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From Chlorogermylenes to Stable Hydroxy- and Siloxy-Germylene−Tungsten Complexes

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Reaction of the chlorogermylene ArGeCl [Ar = 2,6-bis((diethylamino)methyl)phenyl] with lithium amides afforded the aminogermylenes $ArGeNR_2$ **1** (**1a**, R = $SiMe_3$; **1b**, R = ^{i}Pr); **1a** was structurally analyzed by X-ray diffraction. A protic reagent such as 2,4,6-trimethylphenol (Ar′OH) reacts with **1b**, leading to the mesityloxygermylene ArGeOAr′ **2**. Subsequent hydrolysis of tungsten complexes $\mathbf{1}\cdot W(CO)_5$ gave $ArGeOH\cdot W(CO)_5$, **3**. From **1a**, $ArGeOSiMe_3\cdot W(CO)_5$ (**4**) also was obtained. Compounds **3** and **4** are the first stable hydroxy- and siloxygermylene complexes. X-ray analysis of **3** shows an increased coordination of the side-chain nitrogen atoms to the germanium resulting from the complexation Ge→W. This complexation can also explain the significant acidity of the hydroxy group in **3**, in the same range as triphenylgermanol Ph_3GeOH.

Introduction

Donor-stabilized germanium(II) compounds have been developed into an active area of research during the last two decades. Compounds with side-chain substituents bearing nitrogen,[1] phosphorus,[2] and oxygen donors[3] are now known. From this range of compounds, halogermylenes are of particular utility for the synthesis of many functionalized germylenes using nucleophilic substitution reactions at germanium. We can expect an increase in the Lewis base character due to donation of electron density to the germanium center by the donor heteroatom and, as a result, a greater ability to form complexes with Lewis acids such as transition metals.

From a chlorogermylene ArGeCl[4] [Ar = 2,6-bis((diethylamino)methyl)phenyl], we report the synthesis of two new functionalized germylenes $ArGeNR_2$ (R = $SiMe_3$ or ^{i}Pr) **1**. $ArGeN(SiMe_3)_2$, **1a**, was used to prepare the first stable hydroxygermylene, stabilized as a pentacarbonyltungsten complex, $ArGeOH\cdot W(CO)_5$, **3**, and the siloxygermylenetungsten complex $ArGeOSiMe_3\cdot W(CO)_5$, **4**. The 2,6-bis((diethylamino)methyl)phenyl group [Ar] allowed us to obtain the stable chlorogermylene ArGeCl and diazogermylene $ArGeC(N_2)SiMe_3$, precursor of a germa-alkyne $ArGe{\equiv}CSiMe_3$.[5]

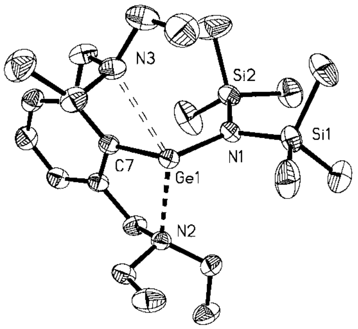

Figure 1.

Results and Discussion

Reaction of ArGeCl[4] with lithium bis(trimethylsilyl)amide in Et_2O in 1:1 ratio at −78 °C afforded $ArGeN(SiMe_3)_2$, **1a**, in 80% yield. The aminogermylene **1b** (R = ^{i}Pr) was prepared in similar manner. The structure of **1a** is shown in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles in Table 2. The Ge(1)−N(1) distance (1.956(0) Å) is the longest observed σ-Ge(II)−N bond in similar structures; for example, in $[(Me_3Si)_2N]_2Ge$, the Ge−N bond distances are 1.873(5) and 1.878(5) Å,[6] and in $[Me_3SiNC(tBu)NSiMe_3]GeN(SiMe_3)_2$, it is 1.910(1) Å.[1j] The Ge(1)−N(2) dative bond (2.390(3) Å) is as expected much longer than the covalent Ge(1)−N(1) bond. On the other hand, the Ge(1)···N(3) distance (2.699(1) Å) shows that significant coordination between these two atoms is absent.

