Synthesis and Crystal Structure of the First Base-Free Diarylgermylene–Transition Metal Mononuclear Complexes

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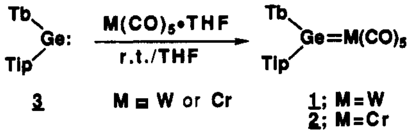
The first base-free diarylgermylene–transition metal mononuclear complexes Tb(Tip)Ge=M(CO)$_5$ (**1**, M = W; **2**, M = Cr; Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl) were synthesized by the reaction of a new type of kinetically stabilized diarylgermylene Tb(Tip)Ge: (**3**), obtained by the treatment of germanium(II) iodide with bulky aryllithiums (TbLi and TipLi), with the corresponding pentacarbonylmetal(0)–tetrahydrofuran complexes of group 6 metals (W and Cr). Of the two diarylgermylene–group 6 metal complexes (**1** and **2**), the molecular structure of **1** was determined by X-ray crystallographic analysis. Crystal data with Mo Kα radiation (λ = 0.710 69 Å): **1**, $C_{47}H_{82}GeO_5Si_6W$, triclinic, space group $P\bar{1}$, a = 12.490(2) Å, b = 23.890(3) Å, c = 10.254(1) Å, α = 96.21(1)°, β = 105.52(1)°, γ = 89.82(1)°, V = 2930(1) Å^3, Z = 2, R = 0.045, R_w = 0.045 based on 8032 reflections with $I > 3\sigma(I)$ together with 541 variable parameters.

Introduction

The coordination chemistry of germylenes, well-known as highly reactive, unstable, low-coordinate germanium species, has been an active area of fascinating research for both organometallic and inorganic chemists.[1] Although there have been a number of reports concerning the synthesis and characterization of germylene–transition metal complexes including both base-stabilized[1b] and base-free[1f–h] species, they are restricted to examples of dialkyl- and heteroatom-substituted germylenes.[2] Numerous complexes of this type, but not with aryl attachments, are also described in a recent review dealing with the role of heavy group 14 element carbene analogues in transition metal chemistry.[1c] The lack of diarylgermylene complexes is mainly due to the absence of a suitable precursor, i.e., a diarylgermylene stable at ambient temperature. With regard to dialkylgermylenes, Lappert et al. have described the first stable compound $[(Me_3Si)_2CH]_2Ge$: in 1976,[2a,b] and very recently a genuinely monomeric dialkylgermylene $[(Me_3Si)_3C][(Me_3Si)_2CH]Ge$: has been synthesized and characterized by Jutzi et al.[3] However, as for the diaryl-substituted counterpart there have been no examples of stable germylenes at ambient temperature. We describe here the first synthesis of base-free diarylgermylene–pentacarbonylmetal(0) mononuclear complexes of group 6 metals (**1**, M = W; **2**, M = Cr) by the reaction of a new type of kinetically stabilized diarylgermylene Tb(Tip)Ge: (**3**) with the corresponding pentacarbonylmetal(0)–tetrahydrofuran complexes (Scheme 1). We also report the X-ray crystallographic structural analysis of the germylene–tungsten(0) complex **1**.

Scheme 1



Results and Discussion

1. Preparation of a Kinetically Stabilized Diarylgermylene Tb(Tip)Ge:, 3. In advance of metal complexation, we examined the preparation of a new type of kinetically stabilized diarylgermylene Tb(Tip)Ge: (**3**, Tip = 2,4,6-triisopropylphenyl) by taking advantage of an effective steric protective group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb in this paper), which was recently developed by us.[4] Germylene **3** was readily obtained by the treatment of a THF solution of TbLi[5] with a THF suspension of germanium(II) iodide (1.0 equiv)[6] in the presence of hexamethylphosphoramide (HMPA, 5.0 equiv) at −78 °C and stirring of the solution at −45 °C for 10 h, followed by addition of a THF solution of an equimolar amount of TipLi[5] at this temperature and gradual warming to room temperature (Scheme 2). Ger-

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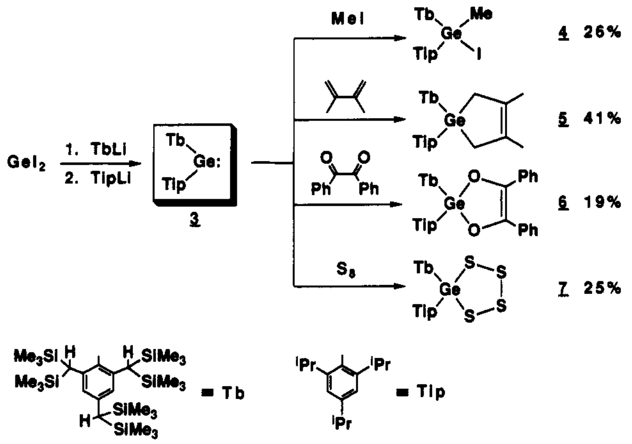
Scheme 2



