Tantalum-Mediated Substitution at Germanium: A Germolyl-to-Germole Transformation Leading to η^4-$C_4Me_4GeMeCl$ Complexes

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The germole reagent $C_4Me_4GeMeSiMe_3$ (**1**), synthesized via reaction of $K[C_4Me_4GeSiMe_3]$ with MeI, reacted with $TaCl_5$ to give $[(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3(Et_2O)_x]_2$ (**2**; $x = 0.5-1.0$) with loss of Me_3SiCl. Complex **2** reacted with various two-electron donors to give stable adducts $(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3L$ (**3**, L = PPh_3; **4**, L = CNXyl; Xyl = 2,6-dimethylphenyl) and $(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3L_2$ (**5**, L = CNXyl; **6**, L = pyridine). The X-ray structure of $(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3(CNXyl)_2$ (**5**) confirmed η^4-coordination of the germole unit and the *exo* orientation of the Ge−Cl bond. Complex **2** also reacted with CpTl to give air-stable $Cp(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_2$ (**7**), which was also characterized by X-ray crystallography. Attempts to generate η^5-germolyl tantalum complexes are described.

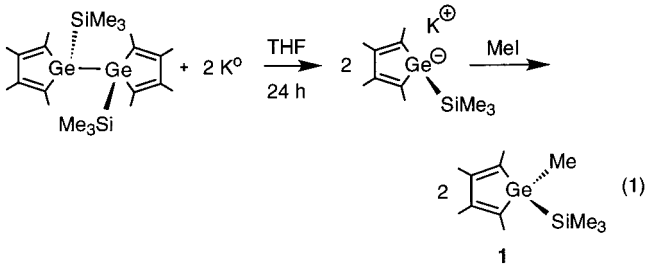
Introduction

Recently, considerable progress has been made in developing the chemistry of silolyl and germolyl anions.[1] Free silolyl and germolyl anions of the type $[C_4Me_4ER]^-$ (E = Si or Ge) have been shown to possess pyramidal Si or Ge centers and bond-localized structures.[2] However, we have shown that coordination of these species to an electron-rich or electron-poor transition metal fragment promotes delocalization of electron density in the heterole ring.[3] Furthermore, it appears that zirconium and hafnium complexes of $[C_4Me_4ER]^-$ exhibit a rich reaction chemistry.[4] Unfortunately, the development of this chemistry has been somewhat limited by the lack of general routes to d^0 complexes with germolyl and silolyl ligands.

The synthesis of early transition metal complexes containing the Cp* (Cp* = C_5Me_5) ligand typically involves reaction of a transition metal halide with an alkali metal derivative of Cp* in a salt metathesis reaction. Initially, we sought to employ an analogous method (starting from $M[C_4Me_4ER]$ reagents, where M = Li or K)[2] in the synthesis of η^5-germolyl and η^5-silolyl complexes of the early transition metals. However, this technique is not general, as only metal complexes of zirconium and hafnium have been synthesized by this route.[3,4] Given the fact that early transition metal Cp* complexes may also be prepared via reaction of Cp^*SiMe_3 with a metal halide,[5] we anticipated that a similar method might be useful in preparing germolyl complexes of the group 4 and 5 metals. Here we report an attempt to employ this strategy in the synthesis of η^5-germolyl complexes of tantalum, which leads to rearrangements that instead give η^4-germole complexes.

Results and Discussion

The synthesis of η^5-germolyl complexes via Me_3SiCl elimination requires a reagent analogous to Cp^*SiMe_3. Reaction of the previously reported dimer $(C_4Me_4GeSiMe_3)_2$ with 2 equiv of potassium metal in THF resulted in formation of a deep red solution of the alkali metal salt $K[C_4Me_4GeSiMe_3]$.[2] Treatment of this solution with a slight excess of MeI cleanly gave the new germole $C_4Me_4GeMeSiMe_3$ (**1**, eq 1). Compound **1** was isolated as a colorless oil in 80% yield after removal of the volatile materials and extraction into pentane.



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Reaction of **1** with $TiCl_4$, $ZrCl_4$, or $HfCl_4$ (CH_2Cl_2, benzene, or THF; room temperature) did not result in

(1) For a review on the recent chemistry of group 14 metalloles see: Dubac, J.; Guérin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds, Part II*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 3, Chapter 34.

(2) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(3) (a) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1744. (b) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8428. (c) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 8245.

(4) (a) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097. (b) Dysard, J. M.; Tilley, T. D. *Organometallics* **2000**, *19*, 2671.

(5) (a) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. (b) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisha, N.; Kasai, N. *Organometallics* **1988**, *7*, 2266. (c) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105. (d) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.

