

Reaction of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})]_4$ with Elemental Sulfur and Selenium: A Facile Chalcogenide Exchange Reaction

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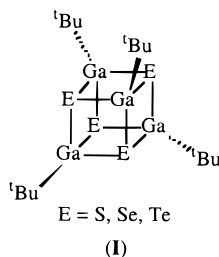
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A facile chalcogenide exchange is observed for the reaction between $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})]_4$ and elemental sulfur or selenium, resulting in the stoichiometric formation of the appropriate cubane, $[(^t\text{Bu})\text{Ga}(\mu_3\text{-E})]_4$ (E = S, Se), and metallic tellurium. Each of the intermediate cubane compounds, $[(^t\text{Bu})_4\text{Ga}_4(\mu_3\text{-E})_x(\mu_3\text{-Te})_{4-x}]$ ($x = 0-4$; E = S, Se) have been characterized by NMR spectroscopy and mass spectrometry. The rate of the chalcogenide exchange is dependent not only on the chalcogen (S faster than Se) but also the allotropic form of the chalcogen (catenasulfur, S_∞ , faster than S_8). The chalcogen exchange reaction is first order with respect to the cubane, and the ΔH^\ddagger and ΔS^\ddagger values have been determined for the reactions with S_8 (64.6 kJ mol⁻¹, 78.7 J K⁻¹ mol⁻¹), catenasulfur (33.3 kJ mol⁻¹, 84.4 J K⁻¹ mol⁻¹), and metallic selenium (73.5 kJ mol⁻¹, 108 J K⁻¹ mol⁻¹). The lack of reactivity of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Se})]_4$ with sulfur is proposed to be related to the strength of the cubane Ga–E bond rather than the relative electrochemical reduction potentials of the chalcogens. The reactions of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})]_4$ with catenasulfur and selenium are inhibited by the deposition of metallic tellurium on the reactant particles, as confirmed by microprobe analysis. The exchange reaction is proposed to be heterogeneous in nature and involve the opening of the cubane core.

Introduction

We have previously reported that the reaction of $\text{Ga}(^t\text{Bu})_3$ with elemental chalcogens ultimately leads to the formation of the cubane compounds $[(^t\text{Bu})\text{Ga}(\mu_3\text{-E})]_4$ (I; E = S, Se, Te).² However, the presence of isolable



intermediate species is dependent on the allotrope of the chalcogen used. For example, reaction of $\text{Ga}(^t\text{Bu})_3$ with red selenium (Se_8) yields only $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Se})]_4$, while that with metallic selenium allows for the isolation of $[(^t\text{Bu})\text{Ga}(\mu\text{-Se}^t\text{Bu})]_2$. After our initial studies, we prepared a number of derivatives with different alkyl substituents, $[(\text{R})\text{Ga}(\mu_3\text{-E})]_4$: E = S, Se, Te; R = $\text{CMe}_2\text{-Et}$, CMeEt_2 , CEt_3 , C_5Me_5 , $\text{C}_5\text{Me}_4\text{Et}$.³ In addition, other group 13–chalcogenide cubane compounds have since been prepared.^{4,5,6}

Cubane clusters of the general class $[(\text{L})\text{M}(\mu_3\text{-E})]_4$ have been extensively studied for both main-group and

transition metals,⁷ and their reactivity has been explored, especially with regard to ligand (L) exchange,⁸ cage redox chemistry,⁹ and reactions in which the M:E:L ratio is altered.¹⁰ Unfortunately, the remarkable stability of the Ga_4S_4 core of the sulfide cubanes, which makes them useful as CVD precursors,^{11,12} essentially pre-

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(4) Stoll, S. L.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 1315.

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(6) (a) Barron, A. R., *Chem. Soc. Rev.* **1993**, 93. (b) Barron, A. R. *Comments Inorg. Chem.* **1993**, *14*, 123.