mylene 3 showed a dark red color in THF and a brownish green color (λ_{max} = 580 nm) after solvent exchange into hexane. Studies on the electronic spectra of a variety of germylenes generated in glass matrices at cryogenic temperatures have revealed that introduction of bulky substituents on a germanium atom resulted in dramatic red shifts of the n-p transition of germylenes [for example: Ph$_2$Ge: (466 nm), Mes$_2$Ge: (550 nm), and Tip$_2$Ge: (558 nm); Mes = 2,4,6-trimethylphenyl].[7] The remarkable red shift observed for the λ_{max} value of 3 (580 nm) is consistent with these results and it is the longest λ_{max} value reported so far for diarylgermylenes. In the absence of HMPA no germylene 3 was formed probably due to the bulkiness of the Tb group which hindered the nucleophilic attack of TipLi onto TbGeI. However, HMPA is not indispensable for the stabilization of germylene 3, since the absence of HMPA was confirmed in the NMR spectra of the hexane solution containing 3 which was separated from insoluble material by decantation under an inert atmosphere.

Under an inert atmosphere germylene 3 was found to be stable in solution, in contrast to bis(2,4,6-tri-*tert*-butylphenyl)germylene prepared by du Mont et al., the sterically most crowded diarylgermylene reported so far, which reportedly survived only below −10 °C and underwent intramolecular cyclization at higher temperatures.[8] It was found that in the UV–vis spectra of 3 the wavelength and absorption coefficient of the absorption at 580 nm were almost unchanged in hexane within a temperature range from −73 to 60 °C, indicating the absence of an equilibrium between monomeric 3 and the corresponding dimer, digermene. The high stability of 3 as a monomer is noteworthy in view of Masamune's report[9] that the reductive coupling of dichloro(2,6-diisopropylphenyl)-mesitylgermane produces the corresponding digermene, Tip(Mes)Ge=Ge(Mes)Tip, which shows no tendency of dissociation into a germylene. However, the possibility cannot be ruled out that germylene 3 exists as an associated chemical species having a weak Ge···Ge interaction, since we have no further conclusive experimental support for the molecularity of 3. The formation of 3 was chemically evidenced by trapping experiments at room temperature using methyl iodide, 2,3-dimethyl-1,3-butadiene, and benzil, giving the expected insertion or [1 + 4] cycloaddition products such as 4 (26%), 5 (41%), and 6 (19%), respectively (Scheme 2). Furthermore, germylene 3 reacted with elemental sulfur in refluxing THF to give the corresponding tetrathiagermolane 7 in 25% yield (Scheme 2).[10]

2. Metal Complexation of Germylene 3 with Transition Metal Carbonyl Complexes. The remarkable stability and versatile reactivities of the sterically protected germylene 3 prompted us to examine its complexation with transition metal carbonyl complexes. When a THF solution of 3 was treated with an excess (2.0 equiv) of W(CO)$_5$·THF,[11] the expected mononuclear germylene–tungsten complex 1 was isolated as reddish-orange crystals in 6% yield (Scheme 1). The analogous pentacarbonylchromium(0) complex 2 was also obtained in 6% yield as bright orange crystals by the reaction of 3 with Cr(CO)$_5$·THF under reaction conditions similar to those used for the tungsten complex 1 (Scheme 1). After chromatographic separation, complexes 1 and 2 were purified by recrystallization from ethanol–dichloromethane (1:1) and they showed satisfactory spectral and analytical data. In the ^{13}C NMR spectrum (CDCl$_3$ at 125 MHz), 1 showed two signals at 198.12 (*cis*-C=O, $^1J_{W-C}$ = 123.6 Hz) and 202.27 (*trans*-C=O, $^1J_{W-C}$ = 139.2 Hz) ppm, while those for 2 were observed at 216.88 and 223.30 ppm. The IR spectra of both the complexes exhibited three bands [2065 (s), 1982 (w), and 1948 cm^{-1} (vs) for 1 and 2052 (s), 1961 (sh), and 1952 cm^{-1} (vs) for 2, respectively], which are attributable to the infrared-active carbonyl stretching frequencies (2A$_1$ + E) predicted by group theoretical consideration on the basis of "local" C_{4v} symmetry for the M(CO)$_5$ fragment.[12] These infrared absorptions in the region of carbonyl stretching vibrations are very similar to those of other group 6 metal complexes with carbene-analogous ligands.[1b,g,13,14] As indicated in the NMR spectra of 1 and 2 as well as by their elemental analysis, no interaction was observed between the germanium atom and the solvent used (THF). The complexes 1 and 2 represent the first examples of base-free, mononuclear diarylgermylene–transition metal complexes, although there have been some examples for dialkyl- and heteroatom-substituted germylenes.[15]

3. Structure Description of Tb(Tip)Ge=W(CO)$_5$ (1). Although the spectroscopic and analytical data for 1 and 2 provided valuable structural information, the detailed bonding of the pentacarbonylmetal(0) to the germanium atom required an X-ray structure analysis. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. Selected bond distances and bond angles are given in Table 1. Of particular note among the structural features is that the steric repulsion between the carbonyl groups of W(CO)$_5$ moiety and the two different types of the bulky aryl groups leads to opening of the angle of W(1)–Ge(1)–C(1) [138.9(2)°] at the expense of that of W(1)–Ge(1)–C(2) [112.2(2)°]. Although such steric hindrance is also responsible for the elongation of

