

# SYNTHESIS AND REACTIVITY OF FUNCTIONALIZED DIMETHYLGERMYL COMPLEXES OF THE FORMULA $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{X})$ ; EQUILIBRIA INVOLVING THE DIMETHYLGERMYLENE COMPLEX $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{GeMe}_2)]^+\text{TfO}^-$

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Addition of  $\text{Me}_2\text{GeCl}_2$  to  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  gives the chiral rhenium dimethylchlorogermyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{Cl})$  (92%), which reacts with  $\text{LiAlH}_4$  and  $\text{Me}_3\text{SiOTf}$  to yield  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{H})$  (74%) and  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{OTf})$  (**3**; 94%), respectively. Reactions of **3** and halide salts give  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{X})$  ( $\text{X} = \text{F}, \text{Br}, \text{I}$ ; 81-83%). All compounds exhibit two  $^1\text{H}/^{13}\text{C}$  NMR signals for the diastereotopic  $\text{GeMe}_2$  groups at ambient temperature, except **3** for which coalescence occurs at 211 K ( $\Delta G^\ddagger = 9.6 \pm 0.2$  kcal/mol). This is interpreted as indicating a rapid equilibrium with the dimethylgermylene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{GeMe}_2)]^+\text{TfO}^-$ .

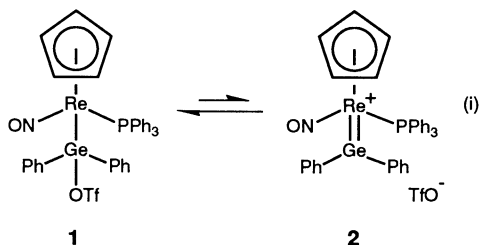
**key words:** Chiral rhenium germyl complexes; germylene intermediate

## INTRODUCTION

This special issue of Phosphorus, Sulfur, Silicon, and the Related Elements commemorates the distinguished career of Professor Alan Cowley. His research accomplishments have had a profound impact upon many areas of contemporary chemistry. In particular, his studies of multiple bonding between the heavier main group elements<sup>1</sup> have had a marked influence on several projects under investigation in our laboratory. For example, we have sought to generate complexes containing metal-silicon<sup>2</sup> and metal-germanium<sup>3</sup> double bonds,  $\text{LM}=\text{XR}_2$ . Cowley pioneered many protocols for enhancing the kinetic stability of compounds with reactive multiple bonds -- introducing rational design in an area historically dominated by empiricism.

A variety of complexes have now been isolated that contain  $\text{M}=\text{Si}$  and  $\text{M}=\text{Ge}$  linkages.<sup>4,5</sup> Others have been observed spectroscopically or trapped with Lewis bases. We have previously reported the synthesis, crystal structure, and dynamic NMR properties of the chiral rhenium

