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Synthesis, Structure, and Reactivity of Germyl(germylene)tungsten Complexes

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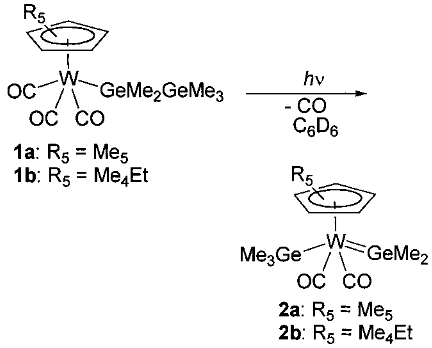
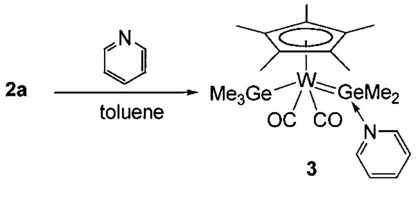
*Summary: Photolysis of a C_6D_6 solution of Cp′W(CO)$_3$-GeMe$_2$GeMe$_3$ (**1a**, Cp′ = Cp*, Cp* = η^5-C$_5$Me$_5$; **1b**, Cp′ = Cp^{Et}, Cp^{Et} = η^5-C$_5$Me$_4$Et) afforded a germyl(germylene)tungsten complex, Cp′W(CO)$_2$(=GeMe$_2$)(GeMe$_3$) (**2a**, Cp′ = Cp*; **2b**, Cp′ = Cp^{Et}), quantitatively. Crystal structure analysis of **2b** revealed a significantly short tungsten−germylene bond (2.4590(16) Å) compared to the tungsten−germyl bond (2.667(3) Å) and planar geometry around the germanium atom of the germylene ligand (sum of the valence angles 357.8°), indicating sp^2 hybridization of the germanium atom.*

Pannell[1] and we[2a] reported that photolysis of the digermanyliron complex CpFe(CO)$_2$GeMe$_2$GeR$_3$ (Cp = η^5-C$_5$H$_5$; R$_3$ = aryl, alkyl) afforded a mixture of the monogermyliron complexes CpFe(CO)$_2$GeMe$_{3-n}$R$_n$ (n = 1−3). This reaction has been proposed to proceed through the formation of the germyl(germylene)iron intermediate CpFe(CO)(=GeMe$_2$)(GeR$_3$) followed by fast 1,3-substituent migration between GeMe$_2$ and GeR$_3$ ligands and substitution of the germylene ligand by free carbon monoxide. Attempts to isolate the germyl(germylene)iron intermediate have not been successful, due to its thermal instability. However, the photolysis of Cp*Fe(CO)$_2$GeMe$_2$GeMe$_2$OMe (Cp* = η^5-C$_5$Me$_5$) afforded an intramolecular methoxy-stabilized germyl(germylene)iron complex.[2a] Hence, the presence of an appropriate base is indispensable to stabilize the germyl(germylene)iron complex. In our previous work on the base-stabilized silyl(silylene) complexes, the tungsten fragment CpW(CO)$_2$ was found to stabilize a silyl(silylene)metal framework efficiently.[3] This prompted us to synthesize a base-free germyl(germylene)tungsten complex. In this paper, we report the synthesis of germyl(germylene)tungsten complexes, Cp′W(CO)$_2$(=GeMe$_2$)(GeMe$_3$) (**2a**, Cp′ = Cp*; **2b**, Cp′ = Cp^{Et}, Cp^{Et} = η^5-C$_5$Me$_4$Et), by the photolysis of the digermanyltungsten complexes Cp′W(CO)$_3$GeMe$_2$GeMe$_3$ (**1a**, Cp′ = Cp*; **1b**, Cp′ = Cp^{Et}). There has been only one germyl−germylene complex reported so far, which is stabilized electronically and sterically by bulky amino groups attached on the germanium atoms.[4] The complexes **2a**,**b** reported in this paper are the first nonbulky alkyl-substituted germyl−germylene complexes, and **2b** is the second example of a structurally characterized germyl−germylene complex.