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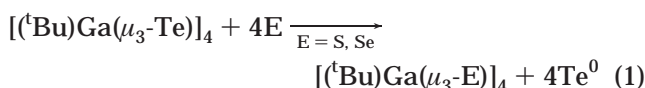
(1) (a) Department of Chemistry. (b) Department of Mechanical Engineering and Materials Science.

(2) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R., *Organometallics* **1992**, *11*, 1055.

cludes an extensive reaction chemistry.¹³ However, we have recently shown that, unlike [(R)Ga(μ₃-S)]₄, the telluride and selenide cubanes undergo significant cleavage during MOCVD,¹⁴ consistent with the decrease in thermochemical bond energies between gallium and the chalcogen down the group.¹⁵ These results suggest that the reaction chemistry of the telluride cubane, [(^tBu)Ga(μ₃-Te)]₄, should be more extensive than that of the lighter chalcogenides. Our investigations in this area are reported herein.

Results and Discussion

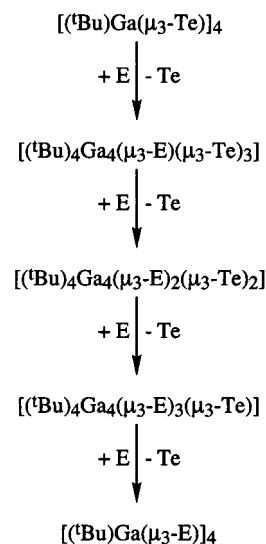
Reaction of a toluene or benzene solution of [(^tBu)-Ga(μ₃-Te)]₄² with excess elemental sulfur or selenium results in the stoichiometric formation of the previously characterized cubane compounds [(^tBu)Ga(μ₃-S)]₄ and [(^tBu)Ga(μ₃-Se)]₄, respectively (eq 1).¹⁶ In both cases



tellurium metal is formed, as confirmed by microprobe analysis (see below). As noted in the Introduction, we have previously observed that the products formed from the reaction of Ga(^tBu)₃ with chalcogens are dependent on the allotrope employed.² However, in the present case, there is no difference in the identity of the reaction products between cyclooctasulfur (S₈) and catenasulfur (plastic sulfur, S_∞) or between metallic gray selenium (Se_∞) and red selenium (α-cubic form, Se₈).

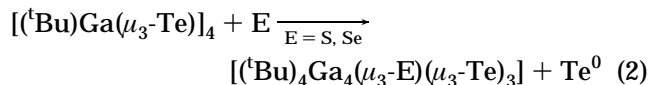
It is possible to follow the stepwise chalcogenide exchange reaction (Scheme 1) by NMR spectroscopy and characterize each of the individual intermediate compounds.¹⁷ For example, Figure 1 shows a ¹H NMR spectrum of the species formed from the incomplete reaction of [(^tBu)Ga(μ₃-Te)]₄ with metallic selenium. It is interesting to note the changes in chemical shift of the *tert*-butyl protons with chalcogenide substitution. Exchange of a tellurium for selenium results in an downfield shift of 0.07–0.08 ppm for the Ga–C(CH₃)₃ moiety adjacent to the exchanged chalcogenide. This shift may be due to both the changes in electronic donor/acceptor ability of the chalcogenide and changes in geometry about the gallium. However, the chemical shift of the Ga–C(CH₃)₃ moiety remote from the replaced chalcogenide also shifts (ca. 0.02–0.03 ppm), presumably due to the small changes in geometry about gallium as a result of cage contraction upon replacement of tellurium for selenium; i.e., Te–Ga–Te = 99.0(2)–99.8(1)° versus Se–Ga–Se = 98.3(1)–98.8(1)°. ^{3b} An analogous process occurs for the [(^tBu)₄Ga₄(μ₃-S)_x(μ₃-

Scheme 1. Stepwise Reaction of [(^tBu)Ga(μ₃-Te)]₄ with Elemental Chalcogen (E = S₈, S_∞, Se_∞, Se₈)



Te)_{4-x}] cubane compounds (see Experimental Section). It should be noted that no noncubane compounds are observed at any time during the reactions.