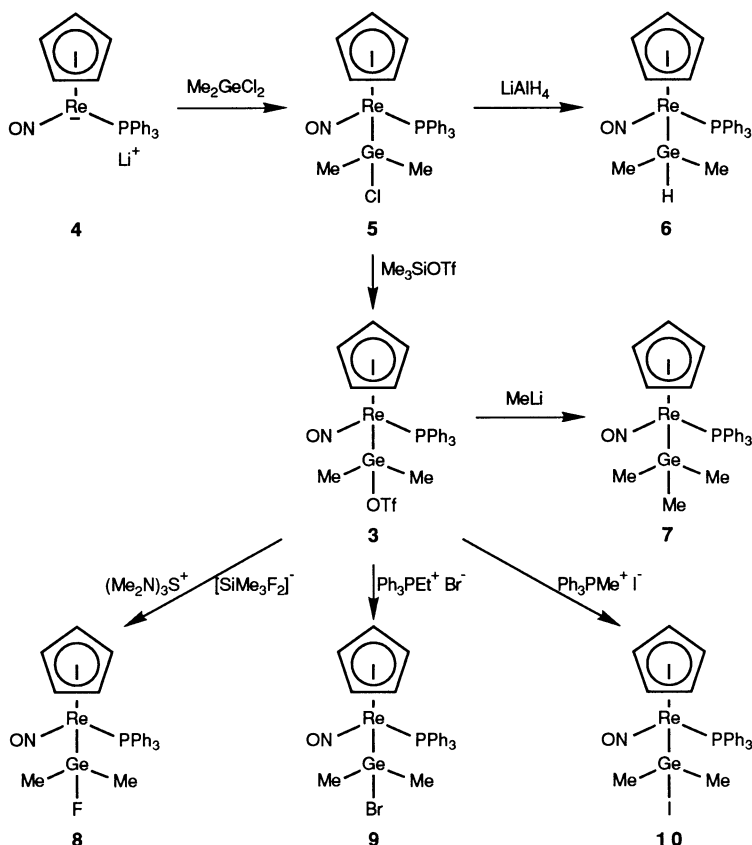
diphenyltriflatogermeryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GePh}_2\text{OTf})$  (**1**).<sup>3</sup> This compound was shown to be in rapid equilibrium with the cationic diphenylgermylene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{GePh}_2)]^+ \text{TfO}^-$  (**2**), as illustrated in equation i. We present here complementary data for the dimethyl analog  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{OTf})$  (**3**). This paper, which constitutes our *chant du cygne* in this series, is dedicated with warm affection to Professor Cowley.



## RESULTS

The anionic rhenium complex  $\text{Li}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  (**4**) was generated as previously described<sup>6</sup> and treated with dimethylgermyl dichloride,  $\text{Me}_2\text{GeCl}_2$ , at  $-80^\circ\text{C}$ . Workup gave the dimethylchlorogermeryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{Cl})$  (**5**) in 92% yield (Scheme I). Complex **5**, and all other new compounds isolated below, were characterized by microanalysis and IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) spectroscopy, as summarized in Table I and the experimental section. Properties were similar to those reported earlier for related germeryl and silyl complexes.<sup>2,3</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5** displayed two signals for the diastereotopic  $\text{GeMe}_2$  groups.

Reactions of the chloride substituent in **5** were attempted. Reduction with  $\text{LiAlH}_4$  ( $25^\circ\text{C}$ ) gave the dimethylhydridogermeryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{H})$  (**6**) in 74% yield after workup (Scheme I). Complex **6** exhibited a diagnostic IR  $\nu(\text{Ge-H})$  absorption ( $1918\text{ cm}^{-1}$ )<sup>7</sup> and a phosphorus-coupled  $\text{GeMe}_2\text{H}$   $^1\text{H}$  NMR signal ( $\delta$  3.62, doublet of heptets; Table I). Reaction of **5** and  $\text{Me}_3\text{SiOTf}$  ( $25^\circ\text{C}$ ) gave the dimethyltriflatogermeryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{OTf})$  (**3**) in 94% yield. The diastereotopic  $\text{GeMe}_2$  groups gave only one broadened  $^1\text{H}$  NMR signal and one broadened  $^{13}\text{C}$  NMR signal at ambient temperature. Additional NMR data are given below.



SCHEME I. Syntheses of functionalized dimethylgermyl complexes  
 $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{X})$ .

TABLE I  
 IR and NMR<sup>a</sup> characterization of new rhenium germyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{X})$

compd (X)	IR (cm <sup>-1</sup> , KBr)	<sup>1</sup> H NMR (ppm)	<sup>13</sup> C{ <sup>1</sup> H} NMR (ppm)	<sup>31</sup> P{ <sup>1</sup> H} NMR (ppm)
<b>5</b> (Cl)	$\nu_{\text{NO}}$ 1652 vs <sup>b</sup>	7.49-7.22 (m, PPh <sub>3</sub> ), 5.10 (s, C <sub>5</sub> H <sub>5</sub> ), 0.63 (s, CH <sub>3</sub> ), 0.53 (s, CH <sub>3</sub> )	PPh <sub>3</sub> at: 137.5 (d, J <sub>CP</sub> = 53.8, i), 133.5 (d, J <sub>CP</sub> = 10.8, o), 130.6 (d, J <sub>CP</sub> = 2.3, p), 128.7 (d, J <sub>CP</sub> = 10.4, m); 89.4 (s, C <sub>5</sub> H <sub>5</sub> ), 13.2 (s, CH <sub>3</sub> ), 11.1 (s, CH <sub>3</sub> )	21.6 (s)

