

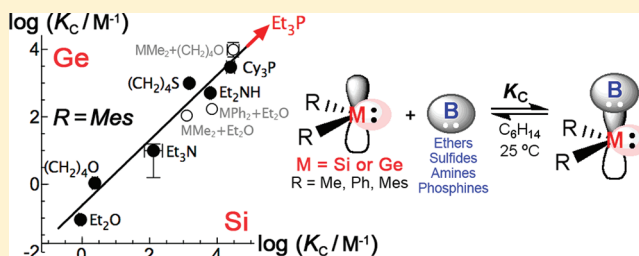
# Electronic and Steric Effects on the Lewis Acidities of Transient Silylenes and Germylenes: Equilibrium Constants for Complexation with Chalcogen and Pnictogen Donors

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## Supporting Information

**ABSTRACT:** The Lewis acid–base complexation reactions of dimethyl-, diphenyl-, and dimesitylsilylene ( $\text{SiMe}_2$ ,  $\text{SiPh}_2$ , and  $\text{SiMes}_2$ , respectively) and their germanium homologues ( $\text{GeMe}_2$ ,  $\text{GePh}_2$ , and  $\text{GeMes}_2$ ) with diethyl ether ( $\text{Et}_2\text{O}$ ), tetrahydrothiophene (THT), triethylphosphine ( $\text{Et}_3\text{P}$ ), and tricyclohexylphosphine ( $\text{C}_6\text{H}_{11}\text{P}$ ) have been characterized in hydrocarbon solvents at 25 °C by laser flash photolysis methods. Together with previously reported (and some new) data for the complexation of the six transient tetrellylenes with methanol ( $\text{MeOH}$ ), tetrahydrofuran (THF), and di- and triethylamine ( $\text{Et}_2\text{NH}$  and  $\text{Et}_3\text{N}$ , respectively), the results allow the first systematic assessment of the thermodynamics of Lewis acid–base complexation of simple dialkyl- and diarylsilylenes and their germanium homologues with chalcogen and pnictogen donors in solution. The equilibrium constants ( $K_C$ ) for complexation of the six species with  $\text{Et}_2\text{O}$  span a range of ca.  $10^5 \text{ M}^{-1}$ , decreasing in the order  $\text{SiPh}_2 > \text{SiMe}_2 > \text{GePh}_2 > \text{GeMe}_2 \gg \text{SiMes}_2 > \text{GeMes}_2$ . For each homologous  $\text{MR}_2$  pair,  $K_C$  is consistently 10–40 times larger for the silylene than the germylene, indicating a systematic difference in binding free energy of 1.5–2.2 kcal mol<sup>-1</sup>. Equilibrium constants have been determined for complexation of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  with all the donors in the series except  $\text{Et}_3\text{P}$ , for which only a lower limit can be determined. Those for  $\text{SiMe}_2$  decrease in the order  $\text{Et}_3\text{P} > \text{C}_6\text{H}_{11}\text{P} > \text{Et}_2\text{NH} > \text{THT} > \text{Et}_3\text{N} > \text{THF} > \text{Et}_2\text{O}$ ;  $\text{GeMe}_2$  is consistently less acidic, but its binding constants follow a similar ordering. The experimental data are supplemented with theoretical (Gaussian-4) calculations of thermochemical parameters for the complexation of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  with 17 O, S, N, and P donors, which are shown to agree with experiment to within 1 kcal mol<sup>-1</sup> for the 6 systems that have also been studied experimentally. The calculations confirm that, in general, trialkylphosphines bind most strongly, followed by amines, sulfides, and then ethers and alcohols.  $\text{SiMe}_2$  and  $\text{GeMe}_2$  are borderline-soft Lewis acids, stronger and softer than trimethylborane in both cases.