Digermanyltungsten complexes **1a**,**b** were prepared by the reaction of Li[Cp′W(CO)$_3$][5a] with Me$_3$GeGeMe$_2$-Cl[5b] as air-stable yellow crystals in 31 and 42% yields, respectively.[6] Irradiation of a benzene-d_6 solution of **1a** or **1b** in a sealed Pyrex NMR sample tube using a 450 W mercury arc lamp resulted in the quantitative formation of the germyl(germylene)tungsten complex **2a** or **2b**, respectively (eq 1). Complexes **2a**,**b** were isolated as yellow crystals by large-scale photolysis of **1a**,**b** in hexane in 60 and 33% yields, respectively, and were fully characterized by NMR, mass, and IR spectroscopy and elemental analysis.[7] The photochemical formation and isolation of **2a**,**b** is the evidence for the formation of a germyl(germylene)iron intermediate postulated in the photolysis of CpFe(CO)$_2$GeMe$_2$GeR$_3$ complexes.[1,2a] The π-acidic character of the germylene ligand in **2a** was confirmed by the fact that complex **2a** reacts with pyridine to afford the pyridine-coordinated germyl(germylene)tungsten complex Cp′W(CO)$_2$(=GeMe$_2$·pyridine)(GeMe$_3$) (**3**) in 89% yield (eq 2).[8]



(1)



(2)

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10.1021/om990607s CCC: $18.00

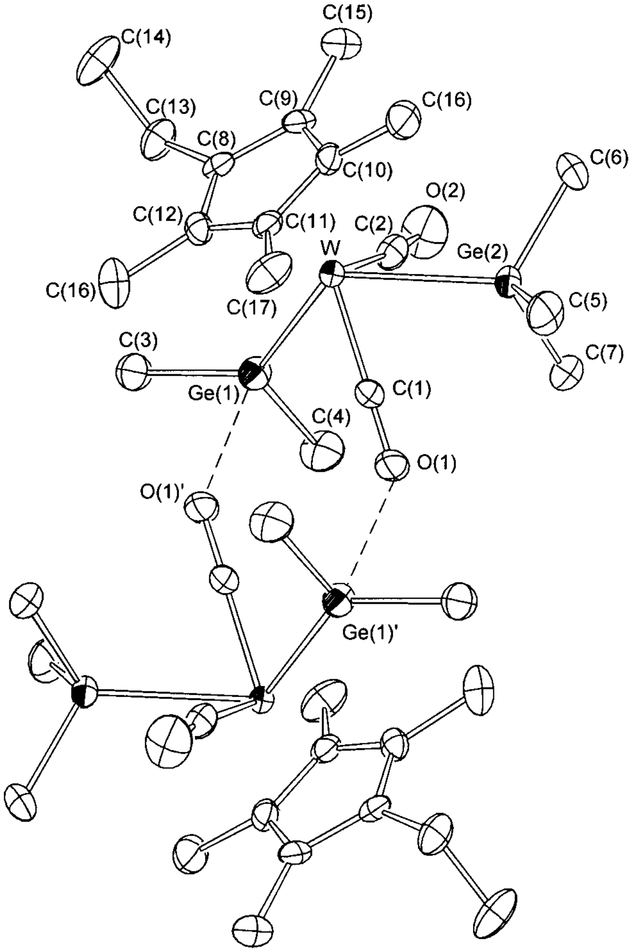

Figure 1. ORTEP drawing of **2b** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg): W−Ge(1) = 2.4590(16), W−Ge(2) = 2.667(3), W−C(1) = 1.937(9), W−C(2) = 1.941(13), C(1)−O(1) = 1.178(11), C(2)−O(2) = 1.142(14), Ge(1)−C(3) = 1.949(11), Ge(1)−C(4) = 1.940(11), Ge(1)···O(1)′ = 2.490(7); Ge(1)−W−Ge(2) = 121.58(6), C(1)−W−C(2) = 103.6(4), W−Ge(1)−C(3) = 132.0(4), W−Ge(1)−C(4) = 121.0(4), C(3)−Ge(1)−C(4) = 104.8(6).