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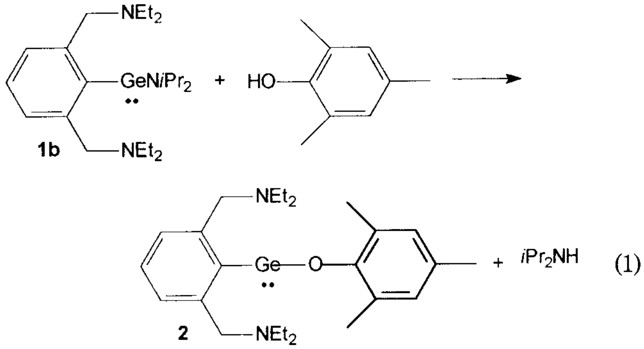
Table 1. Crystal Data and Structure Refinement Details for 1a and 3

empirical formula	$C_{22}H_{45}GeN_3Si_2$	$C_{21}H_{28}GeN_2O_6W$
fw	480.38	660.89
temp [K]	193(2)	193(2)
wavelength [Å]	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a [Å]	16.7379(8)	10.7885(4)
b [Å]	10.4602(5)	19.5121(8)
c [Å]	15.9656(8)	12.2126(5)
β [deg]	103.204(1)	107.050(1)
volume [Å^3]	2721.4(2)	2457.8(2)
Z	4	4
density(calcd) [Mg/m^3]	1.172	1.786
abs coeff [mm^{-1}]	1.226	5.936
F(000)	1032	1288
cryst size [mm^3]	0.3 × 0.6 × 0.8	0.4 × 0.1 × 0.05
θ range for data collection [deg]	2.31−29.53	2.03−28.28
range of hkl	$-21 \leq h \leq 22$ $-14 \leq k \leq 12$ $-15 \leq l \leq 21$	$-14 \leq h \leq 13$ $-26 \leq k \leq 26$ $-16 \leq l \leq 16$
no. of reflns collected	16 519	36 524
no. of ind reflns	6928 [$R_{int} = 0.0371$]	6108 [$R_{int} = 0.0680$]
abs corr	semiempirical	semiempirical
max./min. transmn	1.000000/0.588755	1.000000/0.493596
no. of data/restaints/params	6928/0/263	6108/0/285
goodness-of-fit on F^2	1.029	1.051
final R indices [$I > 2\sigma(I)$]	R1 = 0.0307	R1 = 0.0266
R indices (all data)	wR2 = 0.0873	wR2 = 0.0719
largest diff peak and hole [e Å^{-3}]	0.0571 and −0.576	1.826 and −2.188

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1a

Ge(1)−N(1)	1.956(0)	N(1)−Ge(1)−C(7)	103.68(6)
Ge(1)−N(2)	2.390(3)	N(2)−Ge(1)−C(7)	78.20(5)
Ge(1)−N(3)	2.699(1)	N(1)−Ge(1)−N(2)	97.90(5)
Ge(1)−C(7)	2.022(5)		

A major interest of such germylenes **1** is the high reactivity of the covalent germanium−nitrogen bond enhanced by the diethylamino N→Ge donor interaction. **1** react readily with protic acids A−H and thus are a suitable starting material for the preparation of heteroleptic germylenes ArGe−A. For instance, on reaction of **1b** with 2,4,6-trimethylphenol, the crowded mesityloxygermylene **2** was obtained (eq 1):



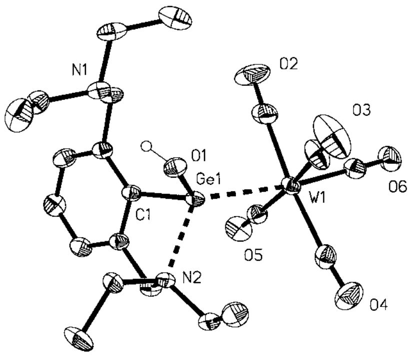
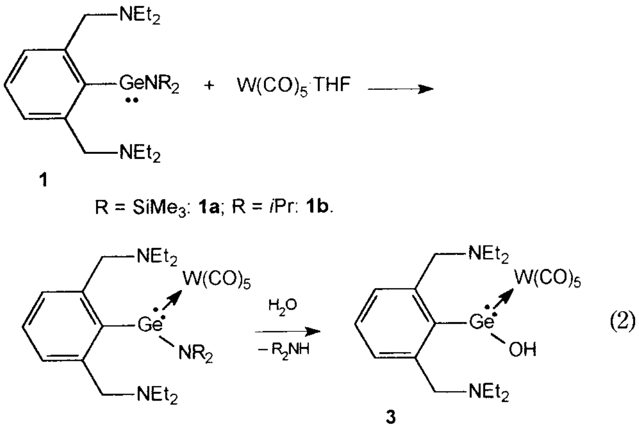


