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Notes

Synthesis and Crystal Structure of a Novel Heterocyclic Compound Bearing a Pentacoordinate Germanium Atom and a Deprotonated HMPA Moiety

Naokazu Kano, Satoshi Goto, and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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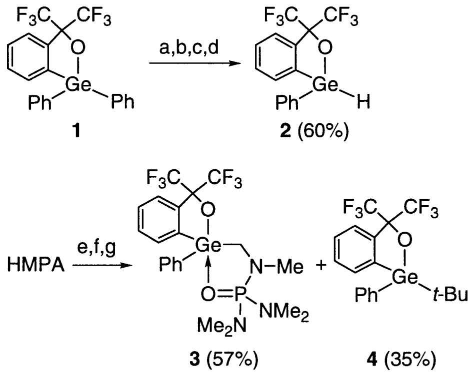
Summary: A novel heterocyclic compound, 1,3,2,5-oxazaphosphagermolidin-2-ium-5-uide, was synthesized by sequential treatment of HMPA with t-BuLi and a hydrogermane, and its crystal structure was established by X-ray crystallographic analysis.

Hexamethylphosphoric triamide (HMPA) has been known to be one of the most useful solvents and additives in organic synthesis because of its high solvating power and coordination ability as an aprotic polar molecule.[1] The coordination ability of HMPA has been utilized as a monodentate ligand for the construction of several main-group-element species with high coordination states.[2] If a heavier main-group element with high Lewis acidity is introduced in the vicinity of an HMPA moiety, a new type of heterocycle bearing a high-coordinate main-group element and an HMPA moiety could be constructed by the successive intramolecular coordination of the oxygen atom to the main-group element. Metalation of HMPA is expected to be a direct and facile method for the synthesis of such a heterocyclic compound. To the best of our knowledge, however, metalation of a part of HMPA as a substrate is limited to one example of the proton abstraction from the methyl group of HMPA by *sec*-BuLi at low temperature.[3] In our study on the generation of germyllithium by abstraction of a proton from a hydrogermane bearing the Martin ligand,[4] this method was found to be useful for the synthesis of a heterocycle including a deprotonated HMPA moiety as its component. We report here the synthesis and structure of a novel heterocyclic compound bearing both a pentacoordinate germanium atom and a deprotonated HMPA moiety in the ring. The Martin ligand was used for stabilization of the pentacoordinate state of the germanium atom.

Scheme 1[a]



[a] Legend: (a) CF_3SO_3H (1.2 equiv), 0 °C to room temperature, $CHCl_3$; (b) evaporation; (c) $LiAlH_4$ (4.0 equiv), room temperature, Et_2O; (d) aqueous $NaHCO_3$, room temperature; (e) *t*-BuLi (1.0 equiv), −30 °C, dimethoxymethane; (f) **2** (1.0 equiv), −30 °C to room temperature; (g) aqueous NH_4Cl.

Results and Discussion

Hydrogermane **2** was prepared in 60% yield by treatment of diphenylgermane **1** bearing the Martin ligand with trifluoromethanesulfonic acid (1.2 equiv) in $CHCl_3$ at 0 °C, followed by reduction of the resulting germyl triflate with lithium aluminum hydride (4.0 equiv) in Et_2O at room temperature after the exchange of the solvent[5] (Scheme 1). *t*-BuLi (1.0 equiv) and hydrogermane **2** (1.0 equiv) were sequentially added to a dimethoxymethane solution of HMPA at −30 °C. The reaction mixture was gradually warmed to room temperature, quenched with aqueous NH_4Cl, and separated by chromatography to give the compound **3** (57%) together with *tert*-butylgermane **4** (35%). The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectral data show that **3** contains both the Martin ligand and a deprotonated HMPA moiety. The structure of **3** was finally determined by X-ray crystallographic analysis, as shown in Figure 1. Selected bond lengths and angles are shown in Table 1. The 1,3,2,5-oxazaphosphagermolidine ring exists in the envelope form close to the planar form; in the former, the O1 atom is located at the tip slightly above the least-squares plane defined by the other four atoms,

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(1) (a) Fieser, L. F.; Fieser, M. In *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 430. (b) Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046. (c) Morrison, R. T.; Boyd, R. N. In *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, MA, 1987; p 230.