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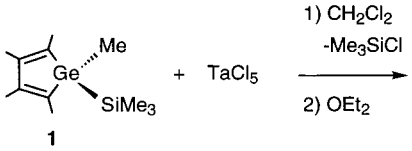
the clean formation of germolyl-containing species (by ^{1}H NMR spectroscopy). In addition, **1** did not react with other Hf-containing starting materials ($CpHfCl_3$, Cp^*HfCl_3, or Cp^*HfMe_2Cl) even after refluxing in CH_2Cl_2 or THF. In contrast, treatment of a suspension of $TaCl_5$ in CH_2Cl_2 with a colorless pentane solution of **1** at room temperature resulted in the immediate formation of a deep purple solution. Addition of Et_2O to this solution, followed by concentration and cooling to −80 °C, gave a green microcrystalline precipitate (71% yield), which was characterized by NMR spectroscopy as a germole complex of tantalum. Additional characterization data (vide infra) allowed us to formulate the product as $[(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3(Et_2O)_x]_2$ (**2**, $x = 0.5-1$, eq 2). Whereas the reaction in eq 2 proceeds in CH_2Cl_2 solvent, no reaction occurs in benzene, toluene, tetrahydrofuran, diethyl ether, or pentane.



1

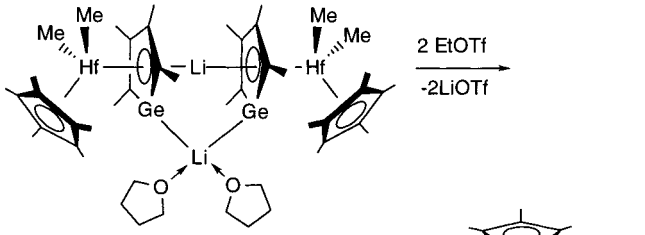
$$[(\eta^4\text{-}C_4Me_4GeMeCl)TaCl_3(OEt_2)_x]_2 \quad (2)$$

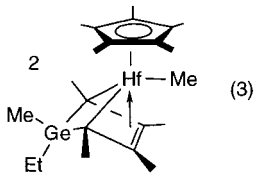
2

The characterization of **2** as a dimer is based on a solution molecular weight measurement (Signer method).[6] Dimer **2** crystallizes with variable amounts of coordinated Et_2O (between 1 and 2 equiv per dimer, by ^{1}H NMR spectroscopy). It is worth noting that the ^{1}H NMR spectrum of **2** exhibits only one set of resonances for the germole ligands, independent of the amount of ether present. Interestingly, **2** could not be isolated in the absence of ether, and exposure of isolated **2** to dynamic vacuum resulted in loss of the ether and decomposition of the dimer to a brown oily material, which exhibited an array of peaks in its ^{1}H NMR spectrum. Given these facts, we assume that the ether is coordinated to the Ta center in **2**, although this has not been proven definitively. Finally, we believe that the chloride atom bound to Ge adopts an *exo* position relative to Ta. This formulation is based on the structure of an adduct of **2** (vide infra).

The ^{1}H NMR spectrum of **2** is quite simple, as it exhibits three resonances at δ 2.31, 3.10 (ring Me protons), and 0.82 (Ge−Me protons) for equivalent η^4-germole ligands (eq 2). The ^{13}C NMR spectrum of **2** contains resonances at δ 109.0 and 145.5 corresponding to the germole ring carbons. The large separation between these shifts, as well as the upfield shift for the resonance of the carbon α to Ge, indicates a $\sigma^2-\pi$ type bonding of the diene portion of the germole ring to tantalum.[4] For comparison, the analogous resonances in the η^5-germolyl complex $Cp^*(\eta^5\text{-}C_4Me_4GeSiMe_3)HfCl_2$ appear at δ 135.8 and 146.0, while the germole complex $Cp^*(\eta^4\text{-}C_4Me_4Ge^tBuMe)HfMe$ exhibits comparable shifts at δ 96.0 and 131.1.[3c,4] It is interesting to note that related processes of this type, involving migration to germanium, seem to pervade the early-metal chemistry of germolyl ligands, as previously observed for a related Hf system (eqs 3 and 4).[4]

(6) (a) Signer, R. *Liebigs Ann. Chem.* **1930**, *478*, 246. (b) Zoellner, R. W. *J. Chem. Educ.* **1990**, *67*, 714.





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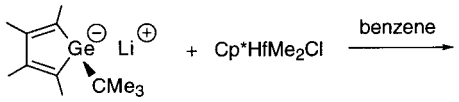
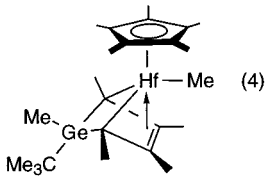
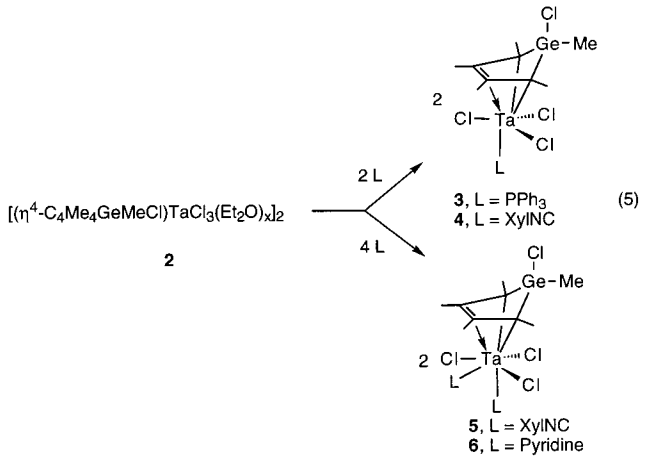