The chalcogen exchange reaction between [(^tBu)Ga(μ₃-Te)]₄ and the chalcogens shows a first-order dependence on the concentration of the cubane. Such a rate dependence precludes any mechanism involving a preequilibrium of the cubane to form dimers or monomers.¹⁸ Using ¹H NMR spectroscopy, the temperature dependence on the rate of the initial chalcogenide exchange (i.e., eq 2) may be determined, from which the



enthalpy (Δ*H*[‡]) and entropy (Δ*S*[‡]) of activation may be determined using the appropriate Eyring plot (Table 1).¹⁹ The difference in Δ*H*[‡] values between the reactions with selenium and sulfur must include some contribution of reaction with the elemental chalcogen, since Ga–Te bond breaking should be independent of other reagents. It is possible, therefore, that the rate-determining step may involve adsorption of [(^tBu)Ga(μ₃-Te)]₄ on the chalcogen surface. On the basis of a Langmuir–Hinshelwood mechanism the first-order rate dependence would be consistent with this proposal. However, given the magnitude of Δ*H*[‡] for each of these reactions, the rate-determining step clearly involves more than surface adsorption. In addition, if surface adsorption was the rate-determining step, a negative or small Δ*S*[‡] would be expected. This is not observed (see below and Table 1).

The rate of the chalcogenide exchange and enthalpy of activation are dependent on the identity of the chalcogen; the allotropes of sulfur react faster than those

(18) There is no evidence to suggest that [(^tBu)Ga(μ₃-Te)]₄ is in equilibrium with either dimers, “[(^tBu)Ga(Te)]₂”, or monomeric, “[(^tBu)GaTe]”, species. In addition, if such species were formed, it is likely that non-cubane products would be observed, especially in the case of the reaction with sulfur: i.e., [(^tBu)Ga(μ₃-E)]_{*n*} (*n* = 6–8).¹³

(19) All kinetic measurements were carried out with a sufficient excess of S or Se such that the amount of [(^tBu)Ga(μ₃-Te)]₄ was sufficient to provide approximately 1% of a monolayer coverage of the surface of the sulfur or selenium.

(12) MacInnes, A. N.; Power, M. B.; Barron, A. R. *Chem. Mater.* **1993**, *5*, 1344.

(13) The only reactivity we have observed involves a series of unique topological reorganization reactions; see: Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 2783.

(14) Gillan, E. G.; Barron, A. R. *Chem. Mater.* **1997**, *9*, 3037.

(15) (a) *Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985. (b) *Lange's Handbook of Chemistry*, 14th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1992. (c) Kubaschewski, O. Alcock, C. B.; Spencer, P. J. *Materials Thermochemistry*, 6th ed.; Pergamon Press: New York, 1993.

(16) It should be noted that no chalcogenide exchange occurs between preformed cubane compounds.

(17) We have been unable, at this time, to separate the individual compounds by fractional crystallization.