## INTRODUCTION

Silylenes and germylenes, the silicon and germanium analogues of (singlet) carbenes, have been studied extensively over the past few decades in the gas phase, in solution, and in solid matrices at low temperatures and have also been the subject of numerous theoretical studies.<sup>1–5</sup> The parent derivatives,  $\text{SiH}_2$  and  $\text{GeH}_2$ , have received particular attention,<sup>4a</sup> both because of their fundamental importance and because they are critical intermediates in the chemical vapor deposition of solid silicon and germanium, respectively.<sup>6</sup> There have also been great advances made in the synthesis and study of isolable silylene and germylene derivatives, rendered so by some combination of steric and electronic stabilization of the intrinsically reactive divalent tetrel center by substituents.<sup>5,7,8</sup>

The primary driving force for the reactivity of these species is their intrinsically high electrophilicity, which results from their electropositive character and the vacant 3p or 4p orbital on the tetrel center. As a result, most of their known reactions begin with an interaction between the vacant p orbital and a nucleophilic site in the substrate, often in the form of a discrete Lewis acid–base complex as reaction intermediate. Intra- or

intermolecular Lewis acid–base coordination is well-known to reduce the reactivity typical of these molecules (e.g., dimerization)<sup>1,9</sup> and is hence a useful tool for the preparation of isolable derivatives.<sup>10–13</sup> Depending on the donor, the increase in nucleophilicity at silicon or germanium that accompanies complexation<sup>14</sup> can be sufficient to result in an altogether different reactivity for the complex in comparison to that of the free species.<sup>11b,c,13b,15,16</sup> This has been shown to be particularly true of phosphine and N-heterocyclic carbene (NHC) donors, which have been shown not only to be particularly effective stabilizers of transient silylenes<sup>17,18</sup> and germylenes<sup>12,13,19</sup> but also to alter their reactivities in intriguing and potentially useful ways.

The Lewis acid–base complexation of transient silylenes<sup>20</sup> and germylenes<sup>21</sup> with chalcogen and pnictogen donors was first studied experimentally by low-temperature spectroscopic methods in the 1980s by West and Ando and their co-workers, following an early theoretical study of the complexation and X–

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H insertion reactions of  $\text{SiH}_2$  with the parent hydride donors by Raghavachari and co-workers.<sup>22</sup> A later computational study of the complexation of  $\text{SiH}_2$ ,  $\text{GeH}_2$ , and  $\text{SnH}_2$  with the chalcogen and pnictogen hydrides predicted the Lewis acidities of the species to decrease in the order  $\text{Si} > \text{Ge} > \text{Sn}$  and demonstrated the more pronounced ylide character of the complexes with the third-row donors in comparison to those with the corresponding second-row homologues;<sup>14</sup> more sophisticated theoretical studies of the bonding in  $\text{SiH}_2$ -phosphine ylides and comparisons to those in methylenephosphorane<sup>23</sup> and other, related systems<sup>24</sup> have been carried out more recently. Other theoretical studies have ranked a variety of substituted silylenes<sup>25</sup> and germylenes<sup>25a</sup> according to their electrophilicities and hardness; the latter is based on calculated binding energies with  $\text{NH}_3$  and  $\text{PH}_3$ , the relative magnitudes of which have led to the general classification of simple silylenes and germylenes as “hard” electrophiles.<sup>25a</sup> A more recent DFT study by De Proft and co-workers examined the thermodynamics of Lewis acid–base complexation of dihalogermylenes with a variety of  $\sigma$  (O, S, and N) donors, in a comparative study of the complexation of dihalogermylenes and -stannylenes with aromatic  $\pi$  donors.<sup>26</sup>

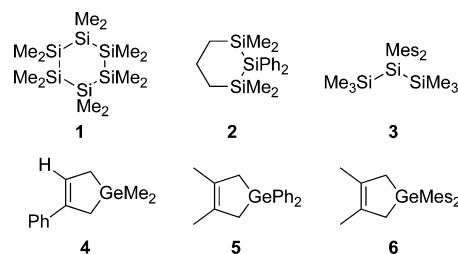
Early fast kinetic studies of the complexation of  $\text{SiMe}_2$  with various donors in solution<sup>27,28</sup> and with ethers in the gas phase<sup>29</sup> established the first absolute rate constants for silylene Lewis acid–base complexation reactions and showed them to be essentially diffusion- or encounter-controlled in all cases, consistent with an enthalpically barrierless process. This has been extended by our own, more recent solution-phase studies of the reactivities of  $\text{SiMe}_2$ ,  $\text{GeMe}_2$ , and the corresponding diphenyl and dimesityl derivatives,<sup>30,31</sup> which show that complexation with THF, alcohols, and amines is invariably quite fast, the rates varying only modestly with variations in structure or substitution in either the tetrellylene or the donor or with the overall thermodynamics of the complexation process. Equilibrium constants have been measured or estimated in only a handful of cases—for the complexation of the three germylene derivatives with methanol ( $\text{MeOH}$ ) and  $\text{THF}$ <sup>31c</sup> and of  $\text{SiMe}_2$  with diethylamine ( $\text{Et}_2\text{NH}$ ) in hexanes<sup>30d</sup> and of  $\text{SiMe}_2$  with dimethyl ether ( $\text{Me}_2\text{O}$ ) and tetrahydrofuran (THF) in the gas phase.<sup>29,32</sup> The available thermodynamic data are thus fairly sparse but are nevertheless consistent with the indication from theory that silylenes are stronger Lewis acids than germylenes of homologous structures and that both species form stronger complexes with amines than with O donors. The differences have never been quantified, however. Similarly, the complexation reactions of these species with sulfides and phosphines have not yet been studied in a systematic way.