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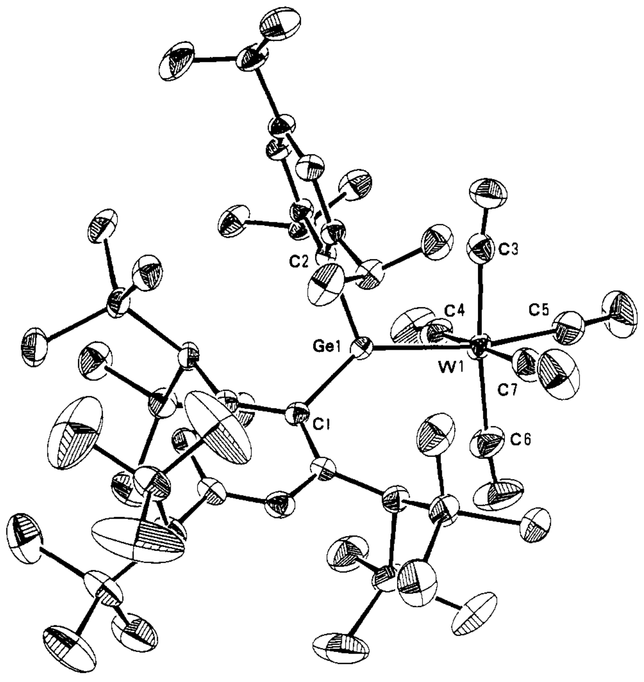

Figure 1. ORTEP drawing of $\mathrm{Tb(Tip)Ge{=}W(CO)_5}$ (**1**) with the thermal ellipsoid plot (30% probability).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Tb(Tip)Ge{=}W(CO)_5}$ (1)

W(1)–G(1)	2.5934(8)	Ge(1)–C(1)	1.988(6)
Ge(1)–C(2)	1.999(6)	W(1)–C(3)	2.017(8)
W(1)–C(4)	1.999(9)	W(1)–C(5)	1.971(9)
W(1)–C(6)	2.005(9)	W(1)–C(7)	2.00(1)
C(1)–Ge(1)–W(1)	138.9(2)	C(2)–Ge(1)–W(1)	112.2(2)
C(1)–Ge(1)–C(2)	108.4(2)	Ge(1)–W(1)–C(3)	84.9(2)
Ge(1)–W(1)–C(4)	91.0(2)	Ge(1)–W(1)–C(5)	169.8(2)
Ge(1)–W(1)–C(6)	101.2(2)	Ge(1)–W(1)–C(7)	93.0(2)
C(3)–W(1)–C(4)	96.1(3)	C(3)–W(1)–C(5)	85.0(3)
C(3)–W(1)–C(6)	173.8(3)	C(3)–W(1)–C(7)	86.8(3)
C(4)–W(1)–C(5)	88.5(3)	C(4)–W(1)–C(6)	84.7(3)
C(4)–W(1)–C(7)	175.3(3)	C(5)–W(1)–C(6)	88.9(3)
C(5)–W(1)–C(7)	88.0(3)	C(6)–W(1)–C(7)	92.1(4)

the Ge–W bond distance [2.5934(8) Å] in comparison with those observed in the closely related compounds [2.528(1) Å for $\mathrm{(ArSe)_2Ge{=}W(CO)_5}$[1h] (Ar = 2,4,6-tri-*tert*-butylphenyl) and 2.511(1) Å for $\mathrm{(C_5Me_5)ClGe{=}W(CO)_5}$[16]], the Ge—W bond length of **1** is still shorter than that of $\mathrm{(C_5Me_5)[(Me_3Si)_2CH]Ge{=}W(CO)_5}$ [2.632(2) Å].[17] These facts suggest that the character of the Ge—W bond of this family seems to be affected to a considerable extent by the electronic effect of the substituents on the germanium atom.

The noticeable stability of the diarylgermylene **3** and its group 6 metal complexes **1** and **2** here obtained is most likely due to the great steric demand of the combination of Tb and Tip groups.

Experimental Section

General Procedure. All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. Silica gel column chromatography and dry column chromatography (DCC) were performed with Wakogel C-200 and ISN silica DCC 60A, respectively. Preparative thin-layer chromatography was carried out with Merck Kieselgel $60PF_{254}$ Art. 7747. The ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured in $CDCl_3$ with a Bruker AM-500 spectrometer using $CHCl_3$ as an internal standard. In the ^1H NMR spectra of the reaction products some broad singlet signals were observed instead of the expected doublet or septet signals, most likely because of the restricted rotation of Tb and Tip groups caused by their large steric hindrance. In the case of tetrathiagermolane **7** the ^1H and ^{13}C NMR spectra were described as coalesced at 67 °C because of the complexity and obscurity of those observed at room temperature. In the ^1H and ^{13}C NMR spectral data of **1**, **2**, and **4–7** assignments of the observed signals except for quaternary carbons are given in parentheses. Infrared spectra were obtained with a Horiba FT-200 spectrometer. Electronic spectra were measured on a JASCO Ubest-50 spectrometer. Melting points were determined on a Yanaco micro melting point apparatus.