(4)

We sought to obtain structural information on **2** to define the coordination mode of the germole ring. Unfortunately, X-ray quality crystals of **2** could not be obtained despite repeated attempts. Fortunately, compound **2** reacts with two-electron donors to give stable adducts (eq 5, Xyl = 2,6-dimethylphenyl). The formulation of compounds **3** and **4** as monomers is based on a solution molecular weight determination of the xylylisocyanide adduct **4**.[6]



(5)

Compounds **4**, **5**, and **6** are formed in excellent yields (86−94%), while **3** could only be isolated as a somewhat impure, green solid in 67% yield (ca. 90% pure by ^{1}H NMR spectroscopy). All of these compounds, like **2**, display very large differences in the ^{13}C NMR chemical shifts for their germole ring carbons, suggesting η^4-coordination. It is worth noting that the ^{1}H NMR spectra for the monoadducts **3** and **4** exhibit rather broad resonances at room temperature which sharpen upon warming to 70 °C. This may indicate a ligand dissociation/association process.

X-ray quality crystals of bright green **5** were obtained by slow cooling of a concentrated toluene solution to −35

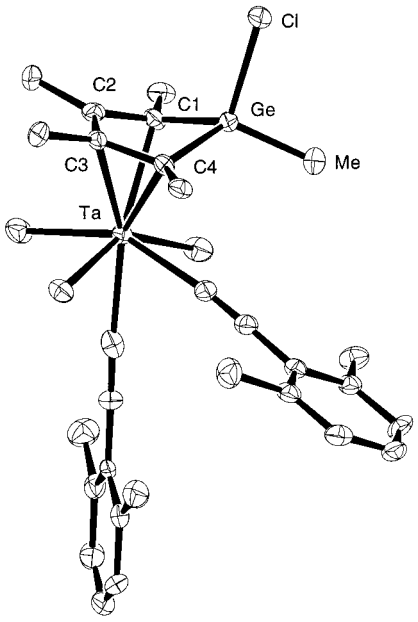
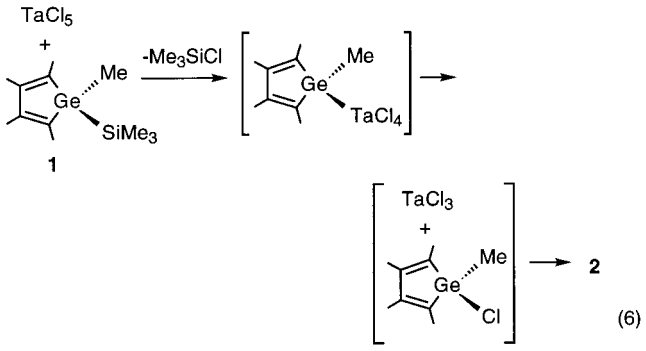


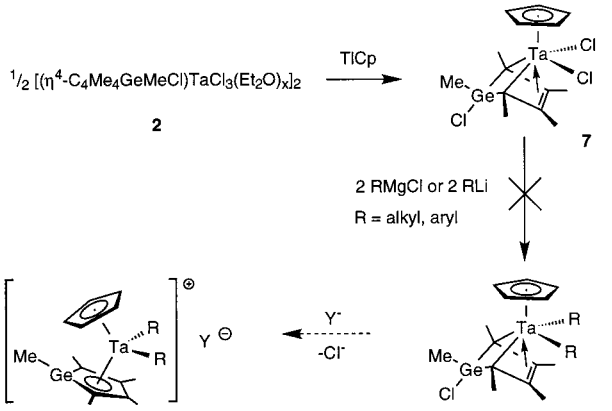
Figure 1. ORTEP diagram of (η^4-$C_4Me_4GeMeCl$)$TaCl_3$-$(CNXyl)_2$ (**5**).

°C, and the molecular structure is shown in Figure 1. X-ray crystallography clearly confirmed η^4-coordination of the germole ring to the Ta center of **5**. Interestingly, the chlorine atom bonded to Ge is *exo* to the metal atom. This suggests that the process by which the chlorine atom shifts to Ge may not involve simple migration to an η^5-germolyl ligand and that the reaction may occur via bimolecular chlorine transfer or ionization of a chloride ligand. Alternatively, the germole Me_4C_4-GeMeCl may form by reductive elimination from an η^1-germole complex (eq 6). The germole ligand may then simply bind preferentially to the face of the ring which allows for back-donation into the Ge−Cl σ^* orbital. The lengthening of the Ge−Cl bond in **2** (vide infra) suggests that such donation may significantly influence the energy of the germole−tantalum bonding.