TABLE I (continued)

compd (X)	IR (cm <sup>-1</sup> , KBr)	<sup>1</sup> H NMR (ppm)	<sup>13</sup> C{ <sup>1</sup> H} NMR (ppm)	<sup>31</sup> P{ <sup>1</sup> H} NMR (ppm)
<b>6</b> (H)	$\nu_{\text{NO}}$ 1636 vs $\nu_{\text{GeH}}$ 1918 m	7.51-7.29 (m, PPh <sub>3</sub> ), 4.89 (s, C <sub>5</sub> H <sub>5</sub> ), 3.62 (dh, J <sub>HP</sub> = 3.6, J <sub>HH</sub> = 1.4, GeH), 0.31 (d, J <sub>HH</sub> = 3.7, CH <sub>3</sub> ), 0.21 (d, J <sub>HH</sub> = 3.6, CH <sub>3</sub> )	PPh <sub>3</sub> at: 137.8 (d, J <sub>CP</sub> = 52.9, i), 133.9 (d, J <sub>CP</sub> = 10.6, o), 130.4 (s, p), 128.5 (d, J <sub>CP</sub> = 10.3, m); 87.2 (s, C <sub>5</sub> H <sub>5</sub> ), 0.8 (s, CH <sub>3</sub> ), -0.2 (s, CH <sub>3</sub> )	22.9 (s)
<b>3</b> (OTf)	$\nu_{\text{NO}}$ 1675 vs <sup>b</sup> $\nu_{\text{SO}_3\text{CF}_3}$ 1336 vs 1198 s	7.62-7.23 (m, PPh <sub>3</sub> ), 5.20 (s, C <sub>5</sub> H <sub>5</sub> ), 0.73 (br s, 2CH <sub>3</sub> )	PPh <sub>3</sub> at: 137.0 (d, J <sub>CP</sub> = 55.2, i), 133.4 (d, J <sub>CP</sub> = 11.1, o), 131.2 (d, J <sub>CP</sub> = 2.3, p), 129.2 (d, J <sub>CP</sub> = 10.5, m); 119.5 (q, J <sub>CF</sub> = 319.7, CF <sub>3</sub> ), 89.6 (s, C <sub>5</sub> H <sub>5</sub> ), 12.3 (br s, 2CH <sub>3</sub> )	18.2 (s)
<b>7</b> (Me)	$\nu_{\text{NO}}$ 1636 vs	7.60-7.13 (m, PPh <sub>3</sub> ), 4.86 (s, C <sub>5</sub> H <sub>5</sub> ), 0.10 (s, 3CH <sub>3</sub> )	PPh <sub>3</sub> at: 138.7 (d, J <sub>CP</sub> = 52.0, i), 133.7 (d, J <sub>CP</sub> = 11.0, o), 130.9 (d, J <sub>CP</sub> = 2.3, p), 128.4 (d, J <sub>CP</sub> = 10.0, m); 87.2 (s, C <sub>5</sub> H <sub>5</sub> ), 5.4 (s, 3CH <sub>3</sub> )	25.9 (s)
<b>8</b> (F)	$\nu_{\text{NO}}$ 1654 vs	7.58-7.23 (m, PPh <sub>3</sub> ), 5.06 (s, C <sub>5</sub> H <sub>5</sub> ), 0.45 (d, J <sub>HF</sub> = 7.8, CH <sub>3</sub> ), 0.35 (d, J <sub>HF</sub> = 7.6, CH <sub>3</sub> )	PPh <sub>3</sub> at: 138.0 (d, J <sub>CP</sub> = 53.8, i), 133.8 (d, J <sub>CP</sub> = 10.9, o), 130.6 (d, J <sub>CP</sub> = 2.4, p), 128.7 (d, J <sub>CP</sub> = 10.5, m); 87.8 (s, C <sub>5</sub> H <sub>5</sub> ), 9.4 (d, J <sub>CF</sub> = 14.9, CH <sub>3</sub> ), 8.7 (d, J <sub>CF</sub> = 14.2, CH <sub>3</sub> )	20.6 (s)
<b>9</b> (Br)	$\nu_{\text{NO}}$ 1664 vs	7.55-7.26 (m, PPh <sub>3</sub> ), 5.12 (s, C <sub>5</sub> H <sub>5</sub> ), 0.86 (s, CH <sub>3</sub> ), 0.65 (s, CH <sub>3</sub> )	PPh <sub>3</sub> at: 137.6 (d, J <sub>CP</sub> = 54.1, i), 133.6 (d, J <sub>CP</sub> = 11.1, o), 130.8 (d, J <sub>CP</sub> = 2.6, p), 128.9 (d, J <sub>CP</sub> = 10.4, m); 90.2 (s, C <sub>5</sub> H <sub>5</sub> ), 13.7 (s, CH <sub>3</sub> ), 11.4 (s, CH <sub>3</sub> )	19.8 (s)
<b>10</b> (I)	$\nu_{\text{NO}}$ 1665 vs	7.52-7.24 (m, PPh <sub>3</sub> ), 5.12 (s, C <sub>5</sub> H <sub>5</sub> ), 1.15 (s, CH <sub>3</sub> ), 0.84 (s, CH <sub>3</sub> )	PPh <sub>3</sub> at: 137.6 (d, J <sub>CP</sub> = 54.1, i), 133.6 (d, J <sub>CP</sub> = 11.2, o), 130.9 (d, J <sub>CP</sub> = 2.0, p), 128.9 (d, J <sub>CP</sub> = 10.5, m); 91.0 (s, C <sub>5</sub> H <sub>5</sub> ), 13.7 (s, CH <sub>3</sub> ), 11.9 (s, CH <sub>3</sub> )	19.9 (s)