Preparation of a Solution of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germylene (3). To a THF solution (5 mL) of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbBr)[4a] (600 mg, 0.949 mmol) was added *t*-BuLi (1.60 M in pentane; 1.25 mL, 2.1 equiv) at −78 °C to give a yellow solution of TbLi.[5] After the addition of hexamethylphosphoramide (0.83 mL, 5.0 equiv), to this solution was added a THF suspension (13 mL) of germanium(II) iodide (310 mg, 0.949 mmol) in some portions by means of a transfer tube at −78 °C. After stirring for 1.0 h at −45 °C, the reaction mixture was treated with a THF solution (5 mL) of TipLi, which was prepared from 1-bromo-2,4,6-triisopropylbenzene (296 mg, 1.1 equiv) in a manner similar to that of TbLi, to afford a bright yellow solution. The mixture turned dark red by gradual warming to room temperature during 2 h and then the volatile substances were removed in vacuo. To the residual dark brown paste was added 15 mL of degassed dry hexane to give a brownish green hexane solution of germylene **3**.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}iodo(2,4,6-triisopropylphenyl)methylgermane (4). To a hexane solution (5 mL) of germylene **3** prepared according to the procedure described above starting from 400 mg (0.633 mmol) of TbBr was added methyl iodide (0.2 mL, 3.2 mmol) by means of a microsyringe at room temperature, during which time the green color of the reaction mixture faded out and turned yellow. After removal of the solvent under reduced pressure, the residual pale yellow oil was subjected to column chromatography (SiO_2/hexane) followed by GPLC separation to yield {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}iodo(2,4,6-triisopropylphenyl)methylgermane (**4**) as a colorless solid (159 mg, 26%). Pure white crystals of **4** were obtained by recrystallization from $EtOH/CH_2Cl_2$ (1:1). **4**: white crystals, mp 118–120 °C dec; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.06 (s, 9H, $SiMe_3$), −0.01 (s, 9H, $SiMe_3$), 0.04 (s, 27H, 3 × $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 1.03 (br s, 3H, Tip-*o*-CH*Me*Me′), 1.19 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me₂*), 1.24 (br s, 9H, Tip-*o*-CHMe*Me′* + Tip-*o′*-CH*Me₂*), 1.29 (s, 1H, Tb-*p*-methine), 1.64 (s, 3H, GeMe), 2.15 (br s, 1H, Tb-*o*- or Tb-*o′*-methine), 2.25 (br s, 1H, Tb-*o*- or Tb-*o′*-methine), 2.62 (sept, *J* = 7 Hz, 1H, Tip-*p*-methine), 3.16 (br s, 1H, Tip-*o*- or Tip-*o′*-methine), 3.58 (br s, 1H, Tip-*o*- or Tip-*o′*-methine), 6.28 (s, 1H, Tb-*m*- or Tb-*m′*-arom), 6.40 (s, 1H, Tb-*m*- or Tb-*m′*-arom), 6.98 (br s, 1H, Tip-*m*- or Tip-*m′*-arom), 7.01 (br s, 1H, Tip-*m*- or TIp-*m′*-arom); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.89 (q, $SiMe_3$), 0.92 (q, $SiMe_3$), 1.84 (q, $SiMe_3$), 1.89 (q, $SiMe_3$), 2.10 (q, $SiMe_3$), 2.18 (q, $SiMe_3$), 18.71 (q, GeMe), 23.13 (q, Tip-*o*-CH*Me₂*), 23.80 (q, Tip-*p*-CH*Me₂*), 24.46 (q, Tip-*o′*-CH*Me₂*), 26.91 (d, Tb-*o*-CH), 27.36 (d, Tb-*o′*-CH), 30.33 (d, Tb-*p*-CH), 32.86 (d, Tip-*o*- or Tip-*o′*-CH), 33.59 (d, Tip-*o*- or Tip-*o′*-CH), 34.22 (d, Tip-*p*-CH), 121.58 (d, Tip-*m*-arom), 123.56 (d, Tb-*m*-arom), 123.81 (d, Tip-*m′*-arom), 128.71 (d, Tb-*m′*-arom), 131.29 (s), 136.45 (s), 144.11 (s), 149.54 (s), 150.10

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(s), 150.31 (s), 151.49 (s), 154.32 (s). Anal. Calcd for $C_{43}H_{85}GeISi_6\cdot 0.5CH_2Cl_2$: C, 51.60; H, 8.56. Found: C, 51.34; H, 8.95. When germylene **3** prepared from 400 mg (0.633 mmol) of TbBr in 15 mL of THF was treated with 0.2 mL (3.2 mmol) of methyl iodide, 103.3 mg (17%) of **4** was obtained after the same workup procedure as above.