Figure 2.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 3

Ge(1)−N(2)	2.113(3)	C(1)−Ge(1)−N(2)	82.70(1)
Ge(1)−C(1)	1.975(3)	O(1)−Ge(1)−C(1)	106.18(1)
Ge(1)−O(1)	1.787(2)	O(1)−Ge(1)−N(2)	101.11(1)
Ge(1)−W(1)	2.595(0)	O(1)−Ge(1)−W(1)	119.78(8)
		N(2)−Ge(1)−W(1)	118.15(7)
		C(1)−Ge(1)−W(1)	121.63(9)

As expected, **1** are very sensitive toward water, a reaction that probably gives oligomeric germoxanes $(ArGeO)_n$. This is in agreement with the well-known instability of hydroxygermylenes toward self-condensation and could explain the absence, until now, of stable compounds of type RGeOH. However, we have succeeded in stabilizing such a derivative as a transition metal complex, the pentacarbonyltungsten complex **3** that was obtained by stoichiometric hydrolysis of **1**·W(CO)$_5$ (eq 2):



Complex **3** was isolated as a colorless powder, which is soluble in organic solvents. To our knowledge, **3** is the first stable hydroxygermylene complex, and crystals suitable for an X-ray structure analysis (Figure 2) were obtained. Crystallographic data are given in Table 1, and significant bond lengths and angles are reported in Table 3. As expected, the coordinate germanium−nitrogen interaction appears to be enhanced by the germanium−tungsten interaction: the distance Ge(1)−N(2) (2.113(3) Å) in **3** is significantly shorter than in compound **1** (2.390(3) Å). Moreover, the germanium−oxygen bond length (1.787(2) Å) is the shortest observed among covalent Ge(II)−O bonds; compare with Ge−O bond lengths in $(^tBu_3CO)_2Ge$ (1.832(1) and 1.896(6) Å),[7] in $Ge[OC_6H_2\text{-}4\text{-}Me\text{-}2,6\text{-}^tBu_2]_2$ (1.802(8) and 1.812(7) Å),[8] in the binuclear germanium calix[4]arene [^{t}BuCalix]Ge$_2$ (1.844(6) Å),[9] or in alkoxy-substituted compounds such as ArGeO^{i}Pr (1.856(2) Å) and ArGeOEt (1.844(3) Å)

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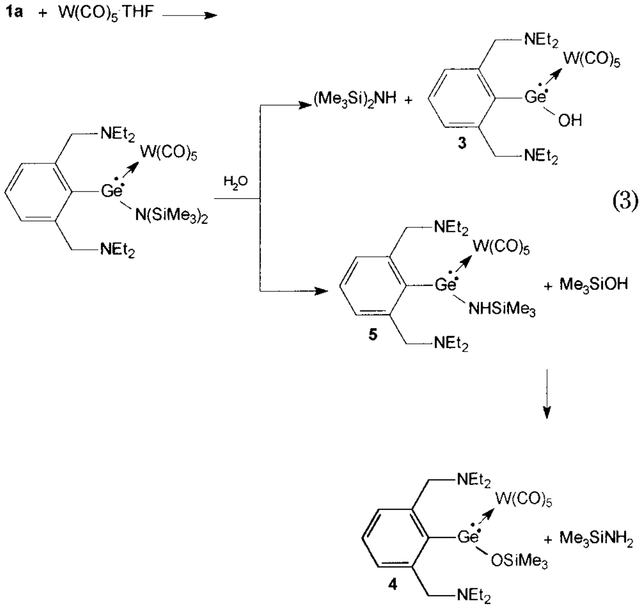
with, in the latter compounds, Ar = [2,4-di-^{t}Bu-6-((dimethylamino)methyl)phenyl].[1i] Among the known germylene–tungsten complexes, only six have been characterized by X-ray analysis: RR′GeW(CO)$_5$ complexes (**A**, R = C$_5$Me$_5$, R′ = Cl;[10] **B**, R = C$_5$Me$_5$, R′ = (Me$_3$Si)$_2$CH;[11] **C**, R = R′ = (2,4,6-^{t}Bu$_3$C$_6$H$_2$)Se;[12] **D**, R = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$, R′ = 2,4,6-^{i}Pr$_3$C$_6$H$_2$[13]) and, more recently, two germyl(germylene)–tungsten complexes (**E**, η^5-C$_5$Me$_4$EtW(CO)$_2$(=GeMe$_2$)(GeMe$_3$), and **F**, η^5-C$_5$Me$_5$W(CO)$_2$(=GeMe$_2$)(GeMe$_3$)).[14]