(2) For examples, see: (a) Yatsenko, A. V.; Aslanov, L. A.; Schenk, H. *Polyhedron* **1995**, *14*, 2371. (b) Ivor, W.; Simard, M. G. *Inorg. Chim. Acta* **1998**, *282*, 30. (c) Ko, B.-T.; Wu, C.-C.; Lin, C.-C. *Organometallics* **2000**, *19*, 1864.

(3) Magnus, P.; Roy, G. *Synthesis* **1980**, 575.

(4) A bidentate ligand, $-C_6H_4C(CF_3)_2O-$, was developed by Martin for stabilizing hypervalent species. See: Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

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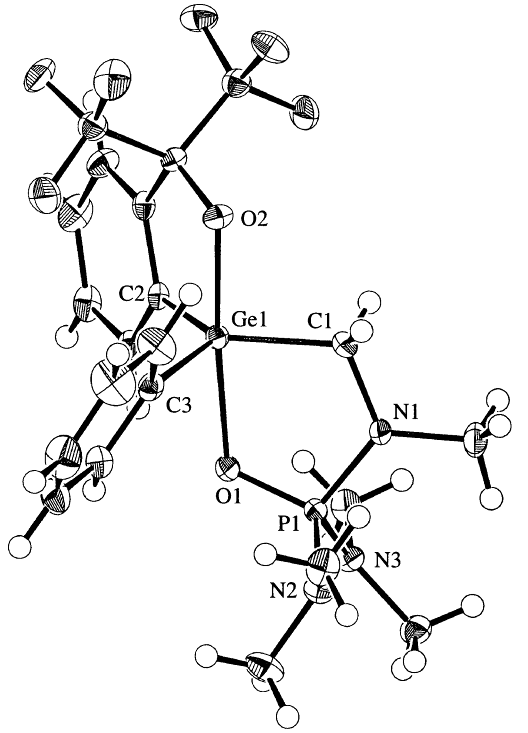


Figure 1. ORTEP drawing of **3** (thermal ellipsoids are at the 50% probability level for all non-hydrogen atoms).

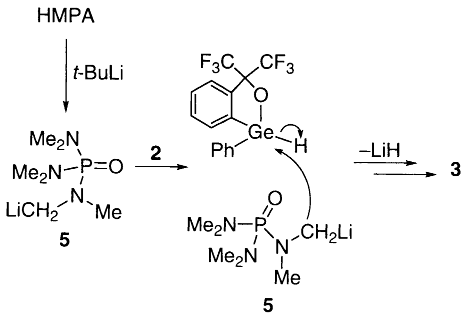
Table 1. Selected Bond Distances and Angles for 3

(a) Bond Distances (Å)			
Ge1−O1	2.1746(14)	P1−O1	1.5060(13)
Ge1−O2	1.9106(13)	P1−N1	1.6309(16)
Ge1−C1	1.9644(18)	P1−N2	1.6410(16)
Ge1−C2	1.9421(17)	P1−N3	1.6426(16)
Ge1−C3	1.9529(18)	C1−N1	1.457(2)
(b) Bond Angles (deg)			
O1−Ge1−O2	171.52(5)	Ge1−C1−N1	113.01(12)
C1−Ge1−C2	123.34(8)	C1−N1−P1	120.22(12)
C1−Ge1−C3	114.92(8)	N1−P1−O1	105.45(8)
C2−Ge1−C3	121.30(7)	P1−O1−Ge1	111.86(7)
C1−Ge1−O1	84.85(6)		