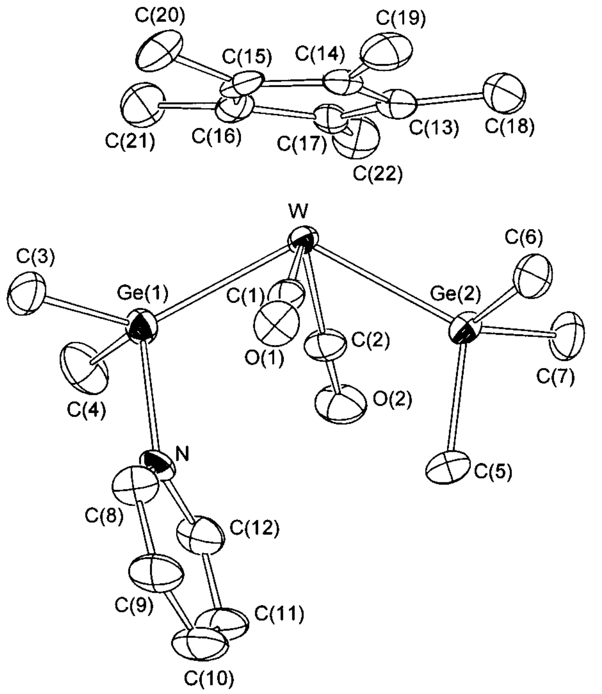

Figure 2. ORTEP drawing of **3** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg): W−Ge(1) = 2.5279(6), W−Ge(2) = 2.6304(6), W−C(1) = 1.946(5), W−C(2) = 1.942(5), C(1)−O(1) = 1.170(6), C(2)−O(2) = 1.176(6), Ge(1)−C(3) = 1.963(6), Ge(1)−C(4) = 1.988(6); Ge(1)−W−Ge(2) = 122.806(18), C(1)−W−C(2) = 107.84(19), W−Ge(1)−C(3) = 124.1(2), W−Ge(1)−C(4) = 122.4(2), C(3)−Ge(1)−C(4) = 103.3(3).

Crystal structure analysis of the germyl(germylene)tungsten complexes **2b** (Figure 1)[9] and **3** (Figure 2)[10] revealed that the germylene ligand occupies the site *trans* to the germyl group: the Ge(1)−W−Ge(2) angles are 121.58(6) and 122.81(2)° for **2b** and **3**, respectively. Similar *trans* geometry has been observed in the HMPA-coordinated silyl(silylene)tungsten complex $\mathrm{CpW(CO)_2({=}SiMe_2{\cdot}HMPA)(SiMe_3)}$.[3a] The *trans* configuration of each complex is attributable to the steric repulsion