The hydrolysis of the aminogermylene–tungsten complex **1a**·W(CO)$_5$ gives not only the hydroxygermylene–tungsten complex **3** but also the siloxygermylene–tungsten complex **4** in appreciate yield (50%); **4** was characterized by ^{1}H and ^{13}C NMR and mass spectrometry. While **3** results by direct hydrolytic cleavage of the Ge–N bond, formation of **4** can be explained by the hydrolysis of a silicon–nitrogen bond to give the monosilylated complex **5** and trimethylsilanol. As it is well known, silanols R$_3$SiOH exhibit a significant acidity,[15] so the formation of **4** could result in the cleavage of the Ge–N bond of **5** by trimethylsilanol (eq 3):



While numerous amino- and thiogermylene–tungsten complexes have been described,[16] alkoxygermylene–tungsten complexes were unknown until now and the siloxygermylene complex **4** is the first example of this class of compounds.

The hydroxygermylene–tungsten complex **3** may be silylated by a standard silylating reagent (eq 4):

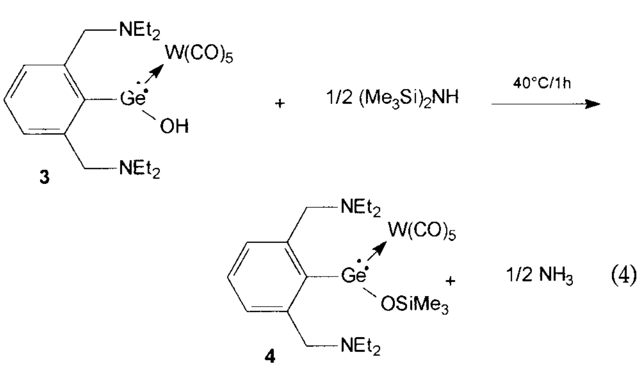


Table 4. Acidity of Several Alcohols and Comparison with 3

compound (solution 0.25 M)	ν(OH)[a] [cm^{-1}]	$\Delta\nu$(Et$_2$O)[b]
(C$_6$H$_5$)$_3$COH	3611	176
(C$_6$H$_5$)$_3$SiOH	3678	317
(C$_6$H$_5$)$_3$GeOH	3650	196
ArGeOH·W(CO)$_5$	3645	194

[a] Frequency of the free O–H band in cm^{-1}. [b] Frequency shift upon hydrogen bonding to diethyl ether in cm^{-1}.

In **3**, the germanol acidity is increased by the dative Ge→W complexation. Due to both side-chain coordination and germanium–tungsten bonding, the germanium atom in hydroxygermylene–tungsten **3** appears to be almost tetracoordinated. Therefore, it would be interesting to compare its acidity and the resulting reactivity with germanols, R$_3$GeOH. The acidity of compounds R$_3$MOH (M = group 14 element) has been examined from the change in OH infrared stretching frequency upon hydrogen bonding to a Lewis base such as diethyl ether.[17] In **3**, the frequency of the free OH bond was found at 3645 cm^{-1}, and the frequency shift upon hydrogen bonding to diethyl ether was 194 cm^{-1}. These values show for **3** an acidity in the same range as that of triphenylgermanol Ph$_3$GeOH (see Table 4). Moreover, our results confirm that the hydroxy compounds of germanium are weaker acids than the analogous silanols.