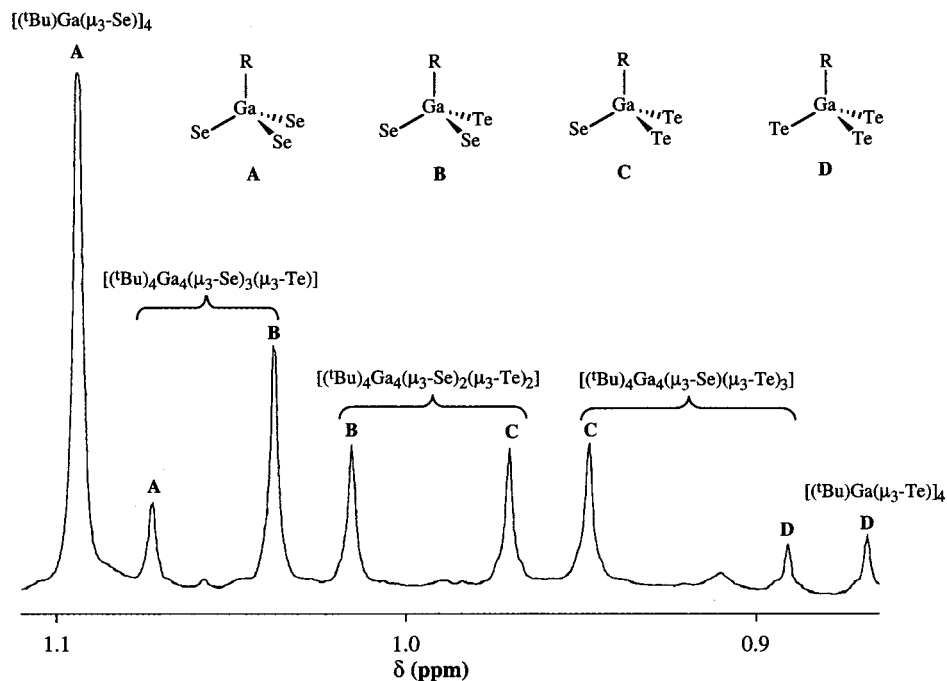


Figure 1. Selected region of the ^1H NMR spectrum of the gallium cubane compounds $[(^t\text{Bu})_4\text{Ga}_4(\mu_3\text{-Se})_x(\mu_3\text{-Te})_{4-x}]$ ($x = 1-4$), formed from the partial reaction between $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ and metallic selenium. The inset diagrams show the assignment of the gallium *tert*-butyl environments.

Table 1. Selected Kinetic Data for the Reaction of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ with Elemental Chalcogens

chalcogen	k_{obs}^a (298 K) (s $^{-1}$)	ΔH^\ddagger (kJ mol $^{-1}$)	ΔS^\ddagger (J K $^{-1}$ mol $^{-1}$)
cyclooctasulfur (S_8)	1.82×10^{-5}	64.5(9)	78.7(5)
catenasulfur (S_∞)	1.24×10^{-4}	33.3(2)	84.3(7)
metallic gray selenium (Se_∞)	1.69×10^{-5}	73.5(2)	108(1)

^a Under pseudo-first-order conditions.

of selenium. However, while the reaction products are independent of the allotropic form of the chalcogen, the rate of reaction and enthalpy of activation for sulfur is highly dependent on its allotropic form, such that the reaction with catenasulfur (plastic sulfur) is significantly faster than with cyclooctasulfur (S_8); $\Delta H^\ddagger = 33.3(2)$ and $64.5(9)$ kJ mol $^{-1}$, respectively. Although the rate of reaction with metallic gray selenium (Se_∞) appears to be slightly faster than that with red selenium (α -cubic form, Se_8), difficulties in obtaining the latter free from the former precluded the exact determination of rate constants. Thus, the rate of chalcogenide exchange follows the order $\text{S}_\infty \gg \text{S}_8 > \text{Se}_\infty \approx \text{Se}_8$, with the enthalpy of activation observing the reverse trend. It should be noted that neither the surface area nor the solubility of the chalcogen appears to be a controlling factor in the difference between allotropes, since the surface area of the more soluble S_8 ($0.270 \text{ m}^2 \text{ g}^{-1}$) is actually higher than that of the sample of catenasulfur used ($0.126 \text{ m}^2 \text{ g}^{-1}$). Although we have been unable to determine the dependence of the chalcogen, the observation of different rates for the different allotropes suggests a heterogeneous reaction which occurs on the chalcogen surface. This would be consistent with either a concerted exchange (I_a) reaction or an associative (A) reaction.²⁰

(20) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965.