The molecular structure of **5** may be described as involving a pseudo-octahedral tantalum center ligated by η^4-germole, Cl, and XylNC ligands. The Ge atom in the ring is pseudo-tetrahedral, and the Ge−C bonds in the ring (1.932(6) and 1.924(6) Å) are similar in length to those for the neutral germole $C_4Me_4GeHSi(SiMe_3)_3$ (1.944(3) and 1.948(3) Å).[7] In addition, the Ge atom is displaced 0.75 Å from the plane defined by the four C atoms of the diene unit. The C(2)−C(3) distance, 1.415(9) Å, is shorter than both the C(1)−C(2) (1.456(8) Å) and C(3)−C(4) (1.425(9) Å) distances, although the differences are relatively small. These C−C distances are very similar to the corresponding ones in TaCl(η^4-$C_{10}H_8$)-$(dmpe)_2$[8] (1.416(7), 1.457(7), and 1.435(7) Å, respectively) and follow a pattern previously observed for Fe−diene complexes.[9] Interestingly, the Ge−Cl bond in **5** is long (2.250(2) Å) and comparable in length with the *exo*-Ge−Cl bond in Cp*RuCl(η^4-$C_4Me_4GeCl_2$) (2.246(2) Å).[3a] For the latter case, the discrepancy between this Ge−Cl bond length and the other (2.151(3) Å) was interpreted in terms of donation of electron density from the Ru atom into the *exo*-Ge−Cl σ^* orbital.[3a] This back-bonding may also be occurring in **5**, and this could explain a thermodynamic preference for the observed germole bonding mode. Finally, the three chlorine atoms bound to Ta and one XylNC ligand are bent away from the germole and define a Cl_3C plane from which the Ta center is displaced by 0.66 Å.

Scheme 1



We envisioned converting the η^4-germole in **2** to an η^5-coordinated ligand via exchange of the chloride atom bound to Ge for a less coordinating anion (Scheme 1). This strategy has been employed previously in attempts to generate η^5-germolyl complexes of the later transition metals, albeit without success.[10]

Reactions of **2** with Cp*Li and Cp*MgCl (tetrahydrofuran or toluene, −80 °C) yielded only complex mixtures of products (by ^{1}H NMR spectroscopy). Also, treatment of **2** with several Cp-transfer reagents (CpNa, CpMgCl, Cp_2Mg, in THF, Et_2O, or benzene) did not produce the desired product cleanly. However, reaction of **2** with CpTl in toluene at −78 °C resulted in formation of a deep green solution, from which Cp(η^4-$C_4Me_4GeMeCl$)-$TaCl_2$ (**7**) was isolated as bright green crystals in 78% yield. Surprisingly, compound **7** is air-stable in both the solid state and in benzene-d_6 solution for a period of days and is only slowly hydrolyzed (several hours, benzene-d_6, room temperature, large excess of water), giving an array of unidentified products as determined by ^{1}H NMR spectroscopy. In addition, as in the case of η^4-germole complexes described earlier, the difference

(7) Freeman, W. P.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L.; Gantzel, P. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1887.

(8) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

(9) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522.

(10) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265−282.

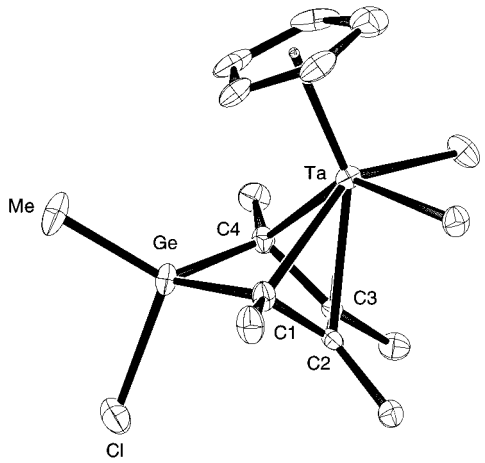


Figure 2. ORTEP diagram of Cp(η^4-$C_4Me_4GeMeCl$)$TaCl_2$ (**7**).

in the ^{13}C NMR shifts for the germole ring carbons of **7** is quite large (53.7 ppm) compared with analogous shifts for an η^5-coordinated germolyl ligand.[3c,4]

The molecular structure of **7** was established by single-crystal X-ray diffraction (Figure 2). As for **5**, the structure of **7** is best described as involving a 1,4-diyl bonding mode for the germole ligand. The Ge atom is displaced 1.07 Å from the least-squares plane defined by C(1), C(2), C(3), and C(4). Also, in contrast to **5**, the C(2)−C(3) bond distance (1.401(5) Å) is somewhat shorter than both the C(1)−C(2) (1.470(5) Å) and C(3)−C(4) (1.465(5) Å) bond lengths, as seen in the related complex $CpTaCl_2(C_4H_6)$.[11] In addition, the Ta−C bond lengths to the diene portion of the η^4-germole ligand (2.411(4), 2.408(4), 2.298(4), 2.282(4) Å) are more similar to the related distances in $CpTaCl_2(C_4H_6)$ (2.424(11), 2.410(12) Å; 2.257(11), 2.258(12) Å) than to those in **5**.[11] Finally, the angle between the C(1)−C(2)−C(3)−C(4) and C(1)−Ta−C(4) planes (91.04°) is similar to the same angles in both **5** (95.24°) and $CpTaCl_2(C_4H_6)$ (94.9°).[11]