<sup>a</sup>At ambient probe temperature in CD<sub>2</sub>Cl<sub>2</sub> and referenced to CHDCl<sub>2</sub> (<sup>1</sup>H,  $\delta$  5.32), CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C, 53.8 ppm), or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P, 0.0 ppm). All coupling constants are in Hz.

<sup>b</sup>IR data in CH<sub>2</sub>Cl<sub>2</sub> (cm<sup>-1</sup>): **5**, 1663 vs; **3**, 1684 vs, 1337 vs, 1198 s.

Substitutions of the triflate moiety in **3** were studied next. Reaction with MeLi (0 °C) gave the trimethylgermyl complex ( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(GeMe<sub>3</sub>) (**7**) in 60% yield (Scheme I). Reactions of **3** and the halide salts (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup> [SiMe<sub>3</sub>F<sub>2</sub>]<sup>-</sup> (TAS-F), Ph<sub>3</sub>Pt<sup>+</sup> Br<sup>-</sup>, or Ph<sub>3</sub>Pt<sup>+</sup> I<sup>-</sup> (-80 °C) gave the corresponding fluorogermyl, bromogermyl, and iodo-germyl complexes ( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(GeMe<sub>2</sub>X) (X = F, **8**; Br, **9**; I, **10**) in 81-83% yields. All of these compounds gave distinct <sup>1</sup>H and <sup>13</sup>C NMR signals for the diastereotopic GeMe<sub>2</sub> groups.

We suspected that the unique NMR properties of the triflate-substituted complex **3** were due to facile exchange of the GeMe<sub>2</sub> groups. Thus, low temperature <sup>1</sup>H NMR spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub>, as shown in Figure 1. At 181 K, two GeMe<sub>2</sub> resonances were present ( $\delta$  0.98, 0.31;  $\Delta\nu$  = 200.2 Hz). These broadened and shifted upon warming, and coalesced at 211 K. Application of the coalescence formula<sup>8</sup> gave a  $\Delta G^\ddagger$ (211 K) value of  $9.6 \pm 0.2$  kcal/mol for methyl group exchange. These data are interpreted as indicating a rapid equilibrium of **3** and the dimethylgermylene complex [( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(=GeMe<sub>2</sub>)]<sup>+</sup> TfO<sup>-</sup> (**12**), as diagrammed in Scheme II and analyzed below.

