.9(8), C1–O1 139.8(6), C8–O2 144.7(8), C6–N1 144.6(5), C1–C6 132.2(6), C7–C8 156.3(7), C7–C7A 154.7(6); O1–Si2–O2 122.3(2), O1–Si2–N1 94.2(3), O1–Si2–Si1 104.1(3), N1–Si2–Si1 136.8(2), C1–O1–Si2 110.6(3), C6–N1–C7 115.8(3), C1–C6–N1 115.8(3).

hydrogenation of the C8 and C8A atoms, presumably by a radical mechanism in which THF functions as the hydrogen source, to afford a hexa-basic bis[amido(enolate)-alkoxide] ligand capable of coordination of two formal $t\text{Bu}_3\text{Si-Si}^{3+}$ fragments. The observed distances and angles (Figure 4) are in the range expected for tetravalent silicon compounds (e.g., amido-alkoxysilanes).^[10] In summary, the deprotonated (anionic) ligand **1** shows remarkable coordination and electron-donor ability even towards tetravalent silicon, leading to the new types of silicon complexes **2** and **4**. Further investigations aimed at isolating the initial colored intermediates during the conversion of the halosilanes with deprotonated **1** and at synthesizing a stable monomeric silicon complex **3** are underway.

Experimental Section

General procedure for the synthesis of 2a–2d: To a mixture of **1** (2 g, 9.38 mmol) and the equimolar amount of the corresponding halosilane (HSiCl_3 for **2a**, SiCl_4 for **2b**, SiBr_4 for **2c**, and PhSiCl_3 for **2d**) in dried, Ar-saturated THF (50 mL) at -78°C was added dropwise three molar equivalents of triethylamine. The reaction mixture was allowed to warm up to room temperature (6 h) and was then stirred for an additional 2 h. All volatiles

were removed in vacuo and the solid residue was extracted with hexane ($3 \times 10\text{ mL}$). After filtration, the solvent was evaporated off and the residue was recrystallized from CH_2Cl_2 to afford a microcrystalline sample of **2a** (0.73 g, 1.52 mmol; 33%); m.p.: $127\text{--}129^\circ\text{C}$; ^1H NMR (CDCl_3): $\delta = 1.18$ (s, 36H; $t\text{Bu}$), 4.22 (brs, 2H; SiH), 5.67 ppm (brs, 4H; NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 27.56$ (s, CH_3), 34.87 (s, $\text{C}(\text{CH}_3)_3$), 106.01 (s, CN), 164.17 ppm (s, CO); ^{29}Si NMR (CDCl_3): $\delta = -81.8$ ppm (d, $J_{\text{Si,H}} = 276.56\text{ Hz}$); EI-MS: m/z (%): 478 ($[M]^+$, 20), 463 ($[M-\text{Me}]^+$, 10), 239 ($[M/2]^+$, 15), 224 ($[M/2-\text{Me}]^+$, 20), 209 ($[M/2-2\text{Me}]^+$, 20), 57 ($t\text{Bu}^+$, 100); correct elemental analyses (C,H,N,Si).

2b: (2.5 g, 4.69 mmol; 100%); m.p.: $120\text{--}122^\circ\text{C}$; ^1H NMR (CDCl_3): $\delta = 1.12$ (s, 36H; $t\text{Bu}$), 5.55 ppm (s, 4H; NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 27.19$ (s, CH_3), 33.84 (s, $\text{C}(\text{CH}_3)_3$), 107.63 (s, CN), 163.83 ppm (s, CO); ^{29}Si NMR (CDCl_3): $\delta = -85.9$ ppm (s); EI-MS: m/z (%): 546 ($[M]^+$, 90), 431 ($[M-\text{Me}]^+$, 20), 511 ($[M-\text{Cl}]^+$, 10), 273 ($[M/2]^+$, 95), 258 ($[M/2-\text{Me}]^+$, 100), 243 ($[M/2-2\text{Me}]^+$, 20); correct elemental analyses (C,H,N,Si).

2c: (2.5 g, 3.94 mmol, 84%); m.p.: $131\text{--}133^\circ\text{C}$ (decomp); ^1H NMR (CDCl_3): $\delta = 1.07$ (s, 36H; $t\text{Bu}$), 5.48 ppm (s, 4H; NCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 27.38$ (s, CH_3), 34.47 (s, $\text{C}(\text{CH}_3)_3$), 107.63 (s, CN), 163.81 ppm (s, CO); ^{29}Si NMR (CDCl_3): $\delta = -107.6$ ppm (s); EI-MS: m/z (%): 636 ($[M]^+$, 100), 621 ($[M-\text{Me}]^+$, 20), 557 ($[M-\text{Br}]^+$, 17), 318 ($[M/2]^+$, 87), 302 ($[M/2-\text{Me}]^+$, 78), 289 ($[M/2-2\text{Me}]^+$, 18); correct elemental analyses (C,H,N,Si).