Preparation of 1-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1-(2,4,6-triisopropylphenyl)-3,4-dimethyl-1-germa-3-cyclopentene (5). To a hexane solution (5 mL) of germylene **3** prepared according to the procedure described above starting from 600 mg (0.949 mmol) of TbBr was added 2,3-dimethyl-1,3-butadiene (0.3 mL, 2.7 mmol) by means of a microsyringe at room temperature, during which time the green color of the reaction mixture faded out gradually. After overnight stirring at room temperature, the reaction mixture became a pale red suspension. After removal of the solvent under reduced pressure, the residual red oil was subjected to column chromatography (SiO_2/hexane) followed by GPLC separation to give 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-(2,4,6-triisopropylphenyl)-3,4-dimethyl-1-germa-3-cyclopentene (**5**) as a colorless solid (350 mg, 41%). Pure white crystals of **5** were obtained by recrystallization from EtOH/CH_2Cl_2 (1:1). **5**: white crystals, mp 177.5–179.5 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.07 (s, 18H, 2 × SiMe$_3$), −0.01 (s, 18H, 2 × SiMe$_3$), 0.02 (s, 18H, 2 × SiMe$_3$), 1.10 (br d, J = 6 Hz, 12H, 2 × Tip-*o*-CH*Me*$_2$), 1.20 (d, J = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.25 (s, 1H, Tb-*p*-C*H*), 1.73 (s, 6H, 2 × Me), 1.83 (s, 1H, Tb-*o*-CH), 1.89 (s, 1H, Tb-*o*′-CH), 2.17 (d, J = 17 Hz, 2H, methylene), 2.39 (d, J = 17 Hz, 2H, methylene), 2.82 (sept, J = 7 Hz, 1 H, Tip-*p*-CH), 3.19 (sept, J = 6 Hz, 2H, Tip-*o*- and Tip-*o*′-CH), 6.23 (s, 1H, Tb-*m*-arom), 6.39 (s, 1H, Tb-*m*′-arom), 6.95 (s, 2H, Tip-*m*- and Tip-*m*′-arom); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.93 (q, SiMe$_3$), 1.92 (q, SiMe$_3$), 2.04 (q, SiMe$_3$), 19.12 (q, –C(*Me*)=C(*Me*)–), 23.55 (q, Tip-*o*-CH*Me*$_2$), 23.95 (q, Tip-*p*-CH*Me*$_2$), 27.17 (d, Tb-*o*-CH), 27.64 (d, Tb-*o*′-CH), 27.81 (q, Tip-*o*′-CH*Me*$_2$), 29.96 (d, Tb-*p*-CH), 34.25 (d, Tip-*p*-CH), 34.39 (d, Tip-*o*- and Tip-*o*′-CH), 36.50 (t, methylene), 121.89 (d, Tip-*m*-arom), 122.64 (d, Tb-*m*-arom), 128.37 (d, Tb-*m*′-arom), 130.99 (s), 134.16 (s), 140.26 (s), 142.25 (s), 148.49 (s), 150.06 (s), 150.36 (s), 152.77 (s). Anal. Calcd for $C_{48}H_{92}GeSi_6\cdot H_2O$: C, 62.10; H, 10.21. Found: C, 62.20; H, 10.02. When germylene **3** prepared from 400 mg (0.633 mmol) of TbBr in 15 mL of THF was treated with 0.2 mL (1.8 mmol) of 2,3-dimethyl-1,3-butadiene, 63 mg (11%) of **5** was obtained after the same workup procedure as above.

Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-diphenyl-3,4-dioxagerma-3-cyclopentene (6). A THF solution (15 mL) of germylene **3** prepared from 600 mg (0.949 mmol) of TbBr in a manner similar to the above experiments was treated with benzil (1.40 g, 6.64 mmol) dissolved in 7 mL of THF at room temperature. The reaction mixture first turned black and then the color of the mixture faded out gradually. After the solution was stirred overnight and concentrated under reduced pressure, the residual yellow oil was submitted to chromatography (SiO_2/hexane) followed by GPLC separation to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-diphenyl-3,4-dioxagerma-3-cyclopentene (**6**) as a colorless solid (187 mg, 19%). Pure white crystals of **6** were obtained by recrystallization from EtOH/CH_2Cl_2 (1:1). **6**: white crystals, mp 244–245 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.07 (s, 18H, 2 × SiMe$_3$), −0.05 (s, 18H, 2 × SiMe$_3$), 0.04 (s, 18H, 2 × SiMe$_3$), 1.19 (br s, 12H, 2 × Tip-o-CH*Me*$_2$), 1.21 (d, J = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.33 (s, 1H, Tb-*p*-CH), 2.30 (br s, 1H, Tb-*o*-CH), 2.60 (br s, 1H, Tb-*o*′-CH), 2.85 (sept, J = 7 Hz, 1H, Tip-*p*-CH), 3.42 (sept, J = 7 Hz, 2H, 2 × Tip-*o*-CH), 6.31 (s, 1H, Tb-*m*-arom), 6.45 (s, 1H, Tb-*m*′-a rom), 7.05 (s, 2H, Tip-*m*-arom), 7.11 (t, J = 7 Hz, 2H, Ph-*p*-arom), 7.15 (m, 4H, Ph-*m*-arom), 7.44 (d, J = 7 Hz, 4H, Ph-*o*-arom); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.89 (q, SiMe$_3$), 1.13 (q, SiMe$_3$), 1.33 (q, SiMe$_3$), 22.69 (q, Tip-*o*-CH*Me*$_2$), 23.86 (q, Tip-*p*-CH*Me*$_2$), 27.73 (d, Tb-*o*-CH), 28.85 (d, Tb-*o*′-CH), 30.77 (d, Tb-*p*-CH), 34.42 (d, Tip-*o*-CH), 34.60 (d, Tip-*p*-CH), 122.02 (d, Tip-*m*-arom), 123.29 (d, Tb-*m*-arom), 126.36 (d, Ph-*p*-arom), 127.50 (d, Ph-*m*-arom), 127.93 (d, Ph-*o*-atom), 128.50 (d, Tb-*m*′-arom), 129.63 (s), 134.55 (s), 135.40 (s), 137.78 (s), 145.86 (s), 150.43 (s), 150.88 (s), 151.35 (s), 153.55 (s). Anal. Calcd for $C_{56}H_{92}GeO_2Si_6\cdot H_2O$: C, 63.67; H, 8.97. Found: C, 63.72; H, 8.68. When germylene **3** prepared from 400 mg (0.633 mmol) of TbBr in 6 mL of hexane was treated with 266 mg (1.27 mmol) of benzil dissolved in 8 mL of hexane, 95.6 mg (15%) of **6** was obtained after the same workup procedure as above.

Preparation of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiagermolane (7). To a THF solution (15 mL) of germylene **3** prepared from 400 mg (0.633 mmol) of TbBr according to the procedure described above was added a THF solution (16 mL) of elemental sulfur (324.8 mg, 1.27 mmol as S_8) at −78 °C. After gradual warming to room temperature, formation of a small amount of 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiagermolane (**7**) was ascertained by thin-layer chromatography (TLC) monitoring. After refluxing further for 3 days the reaction mixture was concentrated under reduced pressure to give a brown residue, which was subjected to dry column chromatography (SiO_2/hexane) followed by GPLC separation to give 149 mg (25%) of **7** as a pale yellow solid. Pure pale yellow crystals of **7** were obtained by recrystallization from EtOH/$CHCl_3$ (1:1). **7**: pale yellow crystals, mp 211–212 °C; ^1H NMR ($CDCl_3$, 500 MHz, 67 °C) δ 0.03 (s, 36H, 4 × SiMe$_3$), 0.07 (s, 18H, 2 × SiMe$_3$), 1.16 (d, J = 7 Hz, 12H, Tip-*o*-CH*Me*$_2$), 1.21 (d, J = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.35 (s, 1H, Tb-*p*-CH), 2.07 (br s, 2H, Tb-*o*-CH), 2.83 (sept, J = 7 Hz, 1H, Tip-*p*-CH), 3.78 (br s, 2H, Tip-*o*-CH), 6.41 (br s, 2H, Tb-*m*- and Tb-*m*′-arom), 7.03 (s, 2H, Tip-*m*- and Tip-*m*′-arom); ^{13}C NMR ($CDCl_3$, 125 MHz, 67 °C) δ 1.01 (q, SiMe$_3$), 2.33 (q, SiMe$_3$), 23.73 (q, Tip-*o*-CH*Me*$_2$), 24.39 (q, Tip-*p*-CH*Me*$_2$), 28.74 (d, Tb-*p*-CH), 30.96 (d, Tb-*o*-CH), 34.27 (d, Tip-*p*-CH), 35.79 (d, Tip-*o*-CH), 123.41 (d, Tb-*m*-arom), 123.63 (d, Tb-*m*′-arom), 129.27 (d, Tip-*m*-arom), 132.74 (s), 137.40 (s), 145.57 (s), 150.67 (s), 151.19 (s), 151.71 (s), 152.55 (s). Anal. Calcd for $C_{42}H_{82}GeS_4Si_6$: C, 52.73; H, 8.64; S, 13.40. Found: C, 52.68; H, 8.48; S, 12.96.