i.e., Ge1, C1, N1, and P1. This five-membered-ring system is interesting as a novel heterocyclic system constituted of C, N, O, P, and Ge elements.[6] Compound **3** has a slightly distorted trigonal-bipyramidal (TBP) structure with two oxygen atoms at apical positions and three carbon atoms at equatorial positions, respectively (% TBP → SP, 24%).[7] The Ge1−O1 bond length (2.1746(14) Å) is much shorter than the sum of the corresponding van der Waals radii (3.50 Å). The P1−O1 bond length (1.5060(13) Å) is longer and the P1−N1 bond length (1.6309(16) Å) is shorter than those of HMPA (1.477(1) and 1.652 Å (average)), respectively, suggesting a strong intramolecular interaction between germanium and oxygen atoms as well as a slight perturbation on the bond lengths of **3** compared to those of HMPA in the solid state.[8]

In the ^{1}H NMR spectrum, the signal due to the ortho proton of the Martin ligand was observed at δ 8.26−8.28 in CDCl$_3$. Such a downfield shift is one of the typical features of the trigonal-bipyramidal structure with a polar apical bond. It indicates that **3** has a TBP structure maintaining the coordination of an oxygen atom of the phosphoryl group also in the solution state. The ^{31}P NMR signal of **3** in CDCl$_3$ was observed at lower field (δ 32.4) than that of free HMPA (δ 25.9). In the ^{31}P CP-MAS solid-state NMR spectra, the signal was observed in a region (δ 32.5) similar to that in the solution state. In the IR spectrum of **3**, a P=O stretching band was observed at 1180 and 1187 cm^{-1} in the KBr disk and in CCl$_4$ solution, respectively, which are lower than that of HMPA (1205 cm^{-1}).[9] These results are consistent with the cationic character of the phosphorus atom in **3** as the result of the coordination of the oxygen atom to the germanium atom. The betaine structure, $-\mathrm{Ge}^{-}-\mathrm{O}-\mathrm{P}^{+}-\mathrm{N}-\mathrm{C}-$, should contribute to the structure of **3**, although the formal negative charge on the germanium atom seems to be localized on the apical oxygen atoms. The combination of the electron-withdrawing property of the Martin ligand and high coordination ability of an HMPA moiety should result in the maintenance of the Ge−O interaction even in the solution state.

Scheme 2



The formation mechanism of **3** was reasonably explained as follows (Scheme 2). Deprotonation of the HMPA molecule with *t*-BuLi gives the corresponding alkyllithium **5** (LiCH$_2$(Me)N(Me$_2$N)$_2$P=O) similarly to the method reported in the literature,[3] and successive nucleophilic substitution of the alkyllithium **5** at the germanium atom results in the formation of **3** with elimination of lithium hydride followed by intramolecular coordination. Competitive substitution of *t*-BuLi at the germanium atom of **2** gave the corresponding *tert*-butylgermane **4**. We have independently confirmed the first process: the generation of **5** by the reaction of HMPA with *t*-BuLi. Furthermore, treatment of hydrogermane **2** with *t*-BuLi and successive addition of benzophenone gave not the adduct of the corresponding germyllithium and benzophenone but *tert*-butylgermane **4** in good yield, as judged by NMR spectra, suggesting that nucleophilic substitution of alkyllithiums at the germanium atom of **2** took place instead of deprotonation. Although the coordination of HMPA or **5** to the germanium atom of **2** to form a pentacoordinated structure might cooperatively increase the electrophilicity of the germanium atom and facilitate the substitution of **2** along with elimination of a hydride, such a coordination was not confirmed by the low-temperature ^{31}P NMR experiments of a THF solution of **2** and HMPA (−60 °C).

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(6) For a 1,5,3,2-oxazaphosphagermolidine, see: Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1991**, *415*, 327.

(7) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(8) Mitzel, N. W.; Lustig, C. *J. Chem. Soc., Dalton Trans.* **1999**, 3177.

(9) Bollinger, J. C.; Yvernault, G.; Yvernault, T. *Spectrochim. Acta* **1985**, *41A*, 399.