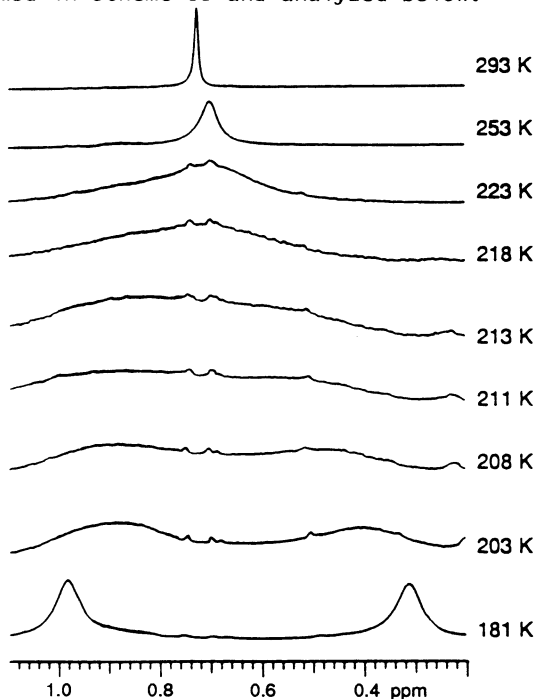
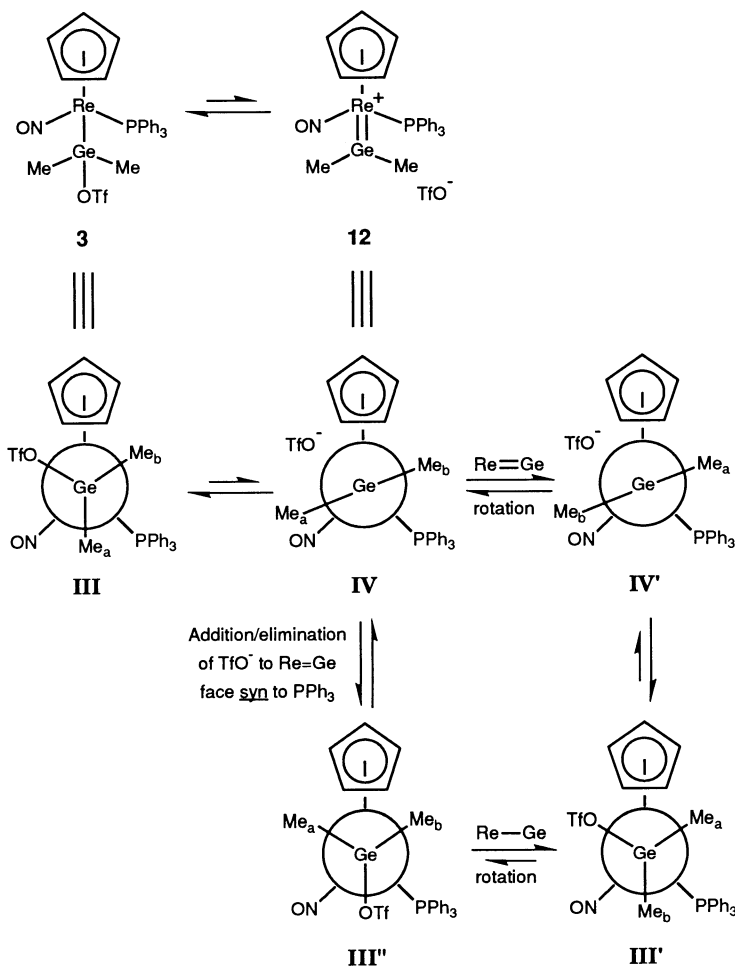


FIGURE1. Variable-temperature <sup>1</sup>H NMR spectra of ( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(GeMe<sub>2</sub>OTf) (**3**).