Preparation of [{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germylidene]pentacarbonyltungsten(0) (1). To a THF solution (15 mL) of germylene **3**, prepared from 1.00 g (1.58 mmol) of TbBr according to the procedure described above, was added an excess amount (2.0 equiv) of $W(CO)_5\cdot THF$, which was prepared by the photolysis of $W(CO)_6$ (1.113 g, 3.16 mmol) in 10 mL of THF using a 400-W medium pressure mercury lamp. After stirring for 2 days at room temperature, the volatile substances were removed in vacuo, and to the residue was added dry hexane (15 mL). After removal of the insoluble substances by filtration, the reaction mixture was evaporated to give an orange solid. The orange solid was subjected to flash column chromatography (SiO_2/hexane) followed by GPLC separation to afford the pentacarbonyltungsten(0) complex **1** (114 mg, 6.3%) as orange crystals. Pure crystals of **1** were obtained by recrystallization from EtOH/CH_2Cl_2 (1:1). **1**: reddish orange crystals, mp 187 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.05 (s, 9H, SiMe$_3$), 0.00 (s, 18H, 2 × SiMe$_3$), 0.04 (s, 9H, SiMe$_3$), 0.08 (s, 9H, SiMe$_3$), 0.11 (s, 9H, SiMe$_3$), 0.94 (br s, 3H, Tip-*o*-CH*Me*Me′), 1.18 (d, J = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.21 (br s, 6H, Tip-*o*′-CH*Me*$_2$), 1.30 (br s, 3H, Tip-*o*-CHMe*Me*′), 1.37 (s, 1H, Tb-*p*-CH), 2.30 (br s, 1H, Tb-*o*-CH), 2.66 (br s, 1H, Tb-*o*′-CH), 2.81 (br s, 1H, Tip-*o*- or Tip-*o*′-CH), 2.82 (sept, J = 7 Hz, 1H, Tip-*p*-CH), 3.32 (br s, 1H, Tip-*o*- or Tip-*o*′-CH), 6.48 (s, 1H, Tb-*m*-arom), 6.51 (s, 1H, Tb-*m*′-arom), 6.75 (s, 1H, Tip-*m*-arom), 6.87 (s, 1H, Tip-*m*′-arom); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.38 (q, SiMe$_3$), 1.08 (q, SiMe$_3$), 1.46 (q, SiMe$_3$), 1.62 (q, SiMe$_3$), 2.09 (q, SiMe$_3$), 2.21 (q, SiMe$_3$), 23.92 (q, Tip-*p*-CH*Me*$_2$), 24.73 (q, Tip-*o*-CH*Me*Me′), 24.77 (q, Tip-*o*′-CH*Me*Me′), 26.38 (d, Tb-*o*-CH), 27.00 (d, Tb-*o*′-CH), 27.69 (q, Tip-*o*-CHMe*Me*′), 29.28 (q, Tip-*o*′-CHMe*Me*′), 31.92 (d, Tb-*p*-CH), 34.24 (d, Tip-*p*-CH), 36.05 (d, Tip-*o*-CH), 37.12 (d, Tip-*o*′-CH), 122.55 (d, Tip-*m*-arom), 122.91 (d, Tip-*m*′-arom), 124.76 (d, Tb-*m*-arom), 130.28 (d, Tb-*m*′-arom), 147.00 (s), 147.92 (s), 148.88 (s), 150.32 (s), 150.41 (s), 150.62 (s), 157.45 (s), 157.61 (s), 198.12 (s, J_{W-C} = 123.6 Hz, *cis*-

CO), 202.27 (s, $J_{\mathrm{W-C}}$ = 139.2 Hz, *trans*-CO); IR ($\mathrm{CCl_4}$) 1948, 1982, 2065 cm^{-1}; UV–vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max}$ 310 (ϵ 5100), 346 (4600), 427 (13 000) nm. Anal. Calcd for $\mathrm{C_{47}H_{82}GeO_5Si_6W}$: C, 49.00; H, 7.17. Found: C, 48.56; H, 7.20.