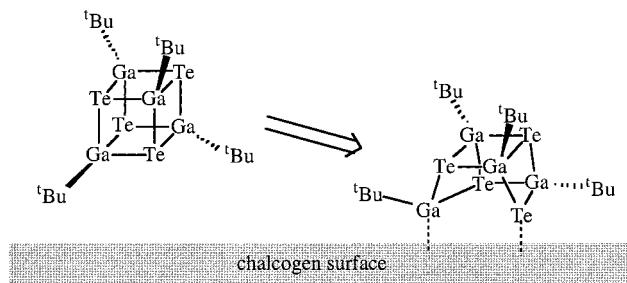


Figure 2. Schematic representation of the proposed cage-opening reaction between $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ and the surface of elemental chalcogen.

The large positive values for ΔS^\ddagger (Table 1) may be compared to the value obtained for the alkyl/hydride exchange reaction between $[\text{HAl}(\mu_3\text{-N}^t\text{Bu})_4]$ and $\text{Cp}_2\text{-ZrMe}_2$ ($18.8(4) \text{ J K}^{-1} \text{ mol}^{-1}$),²¹ for which no cage opening was observed. This suggests that during the chalcogenide exchange reaction opening of the cubane cage occurs, presumably on the surface of the chalcogen, since no cage fluxionality is observed in solution (see Figure 2).²² This reaction is analogous to the latent Lewis acidity of alkylaluminum oxanes in the presence of $\text{Cp}_2\text{-ZrMe}_2$.²³ Given the observation in solution of each stepwise reaction product and the lack of any noncubane products it is likely that the exchange reaction involves a series of consecutive Ga-Te bond-breaking/Ga-E bond-forming reactions.

Although the initial reaction of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ with catenasulfur is faster than that with S_8 , the reaction

(21) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 637.

(22) It should be noted that there is no evidence for scrambling of the alkyl groups between individual cubane molecules which suggests that complete cleavage of the cubane does not occur during the exchange reaction.

(23) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.

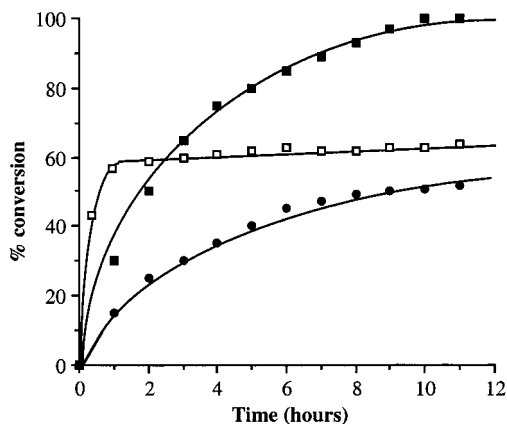


Figure 3. Plot of percentage conversion of $[(t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ to $[(t\text{Bu})\text{Ga}(\mu_3\text{-E})_4]$ upon reaction with a stoichiometric amount of elemental chalcogens: (■) S₈; (□) S_∞; (●) Se_∞.

with the former does not go to completion unless a large excess of catenasulfur is employed; e.g., see Figure 3. Similarly, the reaction with metallic selenium requires a large excess for complete reaction. It would appear that in these cases the rate of subsequent exchanges is inhibited by formation of product. Two possible reasons for this may be proposed. First, the chalcogenide exchange is reversible and the products are actually in equilibrium. However, no reaction is observed between either $[(t\text{Bu})\text{Ga}(\mu_3\text{-S})_4]$ or $[(t\text{Bu})\text{Ga}(\mu_3\text{-Se})_4]$ with tellurium metal. A second explanation is that the tellurium side product from the exchange is coating the chalcogen particles and hence precluding further reaction. Microprobe analyses of catenasulfur or metallic selenium particles after reaction with $[(t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ show a uniform surface coating of tellurium (e.g., Figure 4). This suggests that the reaction between the tellurium cubane and the chalcogens is a surface exchange and the tellurium deposit acts as a diffusion barrier to the sulfur (or selenium) below. Furthermore, interdiffusion of the tellurium or alloy formation does not occur under the conditions investigated. In contrast, the reaction of S₈ proceeds via the formation of other cyclic sulfur molecules and the precipitation of distinct particles of tellurium metal.