Conclusion

Properties of germanium–tungsten complexes often differ from the behavior of carbene analogues, and we can reasonably anticipate a specific activity of these species, especially in organometallic synthesis and in homogeneous catalysis. This study is in progress.

Experimental Section

Air and moisture were excluded from all reactions by use of standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by usual procedures and freshly distilled before use. ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.1 MHz, and ^{13}C NMR spectra at 62.9 MHz; we use C$_6$D$_6$ as deuterated solvent (chemical shifts are relative to SiMe$_4$). EI mass spectra were obtained at 70 eV on a Hewlett-Packard 5989 instrument, and samples were contained in glass capillaries under argon. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Melting points were taken on a Leitz Biomed hot-plate microscope apparatus in sealed capillary tubes under argon and are uncorrected. Elemental analyses were performed by the “Service de Microanalyse de l'Ecole de Chimie

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de Toulouse". The chlorogermylene ArGeCl (Ar = [2,6-bis(diethylamino)methyl]phenyl) was synthesized as described.[4]

ArGeN(SiMe$_3$)$_2$ [Ar = 2,6-(Et$_2$NCH$_2$)$_2$C$_6$H$_3$] **(1a)**. A solution of lithium bis(trimethylsilyl)amide (4.31 mmol) in Et$_2$O (10 mL) prepared by reaction of bis(trimethylsilyl)amine (0.91 mL, 4.31 mmol) with *n*-BuLi (1.6 M in hexane, 2.96 mL, 4.74 mmol) was added to a solution of ArGeCl (1.53 g, 4.31 mmol) in THF (15 mL) at −78 °C. The orange solution was allowed to warm to room temperature and stirred for 3 h. After removal of volatile materials, the residue was extracted with pentane (15 mL) and filtered. The filtrate was kept at −20 °C to give yellow crystals suitable for an X-ray analysis (0.85 g, 41%). Mp: 55 °C. ^{1}H NMR δ [ppm]: 0.08 (s, 9H, SiMe$_3$), 0.58 (s, 9H, SiMe$_3$), 0.92 (t, $^3J_{H/H} = 7.2$ Hz, 12H, CH$_3$(Et)), 2.59 (q, $^3J_{H/H} = 7.2$ Hz, 4H, CH$_2$(Et)), 2.68 (q, $^3J_{H/H} = 7.2$ Hz, 4H, CH$_2$(Et)), 3.39, 3.96 (AB system, $^2J_{H/H} = 14.6$ Hz, 4H, CH$_2$N), 6.98 (d, $^3J_{H/H} = 7.4$ Hz, 2H, 3,5-aryl-H), 7.15 (t, $^3J_{H/H} = 7.4$ Hz, 1H, 4-aryl-H). ^{13}C NMR δ [ppm]: 6.15, 6.87 (SiMe$_3$), 9.56 (CH$_3$(Et)), 45.94 (CH$_2$(Et)), 60.92 (CH$_2$N), 123.95 (3,5-aryl-C), 127.40 (4-aryl-C), 145.39 (2,6-aryl-C), 158.99 (1-aryl-C); EI-MS: *m/z* (%) 481 ($M^{\bullet+}$, 100), 321 (ArGe, 48). Anal. Calcd for $C_{22}H_{45}GeN_3Si_2$ (M_r = 480.38): C, 55.01; H, 9.44; N, 8.75. Found: C, 54.70; H, 9.65; N, 8.61.

