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COMMUNICATION

SYNTHESIS AND REACTIVITY OF FUNCTIONALIZED RHENIUM GERMYL COMPLEXES (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2X$); DYNAMIC EQUILIBRIA WITH GERMYLENE COMPLEX [(η^5-C_5H_5)Re(NO)(PPh_3)(=$GePh_2$)]$^+X^-$

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Abstract—Reaction of Li^+[(η^5-C_5H_5)Re(NO)(PPh_3)]$^-$ with Ph_3GeCl and Ph_2GeCl_2 (THF, −75°C) gives germyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_3$) (84%) and (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2Cl$) (**3**, 82%), respectively. Reaction of **3** and $(CH_3)_3SiOTf$ gives (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$) (**4**, 82%). Several properties show the triflate substituent in **4** to be extremely labile. First, reaction of **4** and pyridine to give [(η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2NC_5H_5$)]$^+$TfO$^-$ (**5**) is complete in < 5 min at −78°C; the pyridine in **5** rapidly exchanges with pyridine-d_5 (CD_2Cl_2, −80°C). Second, the ^{13}C NMR resonances of the diastereotopic germanium phenyl substituents in **4** coalesce upon warming ($\Delta G^{\ddagger}_{268\mathrm{K}}$ (CD_2Cl_2) = 12.6 ± 0.2 kcal mol^{-1}). The most likely mechanisms for this dynamic behaviour entail initial triflate dissociation to give the germylene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=$GePh_2$)]$^+$TfO$^-$.

Metal complexes of unsaturated silicon, germanium, tin and lead containing ligands have been the focus of much recent attention.[1–2] We have previously demonstrated the ready availability of cationic chiral rhenium alkylidene complexes of the formula [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+X^-$.[3,4] The rhenium fragment (η^5-C_5H_5)Re(NO)(PPh_3)$^+$ is a powerful π donor by virtue of the high-lying *d* orbital HOMO shown in **I** below (Scheme 1),[3d] and hence these alkylidene complexes exhibit some of the highest M=C double bond rotational barriers known (18–21 kcal mol^{-1}).[3a,c,d] Thus, we sought to probe the accessibility of analogous germylene complexes, [(η^5-C_5H_5)Re(NO)(PPh_3)(=GeR_2)]$^+X^-$. Neutral germylene complexes with bulky germanium substituents have been previously synthesized,[1] but cationic germylene complexes remain to our knowledge unknown. In this communication, we report the synthesis of functionalized germyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(GeR_2X), and dynamic NMR data that suggest facile equilibria with the corresponding germylene complexes.

The rhenium anion Li^+[(η^5-C_5H_5)Re(NO)PPh_3)]$^-$ (**1**) was generated in THF as previously described[5] and treated with germyl chloride Ph_3GeCl (1.5 equiv.) at −75°C (Scheme 1). Work-up gave the triphenylgermyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_3$) (**2**) in 84% yield.† Next, anion **1** was similarly treated with dichloride Ph_2GeCl_2. The functionalized germyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2Cl$) (**3**) was isolated in 82% yield after work-up. Complex **3** and $(CH_3)_3SiOTf$[2a] were in turn reacted in CH_2Cl_2. Work-up gave the germyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$) (**4**) in 82% yield.

Several observations indicated the triflate substituent in germyl complex **4** to be extremely labile. First, addition of pyridine (2.0 equiv.) to **4** gave the pyridinium salt, [(η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2NC_5H_5$)]$^+$ TfO$^-$ (**5**), in 83% yield after

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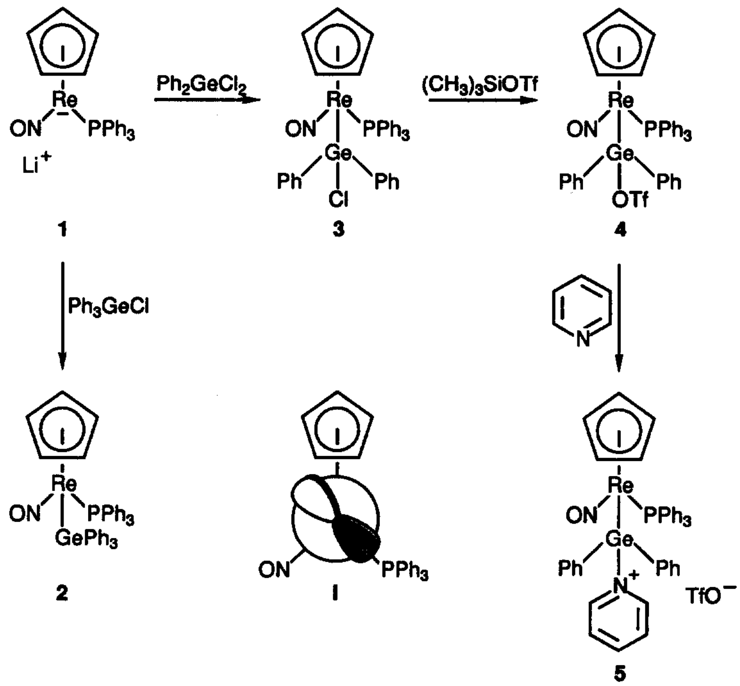
† Reaction conditions, work-up procedures and product spectroscopic properties are similar to those recently described for related silyl complexes.[6]



Scheme 1. Synthesis of functionalized germyl complexes.

work-up. We sought to determine the rate law for this transformation, and specifically the order in pyridine. However, reaction was complete in < 5 min at -78°C, as assayed by ^{31}P NMR monitoring. Similarly, pyridinium salt **5** (0.02 M in CD_2Cl_2) was treated with 2.5 equiv. of pyridine-d_5 at -80°C. Equilibration with **5**-d_5 was complete in < 5 min.