We initially focused on the conversion of **7** to a dialkyl species according to Scheme 1. Reactions with various alkylating reagents (Me_2Zn, MeMgCl, BnMgCl, Bn_2Mg, BnLi(Et_2O), BnK, $ClMgCH_2SiMe_3$, $LiCH_2SiMe_3$, Me_3Al, NpLi, NpMgBr; Bn = CH_2Ph, Np = CH_2CMe_3) gave only complex mixtures of products (by ^1H NMR spectroscopy). In addition, reactions of **7** with lithium amides ($LiN(SiMe_3)_2$, $LiNEt_2$) and LiPhC=CPh−CPh=CPhLi did not result in isolated products. However, analysis of the NMR spectra of these product mixtures suggests that alkylation occurs most rapidly at germanium, as species containing only one alkyl substituent appear to possess mirror-plane symmetry. Finally, reactions of **7** with Me_3SiOTf or AgOTf in benzene-d_6 resulted in an array of unidentified products (by ^1H NMR spectroscopy).

In conclusion, we have shown that loss of Me_3SiCl upon reaction of a germole reagent possessing a Me_3Si substituent with an early metal halide is a viable route to metal germole complexes. The reaction of C_4Me_4-GeMeSiMe$_3$ (**1**) with $TaCl_5$ did not produce the desired η^5-germacyclopentadienyl complex, but instead proceeded via chloride transfer to Ge with formation of an η^4-germole ligand. It would seem that early metal germolyl complexes are prone to this type of process, as it has now been observed in several different systems.[4a] Thus far, the compounds in hand have not proven to be viable precursors to tantalum η^5-germolyl complexes.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed throughout. Pentane, THF, toluene, and diethyl ether were distilled from sodium/benzophenone, CH_2Cl_2 was distilled from CaH_2, and benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. The compounds $[C_4Me_4GeSiMe_3]_2$[2] and CpTl[12] were prepared according to literature procedures. MeI and pyridine were purchased from Aldrich and distilled prior to use. PPh_3 and XylNC were purchased from Aldrich and recrystallized prior to use, while $TaCl_5$ was purchased from Strem and sublimed. NMR spectra were recorded at 300 or 500 MHz (^1H) with Bruker AMX-300 and DRX-500 spectrometers or at 125 MHz ($^{13}C\{^1H\}$) with a DRX-500 spectrometer at ambient temperature unless otherwise noted. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. IR samples of solid materials were prepared as KBr pellets, while IR spectra of oils were obtained with neat samples between CsI plates. All IR absorptions are reported in cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

$C_4Me_4Ge(Me)SiMe_3$ (1). A 200 mL Schlenk tube was charged with $[C_4Me_4GeSiMe_3]_2$ (2.000 g, 3.94 mmol) and K metal (0.320 g, 8.18 mmol), and 100 mL of THF was added to generate a light orange solution. This solution was stirred for 1 week, after which time all of the potassium had been consumed and the solution had turned to a deep red color. The flask was placed in an ice bath, and the solution was cooled to 0 °C. MeI (0.520 mL, 8.27 mmol) was then added to the flask, resulting in formation of a white cloudy suspension. This suspension was allowed to warm to room temperature and was then stirred for 1 h. The volatile materials were removed under dynamic vacuum, and the resulting residue was extracted with pentane (3 × 30 mL). Pentane was removed from the extracts to give the product as a colorless oil in 80% yield (1.690 g, 6.30 mmol). This oil was purified by a short-path distillation (bp 48 °C, 1×10^{-3} Torr). ^1H NMR (benzene-d_6): δ 0.16 (s, 9 H, GeSi*Me*$_3$), 0.43 (s, 3 H, Ge*Me*), 1.82 (s, 6 H, C_4*Me*$_4$Ge), 2.03 (s, 6 H, C_4*Me*$_4$Ge). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ −7.31 (s, Ge*Me*), −0.29 (s, GeSi*Me*$_3$), 16.72, 14.88 (s, C_4*Me*$_4$Ge), 146.02, 135.04 (s, *C*$_4$Me$_4$Ge). Anal. Calcd for $C_{12}H_{24}GeSi$: C, 53.58; H, 8.99. Found: C, 52.66; H, 9.26. IR: 2951 s br, 2905 s br, 2851 s br, 1551 w, 1441 m, 1399 sh, 1245 s, 1058 m, 839 s, 785 s, 741 m, 693 m, 622 m, 578 m, 484 m.