ArGeN(^{i}Pr)$_2$ (1b). The same procedure as for **1a** was used for **1b** (1.45 g, 80%). ^{1}H NMR δ [ppm]: 0.93 (t, $^3J_{H/H} = 7.3$ Hz, 12H, CH$_3$(Et)), 1.01 (d, $^3J_{H/H} = 6.7$ Hz, 6H, CH$_3$(^{i}Pr)), 1.63 (d, $^3J_{H/H} = 6.7$ Hz, 6H, CH$_3$(^{i}Pr)), 2.65 (q, $^3J_{H/H} = 7.3$ Hz, 4H, CH$_2$(Et)), 2.66 (q, $^3J_{H/H} = 7.3$ Hz, 4H, CH$_2$(Et)), 3.48 (sept, $^3J_{H/H} = 6.7$ Hz, 2H, CH(^{i}Pr)), 3.53, 3.85 (AB system, $^2J_{H/H} = 14.0$ Hz, 4H, CH$_2$N), 7.16−7.21 (m, 3H, aryl-H). ^{13}C NMR δ [ppm]: 9.86 (CH$_3$(Et)), 25.0, 30.90 (CH$_3$(^{i}Pr)), 45.23 (CH$_2$(Et)), 53.44 (CH(^{i}Pr)), 60.88 (CH$_2$N), 124.70 (3,5-aryl-C), 127.21 (4-aryl-C), 145.78 (2,6-aryl-C), 158.32 (1-aryl-C). EI-MS: *m/z* (%): 421 ($M^{\bullet+}$, 8), 321 (ArGe, 100). Anal. Calcd for $C_{22}H_{41}GeN_3$ (M_r = 420.18): C, 62.89; H, 9.84; N, 10.0. Found: C, 62.35; H, 10.01; N, 9.83.

ArGeOMes [Mes = 2,4,6-Me$_3$C$_6$H$_2$] **(2)**. A solution of MesOH (0.19 g, 1.39 mmol) in THF (5 mL) was added slowly to a solution of **1b** (0.59 g, 1.39 mmol) in THF (5 mL) at −78 °C. The resulting solution was stirred for 30 min and heated at reflux for 1 h. The solvents were removed under vacuum to give a waxy product (0.48 g, 75%). ^{1}H NMR δ [ppm]: 0.80 (t, $^3J_{H/H} = 7.3$ Hz, 12H, CH$_3$(Et)), 2.25 (s, 3H, p-CH$_3$(Mes)), 2.41 (s, 6H, o-CH$_3$(Mes)), 2.565 (q, $^3J_{H/H} = 7.3$ Hz, 4H, CH$_2$(Et)), 2.57 (q, $^3J_{H/H} = 7.3$ Hz, 4H, CH$_2$(Et)), 3.48, 3.80 (AB system, $^2J_{H/H} = 14.0$ Hz, 4H, CH$_2$N), 6.71−7.16 (m, 5H, aryl-H, Mes-H). ^{13}C NMR δ [ppm]: 9.31 (CH$_3$(Et)), 19.69 (p-CH$_3$(Mes)), 20.69 (o-CH$_3$(Mes)), 44.84, 44.98 (CH$_2$(Et)), 59.15 (CH$_2$N), 123.68 (2,6-Mes-C), 123.89 (3,5-aryl-C), 128.34 (4-aryl-C), 128.74 (4-Mes-C), 129.46 (3,5-Mes-C), 145.43 (2,6-aryl-C), 152.2 (1-Mes-C), 158.78 (1-aryl-C). EI-MS: *m/z* (%): 337 ($M^{\bullet+}$ − Mes, 10), 321 (ArGe, 100). Anal. Calcd for $C_{25}H_{38}GeN_2O$ (M_r = 455.18): C, 65.97; H, 8.41; N, 6.15. Found: C, 66.65; H, 8.78; N, 5.51.

ArGeOH·W(CO)$_5$ (3) and ArGeOSiMe$_3$·W(CO)$_5$ (4). To a solution of W(CO)$_5$·THF (1.27 mmol), prepared by the photolysis of W(CO)$_6$ (0.45 g, 1.27 mmol) in 50 mL of THF using a low-pressure mercury immersion lamp in a quartz tube, was added a solution of **1a** (0.61 g, 1.27 mmol) in THF (10 mL) at room temperature. The resulting yellow solution was stirred for 2 h. Then, a stoichiometric amount of water (1.27 mmol) was added to the mixture, which was stirred for a further 1 h. After removal of the solvent under reduced pressure, the residual yellow oil was subjected to column chromatography (SiO$_2$, MeOH). Two successive yellow fractions were isolated. The first fraction gave **4** as a waxy material (0.46 g, 50%). The second fraction gave pure crystals of **3** suitable for X-ray analysis after storage of the pentane solution at −20 °C for 2 days (0.30 g, 36%).