2d: (1.56 g, 2.73 mmol, 58%); m.p.: $117\text{--}119^\circ\text{C}$ (decomp); ^1H NMR (CDCl_3): $\delta = 1.17$ (s, 36H; $t\text{Bu}$), 5.55 (s, 4H; NCH), 7.3–7.9 ppm (m, 10H; Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 28.73$ (s, CH_3), 34.97 (s, $\text{C}(\text{CH}_3)_3$), 112.39 (s, CN), 127.9 (s, Ph), 129.8 (s, Ph), 135.8 (s, Ph), 149.7 ppm (s, CO); ^{29}Si NMR (CDCl_3): $\delta = -38.3$ (s); EI-MS: m/z (%): 630 ($[M]^+$, 30), 615 ($[M-\text{Me}]^+$, 10), 315 ($[M/2]^+$, 35), 300 ($[M/2-\text{Me}]^+$, 30), 57 ($t\text{Bu}^+$, 100); correct elemental analyses (C,H,N,Si).

4: A solution of BuLi in hexane (Aldrich, 0.76 g, 12 mmol) at -78°C was added to a stirred solution of diisopropylamine (1.21 g, 12 mmol) in THF (10 mL). The solution was allowed to warm up to room temperature and stirred for 0.5 h. To this freshly prepared solution of LDA, a solution of **1** (0.8 g, 3.75 mmol) in THF (10 mL)

was added dropwise at -20°C over 10 min, affording a deep red solution of lithated **1**. The reaction mixture was warmed up to room temperature and stirred overnight. Subsequently, all volatile components were removed in vacuo and the red solid was redissolved in THF. To this solution was added a solution of $(t\text{Bu})_3\text{SiSiF}_3$ (1.06 g, 3.75 mmol) THF (in 10 mL) and the reaction mixture was stirred overnight. The solvent was removed under vacuo and the pale yellow solid was taken up in CH_2Cl_2 (30 mL). The filtrate, a slightly yellow solution, afforded (at -30°C) pale yellow crystals suitable for X-ray diffraction analysis (0.48 g, 0.54 mmol, 29%); ^1H NMR (CDCl_3): δ = 0.88 (s, 54H; $t\text{BuSi}$), 1.22 (s, 18H; $t\text{Bu}$), 1.14 (s, 18H; $t\text{Bu}$), 1.34 (m, 2H; HCN), 1.39 (m, 2H; HCO), 5.21 (s, 2H; NCH); EI-MS: m/z (%): 877 ($[\text{M}]^+$, 40), 862 ($[\text{M}-\text{Me}]^+$, 30), 438 ($[\text{M}/2]^+$, 15), 57 ($[\text{tBu}^+$, 100); correct elemental analyses (C,H,N,Si).

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- [8] Crystal structure analyses of **2c** and **4**: A crystal of **2c** and **4** were each mounted on a glass capillary in perfluorinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector (MoK_α radiation), $\lambda = 0.71073 \text{ \AA}$, ω scan at -60°C . **2c**: ($\text{C}_{24}\text{H}_{40}\text{Br}_2\text{N}_2\text{O}_4\text{Si}_2$): triclinic, $P\bar{1}$, $a = 11.47(2)$, $b = 11.80(2)$, $c = 11.95(2) \text{ \AA}$, $\alpha = 74.76(4)$, $\beta = 89.66(7)$, $\gamma = 76.31(4)^{\circ}$, $V = 1514(4) \text{ \AA}^3$, $Z = 2$, $\mu = 2.786 \text{ mm}^{-1}$. A total of 6817 reflections were collected ($2\theta_{\text{max}} = 50^{\circ}$), 3907 independent, 2921 observed ($F_o > 4\sigma(F_o)$), 307 parameters; $R1 = 0.0792$, $wR2$ (all data) = 0.2273. **4**: ($\text{C}_{48}\text{H}_{96}\text{N}_2\text{O}_4\text{Si}_4$): triclinic, $P\bar{1}$, $a = 8.68(3)$, $b = 10.72(3)$, $c = 15.87(7) \text{ \AA}$, $\alpha = 106.6(2)$, $\beta = 94.4(3)$, $\gamma = 99.1(1)^{\circ}$, $V = 1386(9) \text{ \AA}^3$, $Z = 1$, $\mu = 0.146 \text{ mm}^{-1}$. A total of 4872 reflections were collected ($2\theta_{\text{max}} = 50^{\circ}$), 3652 independent, 3029 observed ($F_o > 4\sigma(F_o)$), 262 parameters; $R1 = 0.0525$, $wR2$ (all data) = 0.1554. Structure solution by direct methods (SHELXS 97), refinement against F^2 with all measured reflections (SHELXTL 97). The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 274140(**2c**) and 274141 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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