[(η^4-$C_4Me_4GeMeCl$)$TaCl_3(OEt_2)_{0.8}$]$_2$ (2). A 150 mL Schlenk tube was charged with $TaCl_5$ (1.92 g, 5.36 mmol). A separate 100 mL Schlenk tube was charged with **1** (1.44 g, 5.36 mmol). Then 50 mL of CH_2Cl_2 was added to the flask containing $TaCl_5$, generating a cloudy white suspension, and **1** was dissolved in 50 mL of pentane. The pentane solution of **1** was added to the flask containing $TaCl_5$ at room temperature via cannula, to give a deep purple solution. This solution was stirred for 1 h, after which time it was filtered via cannula into a 200 mL Schlenk tube. To the resulting purple solution was added 50 mL of Et_2O, and the solution was concentrated until a green precipitate began to form (to ca. 100 mL). The resulting mixture was cooled to −80 °C to give **2** as a green powder in

(11) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(12) Nielson, A. J.; Rickard, C. E. F.; Smith, J. M. *Inorg. Synth.* **1990**, *28*, 315.

71% yield (2.20 g, 3.81 mmol). ^{1}H NMR (benzene-d_6): δ 0.82 (s, 3 H, Ge*Me*), 1.11 (t, 4.8 H, (C*H*$_3$CH$_2$)$_2$O), 2.31 (s, 6 H, C$_4$*Me*$_4$Ge), 3.10 (s, 6 H, C$_4$*Me*$_4$Ge), 3.26 (q, 3.2 H, (CH$_3$C*H*$_2$)$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6): δ 5.94 (s, Ge*Me*), 15.58, 16.93 (s, C$_4$*Me*$_4$Ge), 16.03 (s, (*C*H$_3$CH$_2$)O), 66.37 (s, (CH$_3$*C*H$_2$)O), 109.02, 145.51 (*C*$_4$Me$_4$Ge). Anal. Calcd for C$_{12.2}$H$_{23}$Cl$_4$GeO$_{0.8}$Ta: C, 25.36; H, 4.01. Found: C, 25.67; H, 4.10. IR: 2945 br s, 2909 s, 2856 s, 1442 s, 1379 s, 1319 w, 1108 m, 1014 m, 801 s, 757 br m. Mp: 120−123 °C dec. Molecular weight in CH_2Cl_2: 1110 g mol^{-1}. Calcd for the dimer (including 0.8 mol of OEt_2 per Ta): 1155 g mol^{-1}.

(η^4-C$_4$Me$_4$GeMeCl)TaCl$_3$(PPh$_3$) (3). A 50 mL Schlenk tube was charged with **2** (0.257 g, 0.44 mmol), and a separate 50 mL Schlenk tube was charged with PPh_3 (0.117 g, 0.44 mmol). Then 20 mL of toluene was added to each flask via cannula. The colorless solution of PPh_3 was added to the flask containing the purple solution of **2**. An immediate reaction took place, as evidenced by the precipitation of a green solid. The purple solution was cooled to −35 °C to give **3** as a green microcrystalline solid in 67% yield (0.233 g, 0.30 mmol). This material could not be separated from impurities (ca. 90% pure by ^{1}H NMR), and thus satisfactory combustion analysis data could not be obtained. ^{1}H NMR (toluene-d_8, 70 °C): δ 0.86 (s, 3 H, Ge*Me*), 2.45 (s, 6 H, C$_4$*Me*$_4$Ge), 3.13 (s, 6 H, C$_4$*Me*$_4$Ge), 7.06, 7.34 (br m, 15 H, P*Ph*$_3$). ^{13}C{^{1}H} NMR (toluene-d_8, 70 °C): δ 5.4 (s, Ge*Me*), 15.1, 16.4 (s, C$_4$*Me*$_4$Ge), 109.0 (s, *C*$_4$Me$_4$Ge), 134.2 (br d, P*Ph*$_3$), 137.4, 137.6, 137.8 (s, P*Ph*$_3$), 144.7 (s, *C*$_4$Me$_4$Ge). IR: 2961 br m, 2907 br m, 2854 br m, 1651 m, 1438 s, 1262 w, 1101 m, 1016 w, 1019 m, 746 m.