ArGeOH·W(CO)$_5$ (3). Yield: 36%, 0.30 g. Mp: 110 °C. ^{1}H NMR δ [ppm]: 0.77 (t, $^3J_{H/H} = 7.2$ Hz, 12H, CH$_3$(Et)), 2.44 (q, $^3J_{H/H} = 7.2$ Hz, 4H, CH$_2$(Et)), 2.51 (q, $^3J_{H/H} = 7.2$ Hz, 4H, CH$_2$(Et)), 3.08, 3.79 (AB system, $^2J_{H/H} = 13.7$ Hz, 4H, CH$_2$), 5.78 (s, 1H, OH), 6.83 (d, $^3J_{H/H} = 7.9$ Hz, 2H, 3,5-aryl-H), 6.96 (t, $^3J_{H/H} = 7.9$ Hz, 1H, 4-aryl-H). ^{13}C NMR δ [ppm]: 9.92 (CH$_3$(Et)), 45.55 (CH$_2$(Et)), 58.39 (CH$_2$N), 126.87 (3,5-aryl-C), 129.13 (4-aryl-C), 140.63 (2,6-aryl-C), 153.44 (1-aryl-C), 199.23 (CO), 201.37 (CO). IR (C$_6$D$_6$): 2060, 1970, 1925 cm^{-1} ($\nu_{C=O}$). EI-MS: *m/z* (%) 660 ($M^{\bullet+}$, 1), 642 ($M^{\bullet+}$ − H$_2$O, 2), 604 ($M^{\bullet+}$ − 2CO, 2), 520 ($M^{\bullet+}$ − 5CO, 3), 321 (ArGe, 100). Anal. Calcd for $C_{21}H_{28}N_2GeO_6W$ (M_r = 660.90): C, 38.16; H, 4.27; N, 4.24. Found: C, 37.93; H, 4.04; N, 4.01.

ArGeOSiMe$_3$·W(CO)$_5$ (4). Yield: 50%, 0.46 g. ^{1}H NMR δ [ppm]: 0.13 (s, 9H, OSiMe$_3$), 0.85 (t, $^3J_{H/H} = 7.2$ Hz, 12H, CH$_3$(Et)), 2.65 (q, $^3J_{H/H} = 7.2$ Hz, 8H, CH$_2$(Et)), 3.68, 3.94 (AB system, $^2J_{H/H} = 15$ Hz, 4H, CH$_2$), 7.16−7.32 (m, 3H, aryl-H). ^{13}C NMR δ [ppm]: 2.58 (SiMe$_3$), 11.11 (CH$_3$(Et)), 47.53 (CH$_2$(Et)), 58.49 (CH$_2$N), 124.81 (3,5-aryl-C), 130.19 (4-aryl-C), 143.04 (2,6-aryl-C), 148.75 (1-aryl-C), 199.55 (CO), 200.57 (CO). IR (C$_6$D$_6$): 2061, 1971, 1924 cm^{-1} ($\nu_{C=O}$). EI-MS: *m/z* (%) 732 ($M^{\bullet+}$, 2), 642 ($M^{\bullet+}$ − HOSiMe$_3$, 17), 321 (ArGe, 66), 73 (SiMe$_3$, 100). Anal. Calcd for $C_{24}H_{36}GeN_2O_6SiW$ (M_r = 733.09): C, 39.32; H, 4.95; N, 3.82. Found: C, 40.47; H, 5.53; N, 3.47.

Silylation of 3. Bis(trimethylsilyl)amine (0.019 g, 0.12 mmol) was added slowly via a microsyringe to a stirring solution of **3** (0.15 g, 0.23 mmol) in toluene (5 mL) at room temperature. The mixture was heated at 40 °C for 1 h, and after evaporation of solvent and ammonia, **4** was obtained (0.15 g, 89%).

X-ray Structure Determination for 1a and 3. Data of **1a** and **3** were collected at low temperature on an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. The structures were solved by direct methods (SHELXS-97)[18] and refined by the least-squares method on F^2.[19] The *R* values are defined as R1 = $\sum|F_o| - |F_c|/\sum|F_o|$ and wR2 = $(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. Crystal data and structure refinement details are listed in Table 1.

Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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