In the present paper, we report the results of a fast kinetics study of the Lewis acid–base complexation reactions of the six homologous transient silylenes and germylenes  $\text{MMe}_2$ ,  $\text{MPh}_2$ , and  $\text{MMes}_2$  ( $\text{M} = \text{Si}, \text{Ge}$ ) with diethyl ether ( $\text{Et}_2\text{O}$ ), tetrahydrothiophene (THT), and triethyl- and tricyclohexylphosphine ( $\text{Et}_3\text{P}$  and  $\text{Cy}_3\text{P}$ , respectively) in hexanes or cyclohexane solution at 25 °C. The data are combined with data reported earlier, supplemented where necessary with new measurements for some of the systems, for the reactions of these species with  $\text{MeOH}$ ,  $\text{THF}$ ,  $\text{Et}_2\text{NH}$ , and  $\text{Et}_3\text{N}$  under similar conditions. The experimental data, and their implications, are extended with theoretical (Gaussian-4<sup>33</sup>) calculations of thermochemical parameters for the complexation of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  with a series of 17 chalcogen and pnictogen donors,

including several of those that have been characterized experimentally. The data are compared to various empirical donor basicity scales in order to rank the Lewis acidities and hard–soft behaviors of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  relative to each other and in the context of other, more conventional Lewis acids.

## RESULTS

The transient silylenes and germylenes studied in this work were generated and detected by laser flash photolysis of rapidly flowed, deoxygenated solutions of compounds 1–6 in anhydrous hexanes or cyclohexane<sup>34</sup> and the pulses from a KrF excimer laser (248 nm, 90–105 mJ, ca. 20 ns) for excitation. As reported previously, the species of interest are observed in these experiments as promptly formed transients with UV–vis absorption bands centered at  $\lambda_{\text{max}}$  465 nm ( $\text{SiMe}_2$ ),<sup>27a,34c,35</sup> 290 and 515 nm ( $\text{SiPh}_2$ ),<sup>34c</sup> and 290 and 580 nm ( $\text{SiMes}_2$ ),<sup>34c,36</sup> for the silylenes and at  $\lambda_{\text{max}}$  470 nm ( $\text{GeMe}_2$ ),<sup>34a,37</sup> 300 and 500 nm ( $\text{GePh}_2$ ),<sup>34a</sup> and 325 and 560 nm ( $\text{GeMes}_2$ ),<sup>34a,38</sup> for the germylenes. In the absence of added substrates they each decay on the microsecond time scale with the concomitant formation of longer-lived absorptions in the 360–460 nm range due to the corresponding disilenes and digermenes, formed by dimerization.<sup>34</sup> Silylene formation is accompanied by the formation of minor amounts of a second transient product in the cases of 2 and 3, which gives rise to long-lived residual absorptions (centered at 460 and 440 nm, respectively) on which the spectra of the silylenes and corresponding disilenes are superimposed.<sup>34c,39</sup> These side products are unreactive toward the substrates of interest studied here; therefore, their presence in the photolysis mixtures does not compromise kinetic and/or thermodynamic measurements, and they are sufficiently long-lived that their contributions to the absorption spectra of the resulting silylene-donor complexes (vide infra) can be subtracted out.