SCHEME II. Proposed equilibrium of the dimethyltriflatogermeryl complex **3** and dimethylgermylene complex **12**; possible mechanisms for the exchange of the diastereotopic methyl groups.

## DISCUSSION

The reactions in Scheme I have close analogy in our previous studies of the diphenyltriflatogermeryl complex **1** (equation i), and abundant literature precedent as discussed earlier.<sup>3</sup> The substitution products **6-10** were utilized in other exploratory routes to the dimethylgermylene complex **12** and related species.<sup>9</sup> Although these efforts were not fruitful, the ease of displacement of the triflate group in **3** is in itself suggestive of a facile equilibrium with **12**.

Triflate-containing compounds commonly exhibit several IR absorptions between 900 and 1400  $\text{cm}^{-1}$ .<sup>10</sup> The highest frequency IR band is typically 1395–1365  $\text{cm}^{-1}$  in covalent triflates, and 1280–1270  $\text{cm}^{-1}$  in ionic triflates. Significantly, the highest frequency band of **3** occurs at 1336–1337  $\text{cm}^{-1}$  ( $\text{KBr}/\text{CH}_2\text{Cl}_2$ ). This indicates that the Ge–OTf linkage in **3** has appreciable ionic character. The diphenyltriflatogermyl complex **1** gives an analogous band at 1331  $\text{cm}^{-1}$ .

Exchange of the diastereotopic  $\text{GeMe}_2$  groups of **3** requires both (a) inversion of configuration at germanium or rhenium, and (b) rotation about the rhenium–germanium bond. The unique NMR behavior of **3** – and the generally high configurational stability of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{X})$  compounds at rhenium<sup>11</sup> – implicate germanium as the labile center. Scheme II depicts two possible exchange pathways, both involving initial triflate ionization to give the dimethylgermylene complex **12**. The experimental and stereoelectronic basis for the Re–Ge conformations illustrated for **3** (III) and **12** (IV) have been discussed at length earlier.<sup>3</sup>

In one pathway, the Re=Ge bond of **12** (IV) first rotates by 180° to give IV'. The addition of the triflate anion by the microscopic reverse of the ionization step yields III', simultaneously consummating inversion and exchange. Alternatively, triflate could add to the Re=Ge face of IV opposite to the one it ionized from, and syn to the bulky  $\text{PPh}_3$  ligand. This would give the inverted species III'', and a ca. 120° rotation about the Re–Ge bond would subsequently be required to complete exchange. Since the Re=C moiety in cationic alkylidene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHR})]^+ \text{X}^-$  undergoes nucleophilic attack from a direction anti to the  $\text{PPh}_3$  ligand,<sup>12</sup> we favor the former process.

The  $\Delta G^\ddagger$  (211 K) value for exchange, 9.6 kcal/mol, provides an upper bound for the difference in free energy ( $\Delta G$ ) between **3** and dimethylgermylene complex **12**. In actuality, the difference is likely much less. Phenyl substituents should stabilize an electrophilic germanium center more than methyl groups. Hence, the energy difference between the diphenyltriflatogermyl complex **1** and diphenylgermylene complex **2** should be even lower. However, the  $\text{GePh}_2$  groups of **1** exchange with a higher barrier ( $\Delta G^\ddagger$  (268 K) = 12.6 kcal/mol,  $\text{CD}_2\text{Cl}_2$ ) than the  $\text{GeMe}_2$  groups of **3**. One possible explanation is that Re=Ge bond rotation is

rate limiting in Scheme II ( $\text{IV} \rightarrow \text{IV}'$ ). Thus, the larger phenyl substituents, one of which must pass over the  $\text{PPh}_3$  ligand, would sterically destabilize the transition state.