Germyl complexes **2**–**5** were characterized by microanalysis and by IR, and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as described in supplementary material furnished to the reviewers.* IR $\nu(CF_3SO_3)$ (KBr, cm^{-1}, s) were noted for **4** (1331, 1234, 1200) and **5** (1271, 1224, 1150, 1045). The high frequency band of **5** was in a typical range for ionic triflates (1280–1270 cm^{-1}), whereas that of **4** was outside the typical range for covalent triflates (1395–1365 cm^{-1}).[7]

Importantly, germyl complexes **3** and **5** exhibited separate ^{13}C NMR resonances for the diastereotopic germanium–phenyl substituents in CD_2Cl_2 at room temperature (two *o*, *m*, *p*, *ipso*). However, triflate-substituted complex **4** showed dynamic behaviour. At lower temperatures, separate phenyl carbon resonances were observed as with **3** and **5**. However, these coalesced to a single set of resonances upon warming. The coalescence temperatures were determined from spectra recorded in 5°C increments, and differed for each type of carbon. Standard treatment of the data for the *ipso* carbons gave $\Delta G^{\ddagger}_{268\text{K}}$ $(CD_2Cl_2) = 12.6 \pm 0.2$ kcal mol^{-1} for the process equivalencing the phenyl groups.[8,9] The $\Delta G^{\ddagger}$ significantly increased in the less polar solvent chlorobenzene ($\Delta G^{\ddagger}_{323\text{K}}(C_6D_5Cl) = 15.3 \pm 0.2$ kcal mol^{-1}).

What is the mechanism by which the diastereotopic phenyl groups of **4** are equivalenced? One possibility is to invoke the inversion of configuration at rhenium. However, analogous rhenium alkyl, phosphido, bromo and iodo complexes show good configurational stability.[4a,9,10] Hence, we conclude that a net inversion of configuration at germanium must occur. Accordingly, the most probable inversion mechanisms entail triflate anion dissociation to give the germylene complex, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}GePh_2)]^+TfO^-$ (**6**), as shown in Scheme 2.[11] The Re═Ge conformation of **6** depicted is analogous to Re═C conformations found in corresponding alkylidene complexes.[3] Dissociation would be followed by either (1) Re═Ge bond rotation, and addition of triflate anion to the Re═Ge face *anti* to PPh_3, or (2) addition of the triflate anion to the Re═Ge face *syn* to PPh_3, and Re—Ge bond rotation (Scheme 2). Both mechanisms interconvert the diastereotopic phenyl groups, and account for the solvent polarity trend noted above. However, since nucleophiles preferentially attack the corresponding alkylidene complexes on the Re═C face *anti* to the bulky PPh_3 ligand,[3] we view the first possibility as more likely.

Importantly, the $\Delta G^{\ddagger}_{268\text{K}}$ (CD_2Cl_2) of 12.6 kcal

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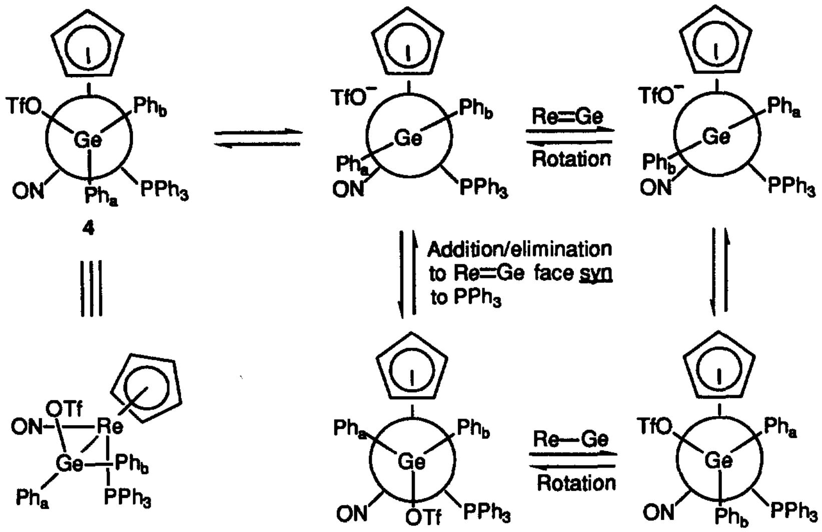
* See footnote † on previous page.



Scheme 2. Possible mechanisms for the equivalencing of diastereotopic phenyl groups Ph_a and Ph_b in germyl complex **4**.

mol^{-1} for the equivalencing of the diastereotopic phenyl groups of germyl complex **4** constitutes the *maximum* ΔG that can separate **4** from germylene complex **6** at 268 K. Since the Re=Ge bond rotational barrier could well contribute to this $\Delta G^{\ddagger}$, the actual ΔG between **4** and **6** may be much less. Hence, appropriate structural variants of **4** have a good chance of being thermodynamically unstable with respect to a germylene complex. Experiments designed to probe this possibility are in progress.

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