Absolute rate and(or) equilibrium constants for complexation of the six tetrellylenes with the four donors ( $\text{Et}_2\text{O}$ , THT,  $\text{Et}_3\text{P}$  and  $\text{Cy}_3\text{P}$ ) were determined by monitoring the effects of varying concentrations of added substrate on the temporal behavior and(or) intensities of the long-wavelength transient absorptions due to the tetrellylenes; all experiments were carried out in hexanes at 25 °C, except those with  $\text{Cy}_3\text{P}$ , which were carried out in cyclohexane owing to its low solubility in hexanes. The kinetic process of interest is a pseudo-first-order approach to equilibrium, which is described by eqs 1 and 2,

$$\Delta A_t = \Delta A_{\text{res}} + (\Delta A_0 - \Delta A_{\text{res}}) \exp(-k_{\text{decay}}t) \quad (1)$$

$$k_{\text{decay}} = k_{-C} + k_C[\text{Q}] \quad (2)$$

where  $k_{\text{decay}}$  is the pseudo-first-order rate coefficient for decay of the tetrellylene,  $k_C$  and  $k_{-C}$  are the forward and reverse rate constants for complexation with the donor (Q),  $\Delta A_0$  and  $\Delta A_t$

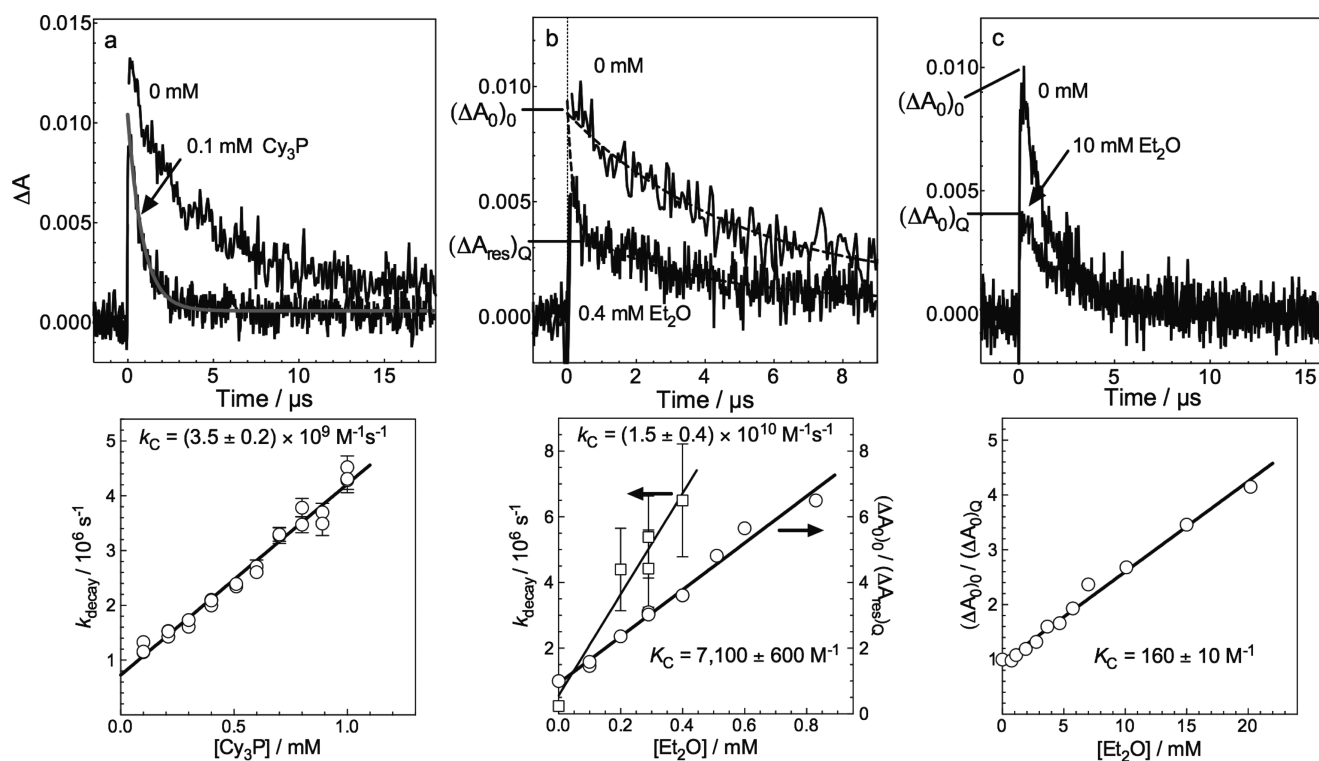
are the transient absorbance values immediately and at time  $t$  after the laser pulse, respectively, and  $\Delta A_{\text{res}}$  is the residual transient absorbance due to free tetrellylene remaining at equilibrium at the end of the initial decay. The latter undergoes a relatively slow subsequent decay owing to dimerization. The variation in the ratio of the initial and residual absorbances ( $(\Delta A_0)_0/(\Delta A_{\text{res}})_Q$ ) with substrate concentration is proportional to the equilibrium constant ( $K_C = k_C/k_{-C}$ ), as shown in eq 3.