The reactivities of **3** with organolithium reagents were tentatively investigated in anticipation of the substitution at the pentacoordinate germanium atom of **3**. Treatment of **3** with phenyllithium (1.4 equiv) or *tert*-butyllithium (1.3 equiv) at −30 °C in THF followed by gradual warming to room temperature resulted in the almost quantitative recovery of **3** without formation of **1** and **4**.

In summary, we have shown the formation of the novel heterocyclic compound **3** using deprotonated HMPA as a component. Intramolecular coordination of the oxygen atom to the germanium atom was confirmed in both crystalline and solution states.

Experimental Section

General Methods. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Bruker DRX500 spectrometer using tetramethylsilane as internal standard. ^{19}F (254 MHz) and ^{31}P (109 MHz) NMR spectra were recorded on a JEOL EXcalibur270 spectrometer using Freon and 85% H_3PO_4 as external standards, respectively. CP-MAS solid-state ^{31}P (122 MHz) NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer using a zirconia rotor (5 mm diameter) at 6.0 kHz in air with triphenylphosphine as an external standard. Silica gel column chromatography was carried out with Wakogel C-200. Preparative gel permeation liquid chromatography (GPLC) was performed with an LC-908 instrument with JAIGEL 1H and 2H columns (Japan Analytical Industry) and chloroform as solvent. Melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Synthesis of Diphenylgermane 1. According to the literature,[5] to a solution of dibromodiphenylgermane (1.27 g, 3.3 mmol) in THF (10 mL) at −72 °C was added dropwise the dilithio derivative of 2,2,2,2′,2′,2′-hexafluorocumyl alcohol, which was prepared from hexafluorocumyl alcohol (0.53 mL, 3.2 mmol), *n*-BuLi (1.59 M, 4.4 mL, 7 mmol), and TMEDA (0.11 mL, 0.7 mmol) in THF (0.5 mL).[4] The reaction mixture was warmed to room temperature, stirred for 1 h, and quenched with aqueous NH_4Cl. After the usual workup, the crude material was separated with column chromatography on silica gel (hexane−CH_2Cl_2) to give **1** (549 mg, 37%). 1,1-Diphenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxagermole (**1**): colorless crystal; mp 104−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.45 (m, 4H), 7.48−7.51 (m, 2H), 7.59−7.60 (m, 6H), 7.75−7.77 (m, 1H), 7.82−7.83 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 84.84 (sept, $^{2}J_{CF}$ = 30.1 Hz), 123.18 (q, $^{1}J_{CF}$ = 287.8 Hz), 126.23 (m), 128.74, 130.62, 130.73, 131.17, 132.02, 132.63 (ipso), 134.27, 135.02 (ipso), 140.01 (ipso); ^{19}F NMR (254 MHz, $CDCl_3$) δ −75.84 (s, 6F); HRMS *m/z* calcd for $C_{21}H_{14}F_6{}^{74}GeO$ 470.0161, found 470.0174. Anal. Calcd for $C_{21}H_{14}F_6GeO$: C, 53.79; H, 3.01. Found: C, 53.91; H, 3.10.