The reactivity of $[(t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ with sulfur and selenium is consistent with the relative magnitudes of the standard reduction potentials (S (−0.508 V), Se (−0.78 V), and Te (−0.92 V)) for the half-reaction shown in eq 3.²⁴ However, from a similar consideration, it is



expected that $[(t\text{Bu})\text{Ga}(\mu_3\text{-Se})_4]$ should react with sulfur, which it does not even in refluxing toluene. Thus, the chalcogenide exchange reaction must also depend on the opening of the Ga₄E₄ cage. Such a proposal is in line with the decrease in bond energies between gallium and the chalcogen down the group: Ga–S (318 kJ mol^{−1}), Ga–Se (274 kJ mol^{−1}), and Ga–Te (251 kJ mol^{−1}).¹⁵

Metal exchange (transmetalation) reactions are well-known for metal complexes and clusters. For example, transition-metal complexes of monoanionic Schiff bases have been shown to be stoichiometric transmetalating

(24) (24) *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1980; p D-155.

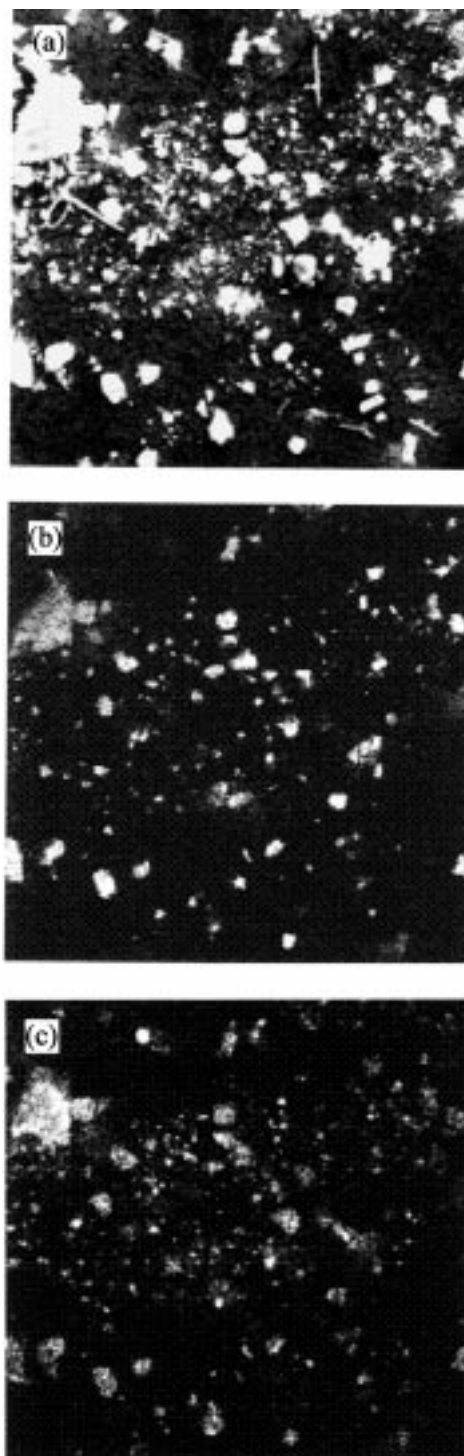


Figure 4. SEI micrograph of selenium, embedded in carbon paste, after partial reaction with $[(t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ (a), with associated Se (b) and Te (c) EDX maps, showing the presence of tellurium on the surface of the selenium particles.

agents for the replacement of copper in various tetranuclear complexes.²⁵ In Schiff base transmetalations,

(25) See for example: (a) Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidus, M. *Inorg. Chim. Acta* **1984**, *84*, 41. (b) El-Toukhy, A.; Cai, G.-Z.; Davies, G.; Gilbert, T. R.; Onan, K. D.; Veidus, M. *J. Am. Chem. Soc.* **1984**, *106*, 4596. (c) Cai, G.-Z.; Davies, G.; El-Toukhy, A.; Gilbert, T. R.; Henary, M. *Inorg. Chem.* **1985**, *24*, 1701. (d) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 2269. (e) Kareiva, A.; Harlan, C. J.; MacQueen, D. B.; Cook, R.; Barron, A. R. *Chem. Mater.* **1996**, *8*, 2331.