A silicon analog of **3**,  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{SiMe}_2\text{OTf})$  (**13**), has been similarly synthesized.<sup>2</sup> Complex **13** gives distinct  $^1\text{H}$  and  $^{13}\text{C}$  resonances for the diastereotopic  $\text{SiMe}_2$  groups near the reflux point of  $\text{CD}_2\text{Cl}_2$ . These data allow a lower bound of 14.8 kcal/mol ( $\Delta G^\ddagger(307\text{ K})$ ) to be placed on any process that can exchange the  $\text{SiMe}_2$  groups. Also, the highest frequency triflate IR band occurs at 1366  $\text{cm}^{-1}$ . Hence, the Si-OTf linkage in **13** has much less ionic character than the Ge-OTf linkage in **3**.

In conclusion, we have established that triflate-substituted germyl complexes of the formula  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeR}_2\text{OTf})$  undergo facile ionization to cationic germylene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{GeR}_2)]^+\text{TfO}^-$ . Although these equilibria are endergonic, strategies for lowering  $\Delta G$  and  $\Delta G^\ddagger$  can be envisioned. For example, larger germanium substituents would increase the driving force for the formation of a trigonal center. Pentamethylcyclopentadienyl ligands, which are more electron-releasing (and bulkier), should better stabilize the electron deficient germanium. These data and considerations should aid future syntheses of complexes with metal-germanium (and metal-silicon) double bonds.

## EXPERIMENTAL<sup>1,3</sup>

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{Cl})$  (**5**). A Schlenk tube was charged with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ <sup>6</sup> (0.500 g, 0.919 mmol), THF, and a stir bar, and was cooled to  $-15^\circ\text{C}$  ( $\text{HOCH}_2\text{CH}_2\text{OH}/\text{CO}_2$ ). Then  $n\text{-BuLi}$  (0.640 mL, 1.58 M in hexane) was added with stirring. After 0.5 h, the resulting red solution was cooled to  $-80^\circ\text{C}$  (acetone/ $\text{CO}_2$ ), and  $\text{Me}_2\text{GeCl}_2$  (0.175 g, 1.01 mmol) was added with stirring. After 0.5 h, the cold bath was removed. After 4 h, the solvent was removed in vacuo. The yellow powder was extracted with  $\text{CH}_2\text{Cl}_2$ , and the extract was filtered through Celite (1 cm) on a fritted funnel. The solvent was removed in vacuo, and the residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /hexane. Dark yellow needles formed, which were collected by filtration and dried in vacuo to give  $5 \cdot 0.5(\text{CH}_2\text{Cl}_2)$  (0.574 g, 0.843 mmol, 92%), mp  $183\text{--}186^\circ\text{C}$ .



The presence of the solvate was verified by  $^1\text{H}$  NMR ( $\delta$  5.28 (s) vs  $\text{CHCl}_3$ ;  $\text{CDCl}_3$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{ClGeNOPRe}\cdot 0.5(\text{CH}_2\text{Cl}_2)$ : C, 42.29; H, 3.76; Cl, 9.79. Found: C, 42.30; H, 3.76; Cl, 9.60.

**$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{H})$  (6).** A Schlenk tube was charged with **5** (0.200 g, 0.294 mmol), THF (5 mL), and a stir bar. Then  $\text{LiAlH}_4$  (0.011 g, 0.29 mmol) was added with stirring. After 0.5 h, the suspension was filtered and the solvent was removed in vacuo. The residue was extracted with benzene. The extract was filtered through Celite (1 cm) on a fritted funnel. The solvent was removed in vacuo, and the residue was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was filtered through Celite (1 cm) on a fritted funnel. The solvent was removed in vacuo, and the residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /hexane. Irregularly shaped orange plates and cubes formed, which were collected by filtration and dried in vacuo to give **6** (0.140 g, 0.216 mmol, 74%), mp 170–173 °C dec. Anal. Calcd for  $\text{C}_{25}\text{H}_{27}\text{GeNOPRe}$ : C, 46.38; H, 4.20. Found: C, 46.03; H, 4.32.