$$(\Delta A_0)_0/(\Delta A_{\text{res}})_Q = 1 + K_C[Q] \quad (3)$$

The observed response of the tetrellylene absorptions to added substrate adopts one of three forms, depending on the relative magnitudes of the forward rate ( $k_C$ ) and equilibrium constants ( $K_C$ ) for complexation, and each situation requires a somewhat different procedure for analysis of the data and determination of kinetic and/or thermodynamic parameters.<sup>31c</sup> The simplest (and least informative) situation arises when  $K_C$  is in excess of ca. 25 000  $M^{-1}$  or when there is a fast secondary reaction of the complex that renders the complexation process irreversible. When either of these situations pertains, the signal decays to a level indistinguishable from the prepulse signal level (i.e.,  $\Delta A_{\text{res}} \approx 0$ ) at all substrate concentrations monitored and only the forward rate constant for complexation ( $k_C$ ) can be determined, from the slope of a plot of  $k_{\text{decay}}$  vs  $[Q]$  according to eq 2. Figure 1a shows representative transient decays and a plot of  $k_{\text{decay}}$  vs  $[Q]$  for the complexation of  $\text{SiPh}_2$  with  $\text{Cy}_3\text{P}$ , as an example of a system characterized by a  $K_C$  value of this magnitude.

For systems characterized by  $K_C$  values between ca. 1000  $M^{-1}$  and ca. 25 000  $M^{-1}$ , the residual absorption is nonzero at low (substrate) concentrations and undergoes a relatively slow decay due to the dimerization reaction; the latter process is slowed appreciably in the presence of the substrate. In such situations the forward rate constant can be estimated from the rate coefficients associated with the initial fast decay ( $k_{\text{decay}}$ ; eq 2), while the equilibrium constant can be estimated from the variation in the residual signal level ( $(\Delta A_{\text{res}})_Q$ ) with substrate concentration according to eq 3. In practice, the determination of  $k_{\text{decay}}$  values for systems in this "intermediate" range usually required two-exponential fitting of the transient absorbance profiles, and the corresponding  $(\Delta A_{\text{res}})_Q$  values were estimated visually as the break point in the two-exponential decays. These analyses are approximate but nevertheless provide values of the forward rate and equilibrium constants with typical uncertainties in the range of 10–25%.<sup>31a</sup> Figure 1b shows representative data obtained for the complexation of  $\text{SiPh}_2$  with  $\text{Et}_2\text{O}$ , as an example of a system characterized by a  $K_C$  value in this range.

Reactions characterized by equilibrium constants smaller than ca. 1000  $M^{-1}$  require relatively high concentrations of substrate in order to produce a residual signal that is significantly different from  $\Delta A_0$ , such that the approach to equilibrium (i.e., the initial fast decay) is rendered unresolvable from the laser pulse. Thus, addition of the substrate results only in a reduction in the *apparent* initial signal intensity due to the free tetrellylene and a concomitant decrease in its decay rate, the latter due to retardation of the dimerization reaction. In such situations only  $K_C$  can be determined, from analysis of the apparent initial signal intensities as a function of  $[Q]$  according to eq 4; it should be noted that the  $(\Delta A_0)_Q$  term in eq 4 in fact corresponds to  $(\Delta A_{\text{res}})_Q$  in eq 3. The  $(\Delta A_0)_0$  values used in



**Figure 1.** (top) Transient absorbance–time profiles and (bottom) associated data plots according to eqs 2–4, all at 25 °C: (a)  $\text{SiPh}_2$ – $\text{Cy}_3\text{P}$  in cyclohexane; (b)  $\text{SiPh}_2$ – $\text{Et}_2\text{O}$  in hexanes; (c)  $\text{GePh}_2$ – $\text{Et}_2\text{O}$  in hexanes. The corresponding plots of the data from experiments with different concentrations of the respective substrates are shown below each set of absorbance–time profiles.