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(6) (a) **1a**: Chloropentamethyldigermane (1.45 g, 5.66 mmol) was added dropwise under an atmosphere of dry nitrogen at room temperature to a THF (30 mL) solution of $\mathrm{Li[Cp^*W(CO)_3]}$ (5.71 mmol) with vigorous stirring. After the mixture was stirred for 11 h, volatiles were removed under vacuum. The residue was extracted with 50 mL of hexane and the extract filtered through a short silica gel column (3 cm). The filtrate was concentrated and cooled to −18 °C to give yellow crystals of **1a** (1.11 g, 1.78 mmol, 31%). ^{1}H NMR (room temperature, 300 MHz, $\mathrm{C_6D_6}$): δ 0.48 (s, 9H, $\mathrm{GeMe_3}$), 0.85 (s, 6H, $\mathrm{GeMe_2}$), 1.69 (s, 15H, $\mathrm{C_5Me_5}$). ^{13}C NMR (260 K, 75.5 MHz, toluene-d_8): δ 0.3, 0.4 (GeMe), 11.1 ($\mathrm{C_5}\mathit{Me}_5$), 102.9 ($C_5\mathrm{Me_5}$), 220.9, 224.6 (CO). IR (cyclohexane solution): 1984, 1903, 1893 cm^{-1} (ν_{CO}). MS (EI, 70 eV): *m*/*z* 624 ($\mathrm{M^+}$, 9.5), 609 ($\mathrm{M^+ - CH_3}$, 5.7), 581 ($\mathrm{M^+ - CH_3 - CO}$, 15.3), 505 ($\mathrm{M^+ - GeMe_3}$, 100), 221 ($\mathrm{Ge_2Me_5^+}$, 10.6), 119 ($\mathrm{GeMe_3^+}$, 23.1). Anal. Calcd for $\mathrm{C_{18}H_{30}Ge_2O_3W}$: C, 34.67; H, 4.85. Found: C, 34.79; H, 4.60. (b) **1b**: Complex **1b** was synthesized by a method similar to that for **1a** in 42% yield. ^{1}H NMR (room temperature, 300 MHz, $\mathrm{C_6D_6}$): δ 0.51 (s, 9H, $\mathrm{GeMe_3}$), 0.71 (t, 3H, $^3J_{\mathrm{HH}} = 7.6$ Hz, $\mathrm{C_5Me_4CH_2}\mathit{CH}_3$), 0.89 (s, 6H, $\mathrm{GeMe_2}$), 1.68 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 1.74 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 2.14 (q, 2H, $^3J_{\mathrm{HH}} = 7.6$ Hz, $\mathrm{C_5Me_4}\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (260 K, 75.5 MHz, toluene-d_8): δ −0.1, 0.0 (GeMe), 10.4, 10.6 ($\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 15.7, 19.5 ($\mathrm{C_5Me_4}\mathit{Et}$), 102.1, 103.3, 107.6 ($C_5\mathrm{Me_4Et}$), 220.4, 224.0 (CO). IR (cyclohexane solution): 1984, 1903, 1894 cm^{-1} (ν_{CO}). MS (EI, 70 eV): *m*/*z* 638 ($\mathrm{M^+}$, 10.1), 595 ($\mathrm{M^+ - CH_3 - CO}$, 8.8), 519 ($\mathrm{M^+ - GeMe_3}$, 100), 221 ($\mathrm{Ge_2Me_5^+}$, 5.7), 119 ($\mathrm{GeMe_3^+}$, 32.1). Anal. Calcd for $\mathrm{C_{19}H_{32}Ge_2O_3W}$: C, 35.80; H, 5.06. Found: C, 36.19; H, 4.98.

(7) (a) **2a**: A hexane solution (ca. 4 mL) of **1a** (42 mg, 0.067 mmol) in a sealed Pyrex tube (8 mm o.d., 6 mm i.d.) was irradiated for 1 h. During the irradiation, yellow crystals of **2a** precipitated in the solution. The yellow crystals were collected and washed with small amounts of hexane. Yield: 24 mg (0.040 mmol, 60%). ^{1}H NMR (room temperature, 300 MHz, $\mathrm{C_6D_6}$): δ 0.99 (s, 9H, $\mathrm{GeMe_3}$), 1.06 (s, 6H, $\mathrm{GeMe_2}$), 1.85 (s, 15H, $\mathrm{C_5Me_5}$). ^{13}C NMR (room temperature, 75.5 MHz, $\mathrm{C_6D_6}$): δ 4.0 ($\mathrm{GeMe_3}$), 11.7 ($\mathrm{C_5}\mathit{Me}_5$), 26.6 ($\mathrm{GeMe_2}$), 102.5 ($C_5\mathrm{Me_5}$), 223.7 (CO). IR ($\mathrm{C_6D_6}$ solution): 1892, 1828 cm^{-1} (ν_{CO}). MS (EI, 70 eV): *m*/*z* 596 ($\mathrm{M^+}$, 37.8), 581 ($\mathrm{M^+ - Me}$, 100.0), 119 ($\mathrm{GeMe_3^+}$, 40.1). Anal. Calcd for $\mathrm{C_{17}H_{30}Ge_2O_2W}$: C, 34.29; H, 5.08. Found: C, 34.39: H, 4.98. (b) **2b**: Complex **2b** was synthesized by a method similar to that for **2a** in 33% yield. ^{1}H NMR (room temperature, 300 MHz, $\mathrm{C_6D_6}$): δ 0.80 (t, $J_{\mathrm{HH}} = 7.5$ Hz, $\mathrm{CH_2}\mathit{CH}_3$), 0.98 (s, 9H, $\mathrm{GeMe_3}$), 1.05 (s, 6H, $\mathrm{GeMe_2}$), 1.84 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 1.90 (s, 6H, $\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 2.31 (q, $J_{\mathrm{HH}} = 7.5$ Hz, $\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (room temperature, 75.5 MHz, $\mathrm{C_6D_6}$): δ 4.1 ($\mathrm{GeMe_3}$), 11.5, 11.7 ($\mathrm{C_5}\mathit{Me}_4\mathrm{Et}$), 16.0, 20.3 ($\mathrm{C_5Me_4}\mathit{Et}$), 26.4 ($\mathrm{GeMe_2}$), 102.0, 102.8, 108.3 ($C_5\mathrm{Me_4Et}$), 223.6 (CO). IR ($\mathrm{C_6D_6}$ solution): 1892, 1828 cm^{-1} (ν_{CO}). MS (EI, 70 eV): *m*/*z* 610 ($\mathrm{M^+}$, 28.8), 595 ($\mathrm{M^+ - Me}$, 100.0), 581 ($\mathrm{M^+ - Et}$, 56.0), 119 ($\mathrm{GeMe_3^+}$, 45.1). Anal. Calcd for $\mathrm{C_{18}H_{32}Ge_2O_2W}$: C, 35.47; H, 5.29. Found: C, 35.46; H, 5.18.