**$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{OTf})$  (3).** A Schlenk tube was charged with **5** (0.204 g, 0.300 mmol),  $\text{CH}_2\text{Cl}_2$  (5 mL), and a stir bar. Then  $\text{Me}_3\text{SiOTf}$  (0.098 g, 0.441 mmol) was added with stirring. After 5 min, the solvent was removed in vacuo. The residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /hexane. Large, irregularly shaped dark yellow plates and cubes formed, which were collected by filtration and dried in vacuo to give **3** (0.225 g, 0.283 mmol, 94%), mp 172–175 °C dec. Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{F}_3\text{GeNO}_4\text{PReS}$ : C, 39.26; H, 3.29. Found: C, 39.77; H, 3.65.

**$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_3)$  (7).** A 5 mm NMR tube was charged with **3** (0.020 g, 0.025 mmol) and THF (0.5 mL), and capped with a septum. The tube was cooled to 0 °C, and  $\text{MeLi}$  (0.022 mL, 1.3 M in ether) was added with shaking. The tube was warmed to room temperature, and the solvent was removed in vacuo. The residue was extracted with benzene. The extract was filtered through silica gel (1 cm) on a fritted funnel. The solvent was removed in vacuo. The residue was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$ , and petroleum ether (30–60 °C) was added. The solvent was removed in vacuo, and the resulting yellow powder was dried in vacuo (56 °C, 48 h) to give **7** (0.010 g, 0.015 mmol, 60%), mp 172–175 °C. Anal. Calcd for  $\text{C}_{26}\text{H}_{29}\text{GeNOPRe}$ : C, 47.22; H, 4.42. Found: C, 46.27; H, 4.36.

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{F})$  (**8**). A 5 mm NMR tube was charged with **3** (0.026 g, 0.033 mmol) and  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and capped with a septum. The solution was cooled to  $-80^\circ\text{C}$  and then transferred, via a  $\text{N}_2$ -purged cannula, to a NMR tube that had been charged with  $(\text{Me}_2\text{N})_3\text{S}^+[\text{SiMe}_3\text{F}_2]^-$  (0.010 g, 0.036 mmol) and cooled to  $-80^\circ\text{C}$ . The tube was warmed to room temperature, and the solvent was removed in vacuo. The residue was extracted with a minimum of benzene. The extract was filtered through dry cellulose (3 cm) on a fritted funnel. The solvent was removed in vacuo. The residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /pentane. Dark yellow needles formed, which were collected by filtration and dried in vacuo to give  $\text{8}\cdot\text{0.5}(\text{CH}_2\text{Cl}_2)$  (0.018 g, 0.027 mmol, 83%), mp  $172\text{--}173^\circ\text{C}$  dec. The presence of the solvate was verified by  $^1\text{H}$  NMR ( $\delta$  5.28 (s) vs  $\text{CHCl}_3$ ;  $\text{CDCl}_3$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{FGeNOPRe}\cdot\text{0.5}(\text{CH}_2\text{Cl}_2)$ : C, 43.29; H, 3.85. Found: C, 43.47; H, 3.95.

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{Br})$  (**9**). Complex **3** (0.050 g, 0.063 mmol) and  $\text{Ph}_3\text{PEt}^+ \text{I}^-$  (0.026 g, 0.069 mmol) were combined in a procedure analogous to that given for **8**. A similar workup (with crystallization from  $\text{CH}_2\text{Cl}_2$ /hexane) gave yellow needles of **9** (0.037 g, 0.051 mmol, 81%), mp  $206\text{--}209^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{BrGeNOPRe}$ : C, 41.35; H, 3.61. Found: C, 41.42; H, 3.70.

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{GeMe}_2\text{I})$  (**10**). Complex **3** (0.050 g, 0.063 mmol) and  $\text{Ph}_3\text{PMe}^+ \text{I}^-$  (0.028 g, 0.069 mmol) were combined in a procedure analogous to that given for **9**. An identical workup gave yellow needles of **10** (0.040 g, 0.052 mmol, 82%), mp  $206\text{--}208^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{GeINOPRe}$ : C, 38.84; H, 3.39. Found: C, 39.19; H, 3.52.

## ACKNOWLEDGEMENTS

We thank the NSF for support of this research, Dr. T.-S. Peng for assistance with the preparation of the manuscript, and Professor N. Hosmane (Southern Methodist University) for his efforts in organizing this volume.

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