(η^4-C$_4$Me$_4$GeMeCl)TaCl$_3$(CNXyl) (4). To a toluene (10 mL) solution of **2** (0.205 g, 0.35 mmol) was added XylNC (0.047 g, 0.35 mmol) in 10 mL of toluene. The resulting solution was stirred for 1 h and then concentrated to 10 mL and cooled to −35 °C to give **4** as a red crystalline solid in 93% yield (0.214 g, 0.33 mmol). ^{1}H NMR (benzene-d_6): δ 1.14 (br s, 3 H, Ge*Me*), 1.92 (br s, 6 H, C$_4$*Me*$_4$Ge), 2.61 (br s, 6 H, C$_4$*Me*$_4$Ge), 3.03 (s, 6 H, (C$_6$H$_3$*Me*$_2$)NC), 6.43 (br d, $^3J_{HH}$ = 8 Hz, 2 H, (C$_6$*H*$_3$Me$_2$)NC), 6.66 (br t, $^3J_{HH}$ = 8 Hz, 1 H, (C$_6$*H*$_3$Me$_2$)NC). ^{13}C{^{1}H} NMR (benzene-d_6): δ 5.55 (br s, Ge*Me*), 15.83 (s, (C$_6$H$_3$*Me*$_2$)NC), 18.51, 18.85 (s, C$_4$*Me*$_4$Ge), 106.81 (br s, *C*$_4$Me$_4$Ge), 129.81, 130.51, 131.21, 136.75 (s, *Xyl*NC), 136.55 (br s, *C*$_4$Me$_4$Ge), 185.90 (s, XylN*C*). Anal. Calcd for C$_{17}$H$_{24}$Cl$_4$GeNTa: C, 32.02; H, 3.79; N, 2.20. Found: C, 32.41; H, 3.78; N, 1.94. IR: 2960 br s, 2191 s (CN), 1647 m, 1489 m, 1378 w, 1115 w, 1086 w, 1019 m, 782 m. Mp: 137−141 °C dec. Molecular weight in CH_2Cl_2: 615 g mol^{-1}. Calcd: 650 g mol^{-1}.

(η^4-C$_4$Me$_4$GeMeCl)TaCl$_3$(CNXyl)$_2$·0.8PhMe (5). A 50 mL Schlenk tube was charged with **2** (0.206 g, 0.35 mmol) and XylNC (0.093 g, 0.71 mmol). To this flask was added 25 mL of toluene to give a deep green solution. The volume of the solution was concentrated to 15 mL, and the solution was cooled to −35 °C to give **5** as a green crystalline solid in 94% yield (0.262 g, 0.34 mmol). **5** crystallized with 0.8 equiv of toluene, which was not removed under vacuum over 12 h at room temperature. ^{1}H NMR (benzene-d_6): δ 1.08 (s, 3 H, Ge*Me*), 2.08 (s, 6 H, C$_4$*Me*$_4$Ge), 2.17 (s, 6 H, C$_4$*Me*$_4$Ge), 2.91 (s, 6 H, (C$_6$H$_3$*Me*$_2$)NC), 3.03 (s, 6 H, (C$_6$H$_3$*Me*$_2$)NC), 6.33 (d, $^3J_{HH}$ = 8 Hz, 2 H, (C$_6$*H*$_3$Me$_2$)NC), 6.51 (d, $^3J_{HH}$ = 8 Hz, 2 H, (C$_6$*H*$_3$Me$_2$)NC), 6.56 (t, $^3J_{HH}$ = 8 Hz, 1 H, (C$_6$*H*$_3$Me$_2$)NC), 6.70 (t, $^3J_{HH}$ = 8 Hz, 1 H, (C$_6$*H*$_3$Me$_2$)NC). ^{13}C{^{1}H} NMR (benzene-d_6): δ 6.65 (s, Ge*Me*), 15.79, 16.54 (s, (C$_6$H$_3$*Me*$_2$)NC), 18.53, 19.04 (s, C$_4$*Me*$_4$Ge), 103.04 (s, *C*$_4$Me$_4$Ge), 130.88 (s, *C*$_4$Me$_4$Ge), 126.14, 129.01, 129.78, 130.43, 133.00, 135.65, 136.73 (s, *Xyl*NC), 161.60, 169.12 (s, XylN*C*). Anal. Calcd for C$_{29.8}$H$_{39.4}$Cl$_4$GeN$_2$Ta: C, 44.59; H, 4.78; N, 3.40. Found: C, 44.18; H, 4.44; N, 3.46. IR: 2917 br s, 2204 s (CN), 2190 s (CN), 1637 m, 1474 m, 1380 w, 1170 w, 1028 w, 782 m. Mp: 128−130 °C dec.

(η^4-C$_4$Me$_4$GeMeCl)TaCl$_3$(pyr)$_2$ (6). A 50 mL Schlenk tube was charged with **2** (0.216 g, 0.37 mmol) and 25 mL of toluene. A solution of pyridine (0.062 g, 0.74 mmol) in 10 mL of toluene was then added, resulting in generation of a deep green solution. This solution was concentrated to 15 mL and cooled to −35 °C to give **6** as a green crystalline solid in 86% yield (0.214 g, 0.32 mmol). ^{1}H NMR (benzene-d_6): δ 1.28 (s, 3 H, Ge*Me*), 2.78 (s, 6 H, C$_4$*Me*$_4$Ge), 2.94 (s, 6 H, C$_4$*Me*$_4$Ge), 6.28 (dd, $^3J_{HH}$ = 7 Hz, 4 H, C$_5$*H*$_5$N), 6.65 (t, $^3J_{HH}$ = 7 Hz, 2 H, C$_5$*H*$_5$N), 8.99 (d, $^3J_{HH}$ = 7 Hz, 4 H, C$_5$*H*$_5$N). ^{13}C{^{1}H} NMR (benzene-d_6): δ 10.22 (s, Ge*Me*), 16.25, 16.38 (s, C$_4$*Me*$_4$Ge), 106.03 (s, *C*$_4$Me$_4$Ge), 124.15, 137.92, 152.69 (s, *C*$_5$H$_5$N), 135.32 (s, *C*$_4$Me$_4$Ge). Anal. Calcd for C$_{19}$H$_{25}$Cl$_4$GeN$_2$Ta: C, 33.72; H, 3.72; N, 4.14. Found: C, 34.08; H, 4.09; N, 4.37. IR: 2948 br s, 2898 s, 1605 s, 1488 m, 1442 s, 1226 m, 1071 m, 1008 m, 862 br w, 757 m. Mp: 78−80 °C dec.