Synthesis of Hydrogermane 2. To a solution of **1** (931 mg, 1.99 mmol) in $CHCl_3$ (20 mL) was added trifluoromethanesulfonic acid (0.22 mL, 2.5 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 5 h. To change the solvent, the original solvent was evaporated in vacuo and ether (10 mL) was added to the residue. The resulting mixture was added to a suspension of lithium aluminum hydride (309 mg, 8.14 mmol) in ether (20 mL) at room temperature to give a green-brown solution, which was stirred for 15 h. The usual workup and separation with HPLC ($CHCl_3$ as eluent) gave the hydrogermane **2** (561 mg, 60%). 1-Phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxagermole (**2**): colorless viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 7.43−7.46 (m, 2H), 7.50−7.51 (m, 1H), 7.52−7.56 (m, 2H), 7.59−7.62 (m, 2H), 7.69−7.70 (m, 1H), 7.81−7.82 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 85.19 (sept, $^{2}J_{CF}$ = 29.9 Hz), 122.99 (q, $^{1}J_{CF}$ = 286.4 Hz), 123.19 (q, $^{1}J_{CF}$ = 286.5 Hz), 126.17 (m), 128.87, 130.67, 130.85, 131.68, 132.00, 132.96 (ipso), 134.18 (ipso), 134.22, 139.90 (ipso); ^{19}F NMR (254 MHz, $CDCl_3$) δ −76.65 (q, $^{4}J_{FF}$ = 9.1 Hz, 3F), −75.95 (q, $^{4}J_{FF}$ = 9.1 Hz, 3F); HRMS *m/z* calcd for $C_{15}H_{10}F_6{}^{74}GeO$ 393.9848, found 393.9828. Anal. Calcd for $C_{15}H_{10}F_6GeO{\cdot}0.24H_2O$: C, 45.36; H, 2.66. Found: C, 45.10; H, 3.21.

Synthesis of Heterocycle 3. To a solution of HMPA (71 μL, 0.41 mmol) in dimethoxymethane (2 mL) at −30 °C was added dropwise a pentane solution of *t*-BuLi (2.26 M, 0.18 mL, 0.41 mmol). The reaction mixture was stirred for 2 h, treated with **2** (158 mg, 0.40 mmol), and gradually warmed to room temperature. The reaction mixture was quenched with aqueous NH_4Cl, worked up in the usual manner, and separated by chromatography to give **3** (131 mg, 57%) and **4** (64 mg, 35%). 2′,2′-Bis(dimethylamino)-3′-methyl-1-phenyl-3,3-bis(trifluoromethyl)-3*H*-spiro[2,1-benzoxagermole-1,5′-[1,3,2,5]oxazaphosphagermolidin]-2′-ium-1-uide (**3**): colorless crystals; mp 120−121 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (d, $^{3}J_{PH}$ = 10.0 Hz, 6H, N(CH_3)$_2$), 2.58 (d, $^{3}J_{PH}$ = 10.0 Hz, 6H, N(CH'_3)$_2$) 2.64 (d, $^{3}J_{PH}$ = 9.4 Hz, 3H, CH_2NCH_3), 3.00 (dd, $^{3}J_{PH}$ = 6.2 Hz, $^{2}J_{HH}$ = 11.8 Hz, 1H, GeC*H*H), 3.26 (dd, $^{3}J_{PH}$ = 13.5 Hz, $^{2}J_{HH}$ = 11.8 Hz, 1H, GeCH*H*), 7.26−7.30 (m, 3H), 7.45−7.51 (m, 2H), 7.70−7.71 (m, 1H), 7.74−7.76 (m, 2H), 8.26−8.28 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 36.20 (d, $^{2}J_{PC}$ = 4.9 Hz, CH_2N(*C*H_3)), 36.61 (d, $^{2}J_{PC}$ = 4.0 Hz, N(*C*H_3)$_2$), 36.78 (d, $^{2}J_{PC}$ = 3.7 Hz, N(*C′*H_3)$_2$), 44.14 (d, $^{2}J_{PC}$ = 8.5 Hz, Ge*C*H_2N), 82.62 (sept, $^{2}J_{CF}$ = 29.1 Hz, *C*(CF_3)$_2$), 123.84 (q, $^{1}J_{CF}$ = 287.5 Hz, *C*F_3), 124.15 (q, $^{1}J_{CF}$ = 287.5 Hz, *C′*F_3), 125.70 (s), 127.55 (s), 128.67 (s), 129.26 (s), 129.77 (s), 133.46 (s), 134.43 (s), 137.75 (s, *ipso*), 140.21 (s, *ipso*), 140.38 (s, *ipso*); ^{19}F NMR (254 MHz, $CDCl_3$) δ −76.35 (q, $^{4}J_{FF}$ = 8.6 Hz, 3F), −75.93 (q, $^{4}J_{FF}$ = 8.6 Hz, 3F); ^{31}P NMR (109 MHz, $CDCl_3$) δ 32.4 (s); IR (KBr) 1180 cm^{-1} (s, $\nu_{P=O}$). Anal. Calcd for $C_{21}H_{26}F_6GeN_3O_2P$: C, 44.25; H, 4.60; N, 7.37. Found: C, 44.51; H, 4.52; N, 7.18. 1-*tert*-Butyl-1-phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxagermole (**4**): colorless crystals; mp 112.1−113.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 9H), 7.36−7.42 (m, 3H), 7.52−7.58 (m, 4H), 7.73−7.77 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 26.87, 28.68, 85.10 (sept, $^{2}J_{CF}$ = 30.4 Hz), 123.10 (q, $^{1}J_{CF}$ = 286.5 Hz), 123.29 (q, $^{1}J_{CF}$ = 287.5 Hz), 126.21, 128.41, 130.17, 130.25, 130.31, 131.85, 133.31, 134.29, 135.90, 140.04; ^{19}F NMR (254 MHz, $CDCl_3$) δ −76.14 (q, $^{4}J_{FF}$ = 9.1 Hz, 3F), −75.11 (q, $^{4}J_{FF}$ = 9.1 Hz, 3F). Anal. Calcd for $C_{19}H_{18}F_6GeO$: C, 50.83; H, 4.04. Found: C, 50.68; H, 4.06.