it is known that the driving force for the reaction is the formation of insoluble $[\text{CuL}]_x$ or highly stable CuL_2 coproducts. In the present case, we presume that the driving force for transmetalation between $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ and the elemental chalcogen is the formation of tellurium metal via a favorable redox reaction; however, the intracage bond strengths appear to be equally important. We are continuing our investigation of the redox reactions and cage substitutions.

Experimental Section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. NMR spectra were obtained on a Bruker AM-250 spectrometer using C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C). Surface area (BET) analyses were conducted on all samples utilizing a Coulter SA 3100 Plus. Sample tubes were Coulter Rapi-tubes. Sample masses were in the 0.100–0.190 g range and were outgassed at 350 °C for 3 h. Nitrogen gas was used as the absorbate, and helium gas was used to measure the free space in the sample tube. WDS microprobe analyses were obtained on a Cameca SX-50 relative to calibration standards. All reactions were performed under purified nitrogen or argon. Solvents were distilled and degassed prior to use. The synthesis of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ was performed as previously reported.² Cyclooctasulfur (S_8) and metallic gray selenium (Se_∞) were obtained from Aldrich and used without further purification. Catenasulfur (plastic sulfur) and red selenium (Se_8 , $\alpha\text{-Se}$) were prepared according to published procedures.²⁶

Reaction of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ with Sulfur. Method 1. To a hexane (200 mL) solution of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ (0.10 g, 0.098 mmol) was added an excess of S_8 (0.030 g, 0.94 mmol). The reaction mixture was stirred overnight at 40 °C. After the mixture was cooled to room temperature, the unreacted sulfur and tellurium side products were removed by filtration. The volatiles were removed under vacuum to yield a white powder, which from NMR spectroscopy and mass spectrometry was assigned to be a mixture of $[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-S})_x(\mu_3\text{-Te})_{4-x}]$ ($x = 0\text{--}4$). The reaction was found to proceed to quantitative formation of $[(\text{tBu})\text{Ga}(\mu_3\text{-S})_4]$ if the mixture is heated to 60 °C for 12 h. The identity of $[(\text{tBu})\text{Ga}(\mu_3\text{-S})_4]$ was confirmed by comparison with a genuine sample.

Method 2. To a C_6D_6 (10 mL) solution of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ (0.025 g, 2.46×10^{-5} mol) was added an excess of S_∞ (0.010 g, 3.12×10^{-4} mol). The reaction mixture was stirred overnight at 40 °C. After the mixture was cooled to room temperature, the unreacted sulfur and tellurium side products were removed by filtration. ^1H NMR spectroscopy and mass spectrometry indicated the product to be a mixture of $[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-S})_x(\mu_3\text{-Te})_{4-x}]$ ($x = 0\text{--}4$).

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-S})(\mu_3\text{-Te})_3]$. EI-MS (m/z , %): 867 ($\text{M}^+ - \text{tBu}$, 5), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 0.98 [27H, s, $\text{C}(\text{CH}_3)_3$], 0.91 [9H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.0 [$\text{C}(\text{CH}_3)_3$], 26.9 [$\text{C}(\text{CH}_3)_3$].

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-S})_2(\mu_3\text{-Te})_2]$. EI-MS (m/z , %): 828 (M^+ , 5), 771 ($\text{M}^+ - \text{tBu}$, 10), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 1.07 [18H, s, $\text{C}(\text{CH}_3)_3$], 1.02 [18H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.1 [$\text{C}(\text{CH}_3)_3$], 27.0 [$\text{C}(\text{CH}_3)_3$].