Cp(η^4-C$_4$Me$_4$GeMeCl)TaCl$_2$ (7). A 100 mL Schlenk tube was charged with **2** (2.50 g, 4.33 mmol) and 50 mL of toluene. A separate 500 mL round-bottom Schlenk flask was charged with CpTl (1.17 g, 4.33 mmol) and 200 mL of toluene to give a cloudy white suspension. This flask was then cooled in a dry ice/acetone bath to −78 °C. The solution containing **2** was then added to this flask at −78 °C to give a deep green solution. The resulting mixture was allowed to warm to room temperature and was stirred for an additional 10 h. After this time, the volatile substances were removed under dynamic vacuum. The resulting dark green residue was extracted into pentane (3 × 50 mL). The pentane extracts were concentrated to 20 mL, and the bright green solution was cooled to −35 °C to give **7** as bright green crystals in 78% yield (1.86 g, 3.39 mmol). ^{1}H NMR (benzene-d_6): δ 0.73 (s, 3 H, Ge*Me*), 1.78 (s, 6 H, C$_4$*Me*$_4$Ge), 2.53 (s, 6 H, C$_4$*Me*$_4$Ge), 5.84 (s, 5 H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 9.00 (s, Ge*Me*), 14.69, 17.57 (s, C$_4$*Me*$_4$Ge), 82.94, 136.64 (s, *C*$_4$Me$_4$Ge), 113.67 (s, *C*$_5$H$_5$). Anal. Calcd for C$_{14}$H$_{20}$Cl$_3$GeTa: C, 30.67; H, 3.68. Found: C, 30.98; H, 3.74. IR: 3114 s, 2860 br s, 1438 s, 1369 m, 1373 w, 1284 w, 1261 m, 1207 w, 1102 br s, 1017 br s, 850 s, 833 s, 803 s, 750 m, 602 m, 527 m, 425 m. Mp: 198−204 °C dec.

Table 1. Crystallographic Data for Compounds 5 and 7

	5	7
	(a) Crystal Parameters	
formula	$TaGeCl_4C_{27}H_{25}N_2$	$TaGeCl_3C_{14}H_{20}$
fw	772.86	548.21
size mm	0.12 × 0.10 × 0.08	0.19 × 0.11 × 0.09
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
a (Å)	10.0714(2)	8.4579(7)
b (Å)	11.3404(3)	15.917(1)
c (Å)	16.1556(3)	12.535(1)
α, β, γ (deg)	88.569(1), 77.068(1), 67.275(1)	90, 93.308(1), 90
V (Å^3)	1654.92(6)	1684.8(2)
Z	4	4
D_{calc} (g cm^{-3})	3.102	2.161
F_{000}	1496.00	1040.00
	(b) Data Collection	
temp (°C)	−158.0	−151.0
no. of unique/total reflens	5628/9206	3049/7941
R_{int}	0.022	0.020
empirical absorption correction: T_{max}/T_{min}	0.977/0.711	0.745/0.521
	(c) Refinement	
no. of observations [$I > 3\sigma(I)$]	4870	2640
no. of variables	333	172
reflection/param ratio	14.62	15.35
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.034	0.019
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2)]^{1/2}$	0.044	0.028
goodness of fit	1.57	1.43
max. and min. peaks in final diff map (e$^-$/Å^3)	2.23/−2.13	1.15/−1.05

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer

with a CCD area detector, using graphite-monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $4° < 2\theta < 45°$. The frame data were integrated using the program SAINT (SAX Area-Detector Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995). An empirical absorption correction based on measurements of multiply redundant data was performed using the program SADABS. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of the Molecular Structure Corporation, using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically unless otherwise noted, and the hydrogen atoms were included in calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a *p*-factor to downweight the intense reflections. Crystallographic data are summarized in Table 1.

For 5. Crystals were grown from a concentrated toluene solution at −35 °C. The non-hydrogen atoms that displayed no disorder were refined anisotropically. Hydrogen atoms were included but not refined. A molecule of toluene in the structure was displaced about an inversion center. This molecule was modeled as four full occupancy carbon atoms (C(28), C(29), C(30), and C(31)) which were refined isotropically. The other atoms of the toluene were generated using a full symmetry expansion.

For 7. Crystals were grown from a concentrated pentane solution at −15 °C.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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