Reaction of 2 with *t*-BuLi. To a solution of **2** (71.3 mg, 0.18 mmol) in THF (2 mL) at −78 °C was added a pentane solution of *t*-BuLi (2.14 M, 0.17 mL, 0.36 mmol). The reaction mixture was stirred for 2 h, quenched with benzophenone (38.1 mg, 0.21 mmol), and gradually warmed to room temperature. The usual workup afforded a colorless crude solid which contains **3** in 90% yield, as judged by NMR spectra.

Attempted Reaction of 3 with PhLi. To a solution of **3** (28.9 mg, 0.051 mmol) in THF (3 mL) at −30 °C was added a cyclohexanes−ether solution of PhLi (1.02 M, 0.07 mL, 0.071 mmol). The reaction mixture was stirred for 2 h and gradually warmed to room temperature. The usual workup and separation resulted in the recovery of **3** (21.7 mg, 75%).

Attempted Reaction of 3 with *t*-BuLi. Similarly to the reaction with PhLi, the reaction of **3** (29.0 mg, 0.051 mmol) with a pentane solution of *t*-BuLi (2.15 M, 0.03 mL, 0.065 mmol) resulted in the recovery of **3** (22.4 mg, 77%).

X-ray Data Collection and Structure Refinement of 3. Colorless single crystals of **3** were grown by the slow evaporation of its saturated solution in hexane at room temperature. Crystal data of **3**: $C_{21}H_{26}F_6GeN_3O_2P$, fw =

570.01, monoclinic, space group $P2_1/n$, $Z = 8$, $a = 16.288(5)$ Å, $b = 14.097(4)$ Å, $c = 21.237(6)$ Å, $\beta = 97.358(5)°$, $V = 4836(3)$ Å^3, $D_{calcd} = 1.566$ g cm^{-3}, $\mu = 1.403$ mm^{-1}, $T = 120$ K. A colorless crystal of **3** having dimensions of 0.30 × 0.30 × 0.05 mm was mounted within a loop. The data set was collected on a Rigaku MERCURY CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) to $2\theta_{max} = 55°$. The structure was solved by direct methods with SIR-97 and refined with SHELXL-97. The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX methods. The final cycle of full-matrix least-squares refinement was based on 10 761 observed reflections and 623 variable parameters and converged to R1 = 0.032 ($I > 2.00\sigma(I)$) and wR2 = 0.073 (all data) with GOF = 1.119.

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Supporting Information Available: Tables giving crystallographic data of **3**. This material is available free of charge via the Internet at http://pubs.acs.org. These data also have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-185065. 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).

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