(8) **3**: To a toluene solution (ca. 5 mL) of **2a** (44 mg, 0.074 mmol) in a Pyrex tube attached to a vacuum line was added pyridine (10 μL, 0.12 mmol) by conventional trap-to-trap distillation. The reaction mixture was warmed to room temperature and then cooled to −18 °C to give yellow crystals of **3**. Yield: 45 mg (0.066 mmol, 89%). ^{1}H NMR (room temperature, 300 MHz, $\mathrm{C_6D_6}$): δ 0.77 (s, 9H, $\mathrm{GeMe_3}$), 1.02 (s, 6H, $\mathrm{GeMe_2}$), 1.96 (s, 15H, $\mathrm{C_5Me_5}$), 6.41 (m, 2H, pyridine), 6.66 (m, 1H, pyridine), 8.33 (m, 2H, pyridine). ^{13}C NMR (room temperature, 75.5 MHz, $\mathrm{C_6D_6}$): δ 4.2, 9.6 (GeMe), 12.1 ($\mathrm{C_5}\mathit{Me}_5$), 98.9 ($C_5\mathrm{Me_5}$), 124.8, 139.5, 146.1 (pyridine), 234.7 (CO). IR ($\mathrm{C_6D_6}$ solution): 1859, 1784 cm^{-1} (ν_{CO}). MS (EI, 70 eV): *m*/*z* 596 ($\mathrm{M^+}$ − pyridine, 9.2), 581 ($\mathrm{M^+}$ − pyridine − Me, 25.8), 119 ($\mathrm{GeMe_3^+}$, 10.9), 79 (pyridine$^+$, 100). Anal. Calcd for $\mathrm{C_{22}H_{35}Ge_2NO_2W}$: C, 39.17; H, 5.23; N, 2.08. Found: C, 39.04; H, 5.05; N, 2.03.

between the bulky germyl and germylene ligands or between silyl and silylene ligands. The W−Ge distance of the tungsten−germylene bond in **2b** (W−Ge(1) = 2.4590(16) Å) is significantly shorter than those of the tungsten−germylene bond of **3** (W−Ge(1) = 2.5279(6) Å) and the tungsten−germyl bonds of **2b** (W−Ge(2) = 2.667(3) Å) and **3** (W−Ge(2) = 2.6304(6) Å) and is the shortest among the known tungsten−germylene bonds (2.52−2.63 Å).[12] In addition to the short tungsten−germylene bond, the germylene ligand in **2b** is almost planar (the sum of the W−Ge(1)−C(3), W−Ge(1)−C(4), and C(3)−Ge(1)−C(4) angles is 357.8°). These facts indicate the sp^2 hybridization of the germanium atom in the germylene ligand in **2b**. Interestingly, the germylene ligand in **2b** is weakly coordinated by a carbonyl oxygen of a neighboring molecule to form a dimer with a $W_2Ge_2C_2O_2$ eight-membered ring in the solid state. The interatomic distance between Ge(1) and O(1)′ (2.490(7) Å) is shorter than the sum of the van der Waals radii of Ge and O (3.6 Å) but significantly longer than those of Ge←O dative bonds of the known base-coordinated germylene complexes (1.8−2.1 Å).[13]