Preparation of [{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germylidene]pentacarbonylchromium(0) (2). To a THF solution (15 mL) of germylene **3**, prepared from 800 mg (1.24 mmol) of TbBr according to the procedure described above, was added an excess amount (3.5 equiv) of $\mathrm{Cr(CO)_5 \cdot THF}$,[12] which was prepared by the photolysis of $\mathrm{Cr(CO)_6}$ (980 mg, 4.34 mmol) in 10 mL of THF. After stirring for 36 h at room temperature, the volatile substances were removed in vacuo, and to the residue was added dry hexane (15 mL). After removal of the insoluble substances by filtration, the reaction mixture was evaporated to give a yellowish orange solid. The orange solid was subjected to flash column chromatography ($\mathrm{SiO_2}$/hexane) followed by GPLC separation to afford the pentacarbonylchromium(0) complex **2** (71.5 mg, 5.5%) as bright orange crystals. Pure crystals of **2** were obtained by recrystallization from $\mathrm{EtOH/CH_2Cl_2}$ (1:1). **2**: bright orange crystals, mp 157 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ −0.03 (s, 9H, $\mathrm{SiMe_3}$), 0.01 (s, 9H, $\mathrm{SiMe_3}$), 0.03 (s, 9H, $\mathrm{SiMe_3}$), 0.06 (s, 9H, $\mathrm{SiMe_3}$), 0.09 (s, 9H, $\mathrm{SiMe_3}$), 0.11 (s, 9H, $\mathrm{SiMe_3}$), 0.96 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*Me′), 1.15 (d, *J* = 6 Hz, 3H, Tip-*o*-CHMe*Me′*), 1.18 (d, *J* = 7 Hz, 6H, Tip-*p*-CHMe_2), 1.21 (d, *J* = 7 Hz, 3H, Tip-*o′*-CH*Me*Me′), 1.32 (d, *J* = 7 Hz, 3H, Tip-*o′*-CHMe*Me′*), 1.37 (s, 1H, Tb-*p*-C H), 2.26 (s, 1H, Tb-*o*-CH), 2.65 (s, 1H, Tb-*o′*-CH), 2.72 (br s, 1H, Tip-*o*- or Tip-*o′*-CH), 2.82 (sept, *J* = 7 Hz, 1H, Tip-*p*-CH), 3.16 (br s, 1H, Tip-*o*- or Tip-*o′*-CH), 6.50 (s, 1H, Tb-*m*-arom), 6.52 (s, 1H, Tb-*m′*-arom), 6.87 (s, 1H, Tip-*m*-arom), 6.93 (s, 1H, Tip-*m′*-arom); ^{13}C NMR ($\mathrm{CDCl_3}$, 125 MHz) δ 1.07 (q, $\mathrm{SiMe_3}$), 1.42 (q × 2, $\mathrm{SiMe_3}$), 1.66 (q, $\mathrm{SiMe_3}$), 2.15 (q × 2, $\mathrm{SiMe_3}$), 23.88 (q, Tip-*p*-CHMe_2), 24.90 (q, Tip-*o*-CH*Me*Me′), 24.93 (q, Tip-*o*-CHMe*Me′*), 26.33 (d, Tb-*o*-CH), 26.85 (d, Tb-*o′*-CH), 27.85 (q, Tip-*o′*-CH*Me*Me′), 29.14 (q, Tip-*o′*-CHMe*Me′*), 31.85 (d, Tb-*p*-CH), 34.24 (d, Tip-*p*-CH), 36.56 (d, Tip-*o*-CH), 37.25 (d, Tip-*o′*-CH), 122.51 (d, Tip-*m*-arom), 122.81 (d, Tip-*m′*-atom), 124.59 (d, Tb-*m*-atom), 130.02 (d, Tb-*m′*-arom), 147.10 (s), 147.58 (s), 148.34 (s), 150.13 (s), 150.46 (s), 150.49 (s), 157.41 (s), 160.62 (s), 216.88 (s, *cis*-CO), 223.30 (s, *trans*-CO); IR ($\mathrm{CCl_4}$) 1952, 1961, 2052 cm^{-1}; UV–vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max}$ 303 (sh, ϵ 3700), 347 (3600), 434 (9200) nm. Anal. Calcd for $\mathrm{C_{47}H_{82}CrGeO_5Si_6}$: C, 55.33; H, 8.10. Found: C, 55.38; H, 7.87.

Single-Crystal X-ray Diffraction Analysis of 1. Single crystals of **1** suitable for X-ray diffraction analysis were grown by recrystallization from $\mathrm{EtOH/CH_2Cl_2}$ (1:1). All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and a 12-kW rotating anode generator. Initial lattice parameters were determined from 16 accurately centered reflections with 2θ values in the range from 5.0 to 60.0°. Cell constants and other pertinent data were collected and are listed in Table 2. The data were collected at 25 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 60.1°. Of the 17 817 reflections which were collected, 17 097 were unique (R_{int} = 0.032). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 26.7 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied and resulted in transmission factors ranging from 0.76 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was first solved by using the heavy-atom method (Patterson synthesis),[18] which revealed the positions of tungsten and germanium atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located in the calculated positions. The final cycle of full-matrix least-squares refinement was based on 8032 observed reflections [$I > 3\sigma(I)$] and 541 variable parameters and converged (largest parameter shift was 0.04 times its esd) with unweighted and weighted agreement factors of R = 0.045 and R_w = 0.045. Final values of selected bond distances and angles are listed in Table 1. All calculations were performed using the TEXSAN[19] crystallographic software package of the Molecular Structure Corp.

Table 2. Crystal and Intensity Collection Data for Tb(Tip)Ge=W(CO)$_5$ (1)

mol formula	$\mathrm{C_{47}H_{82}O_5GeSi_6W}$
mol wt	1152.11
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.490(2)
b, Å	23.890(3)
c, Å	10.254(1)
α, deg	96.21(1)
β, deg	105.52(1)
γ, deg	89.82(1)
V, Å^3	2930(1)
Z	2
D_{calc}, g cm^{-3}	1.306
cryst dimens, mm	0.30 × 0.30 × 0.30
linear abs coeff, cm^{-1}	26.66
radiation	Mo Kα (λ = 0.710 69 Å)
2θ range, deg	5–60
scan type	$2\theta/\omega$
total no. of rflns scanned	17 817
no. of unique rflns	17 097
no. of obsd rflns	8032 [$I > 3\sigma(I)$]
no. of variables	541
R	0.045
R_{W}	0.045
residual electron density, e Å^{-3}	+0.73/−1.08

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Supplementary Material Available: Tables of crystallographic data, complete bond lengths, angles, thermal and positional parameters, and least-squares planes for 1 (44 pages). Ordering information is given on any current masthead page.

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