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-S})_3(\mu_3\text{-Te})]$. EI-MS (m/z , %): 732 (M^+ , 10), 675 ($\text{M}^+ - \text{tBu}$, 30), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 1.14 [9H, s, $\text{C}(\text{CH}_3)_3$], 1.11 [27H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.2 [$\text{C}(\text{CH}_3)_3$], 27.1 [$\text{C}(\text{CH}_3)_3$].

Reaction of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ with Selenium. To a hexane solution (200 mL) of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ (0.30 g, 0.29 mmol) was added an excess of metallic selenium metal (0.19 g, 2.4 mmol). The reaction mixture was stirred overnight at 40 °C. After the mixture was cooled to room temperature, the unreacted selenium and tellurium side products were removed by filtration. The volatiles were removed under vacuum to yield a white powder, which from NMR spectroscopy and mass spectrometry was assigned to be a mixture of $[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-Se})_x(\mu_3\text{-Te})_{4-x}]$ ($x = 0\text{--}4$). The reaction was found to proceed to quantitative formation of $[(\text{tBu})\text{Ga}(\mu_3\text{-Se})_4]$ if heated to 60 °C with a very large excess of selenium. The identity of $[(\text{tBu})\text{Ga}(\mu_3\text{-Se})_4]$ was confirmed by comparison with a genuine sample. The reaction with red selenium (Se_8) was carried out in a similar manner.

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-Se})(\mu_3\text{-Te})_3]$. EI-MS (m/z , %): 970 (M^+ , 30), 913 ($\text{M}^+ - \text{tBu}$, 25), 856 ($\text{M}^+ - 2 \text{tBu}$, 10), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 0.95 [27H, s, $\text{C}(\text{CH}_3)_3$], 0.89 [9H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.0 [$\text{C}(\text{CH}_3)_3$], 26.9 [$\text{C}(\text{CH}_3)_3$].

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-Se})_2(\mu_3\text{-Te})_2]$. EI-MS (m/z , %): 922 (M^+ , 35), 865 ($\text{M}^+ - \text{tBu}$, 30), 808 ($\text{M}^+ - 2 \text{tBu}$, 5), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 1.01 [18H, s, $\text{C}(\text{CH}_3)_3$], 0.97 [18H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.0 [$\text{C}(\text{CH}_3)_3$], 26.9 [$\text{C}(\text{CH}_3)_3$].

$[(\text{tBu})_4\text{Ga}_4(\mu_3\text{-Se})_3(\mu_3\text{-Te})]$. EI-MS (m/z , %): 874 (M^+ , 10), 817 ($\text{M}^+ - \text{tBu}$, 25), 57 (tBu , 100). ^1H NMR (δ , C_6D_6): 1.07 [9H, s, $\text{C}(\text{CH}_3)_3$], 1.04 [27H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (δ , C_6D_6): 27.0 [$\text{C}(\text{CH}_3)_3$], 26.9 [$\text{C}(\text{CH}_3)_3$].

Kinetic Studies. A sample of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ was accurately weighed (± 0.005 g) and dissolved in toluene- d_8 ; the mass of the solution was determined and thus the concentration of $[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ (ca. 2.5 mM). This standard solution was divided into four 5 mm NMR tubes (ca. 0.25 mL). To each tube was added a solid sample of the appropriate chalcogen. All the samples were prepared such that the chalcogen was in excess, and thus the reactions were run under pseudo-first-order kinetic conditions. All the samples were heated to the appropriate temperature within the NMR spectrometer, and a series of ^1H NMR spectra was collected every 5–15 min for up to 8 h. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol.²⁷ The integration of the *tert*-butyl proton resonances was used to determine the rate of reaction. The pseudo-first-order rate constants (k_{obs}) were determined from a plot of $-\ln[(\text{tBu})\text{Ga}(\mu_3\text{-Te})_4]$ versus time. The temperature dependence of the first-order rate constants allows for the determination of the ΔH^\ddagger and ΔS^\ddagger values. Selected kinetic data are given in Table 1.

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