Although the germylene ligand in **2b** is weakly coordinated by the carbonyl oxygen in the crystal, spectroscopic data indicate that **2a**,**b** exist as monomeric base-free germyl(germylene)tungsten complexes in toluene and benzene solutions. The ^1H NMR spectrum of **2a** in toluene-d_8 showed only one sharp singlet for the $GeMe_2$ ligand even at 200 K. If the dimeric structure observed for **2b** in the solid state (Figure 1) is maintained even in solution, two singlet signals must be observed. The CO stretching bands of **2a** (1892 and 1828 cm^{-1}) in C_6D_6 appear at higher frequencies compared to those of **3** (1859 and 1784 cm^{-1}) in the same solvent. However, the frequency difference between those of **2a** and **3** measured in KBr pellets becomes much smaller: 1876 and 1776 cm^{-1} for **2a** and 1847 and 1767 cm^{-1} for **3**. The high-frequency shift of the ν_{CO} bands of **2a** in C_6D_6 is attributable to the formation of the base-free germyl(germylene)tungsten complex, in which the π-acidic base-free germylene ligand decreases the electron density on the tungsten atom, which in turn decreases the back-donation from the tungsten atom to the carbonyl ligands. These observations indicate that the interaction of the germylene ligand in **2b** with a carbonyl ligand of another molecule is negligible in solution.

The germyl(germylene)iron complex has been proposed to undergo rapid 1,3-substituent migration between two germanium atoms.[1,2a] The VT ^1H NMR investigation of **2a** in decahydronaphthalene-d_{18} showed that the signals assignable to $GeMe_3$ and $GeMe_2$ broadened above 340 K but did not coalesce even at 400 K. This implies that the 1,3-methyl migration from the germyl group to the germylene ligand takes place much more slowly than the NMR time scale. The activation energy of the 1,3-methyl migration was estimated to be $\Delta G^{\ddagger} > 80$ kJ/mol. The slower 1,3-migration in **2a** compared to that postulated for the germyl(germylene)iron complexes is attributable to the large geometric separation between the germyl and the germylene ligands due to the *trans* configuration of the germyl(germylene)tungsten complex (Ge(1)···Ge(2) = 4.475(4) Å).

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Supporting Information Available: Text giving the crystal structure determination details and tables giving crystal data, atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **2b** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Crystal data for **2b**: monoclinic, space group $P2_1/c$, $a = 9.524(6)$ Å, $b = 26.877(7)$ Å, $c = 9.274(10)$ Å, $\beta = 112.18(5)°$, $V = 2198(3)$ Å^3, $Z = 4$, $D_c = 1.841$ g/cm^3. R1 = 0.0483 and wR2 = 0.109 for 3350 reflections with $I > 2.0\sigma(I)$. The structure was solved by Patterson and Fourier transform methods and refined by full-matrix least-squares techniques on all F^2 data (5050 unique reflections) using SHELX-97.[11]

[10] Crystal data for **3**: triclinic, space group $P1$, $a = 10.1727(6)$ Å, $b = 15.7200(12)$ Å, $c = 9.2545(5)$ Å, $\alpha = 92.865(2)°$, $\beta = 116.953(4)°$, $\gamma = 104.836(19)°$, $V = 1251.30(14)$ Å^3, $Z = 2$, $D_c = 1.790$ g/cm^3. R1 = 0.0315 and wR2 = 0.0896 for 5080 reflections with $I > 2.0\sigma(I)$. The structure was solved by Patterson and Fourier transform methods and refined by full-matrix least-squares techniques on all F^2 data (5505 unique reflections) using SHELX-97.[11]

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