$$(\Delta A_0)_0 / (\Delta A_0)_Q = 1 + K_C [Q] \quad (4)$$

these analyses were obtained from transient decay traces recorded in the absence of added substrate, which is appropriate provided the laser intensity is kept the same at each substrate concentration studied and provided the substrate does not absorb significantly at the excitation wavelength over the concentration range employed for the determination. It was ensured that these requirements were met in all of the experiments that were carried out. Figure 1c shows some of the data obtained for the complexation of GePh<sub>2</sub> with Et<sub>2</sub>O, as representative of a system in this “small  $K_C$ ” regime. The equilibrium constants for the SiMes<sub>2</sub>–Et<sub>2</sub>O and GeMes<sub>2</sub>–Et<sub>2</sub>O Lewis pairs were measured using transient absorbance data acquired with solutions containing molar concentrations of added Et<sub>2</sub>O, keeping the solution optical densities at the laser wavelength constant by adding the substrate as optically matched (at 248 nm) solutions of the precursors (3 and 6, respectively) in neat Et<sub>2</sub>O.

Similar experiments were also carried out for the SiMes<sub>2</sub>–THF, GeMe<sub>2</sub>–Et<sub>2</sub>NH, GeMes<sub>2</sub>–Et<sub>2</sub>NH, and GeMes<sub>2</sub>–Et<sub>3</sub>N systems, none of which have been characterized previously. The experiments with the GeMes<sub>2</sub>–Et<sub>3</sub>N pair were limited to maximum substrate concentrations of 1.5 mM because the amine absorbs (weakly) at the laser wavelength; no effect on the germylene signal intensity could be detected over the 0–1.5 mM concentration range in Et<sub>3</sub>N, which establishes an upper limit of  $K_C \leq 100 \text{ M}^{-1}$  for the equilibrium constant. With this discrete evaluation of the screening effects due to Et<sub>3</sub>N in hand, we also re-evaluated the complexation of SiMes<sub>2</sub> with Et<sub>3</sub>N in a more complete fashion than in earlier work<sup>30d</sup> and determined a value of  $K_C = 130 \pm 60 \text{ M}^{-1}$  from data recorded over the 0–1.5 mM concentration range in added amine.

Table 1 gives the absolute rate and equilibrium constants for the 28 tetrellylene-donor systems that were studied in this work, along with those values that have been reported previously for complexation with THF,<sup>30a,31c</sup> Et<sub>2</sub>NH,<sup>30d,31a</sup> Et<sub>3</sub>N,<sup>30d,31a,34a,b</sup> and THT<sup>30c</sup> under similar conditions; the corresponding data plots are shown in Figures 1 and S1–S28 of the Supporting Information. The value measured for the SiMe<sub>2</sub>–Et<sub>2</sub>O pair ( $K_C = 1260 \pm 100 \text{ M}^{-1}$ ) is in reasonable agreement with the value estimated from the data of Baggott et al. for the SiMe<sub>2</sub>–Me<sub>2</sub>O system in the gas phase ( $K_C \approx 3600 \text{ M}^{-1}$ ),<sup>29,40</sup> given the uncertainties and accounting for the

slightly higher Lewis basicity of Me<sub>2</sub>O compared to Et<sub>2</sub>O.<sup>41</sup> The lower limit of  $K_C \geq 25\,000 \text{ M}^{-1}$  for complexation of SiMe<sub>2</sub> with THF in hexanes is also consistent with the estimated gas-phase value of  $K_C \approx 30\,000 \text{ M}^{-1}$ .<sup>29,40</sup>

Transient absorption spectra were recorded for each of the tetrellylene-donor pairs studied, generally in dilute solutions containing the substrate at a concentration just high enough to reduce the equilibrium concentration of the free tetrellylene to undetectable levels. The exceptions were the spectra of the MMes<sub>2</sub>–Et<sub>2</sub>O and MMes<sub>2</sub>–THF complexes, which were recorded either in hexanes containing 4–5 M of the substrate or in the neat substrate as solvent.

The spectra of the complexes were obtained by subtraction of the spectrum remaining at the end of the monitored time window from that immediately after the laser pulse (see Figures S1–S28, Supporting Information) and are summarized in Table 2. Spectra recorded of the GeMes<sub>2</sub> precursor (6) in hexanes

**Table 2. UV–vis Absorption Maxima of the Lewis Acid–Base Complexes of Transient Silylenes and Germylenes with Chalcogen and Pnictogen Donors in Hexanes at 25 °C<sup>a</sup>**

donor	$\lambda_{\text{max}}$ (nm)					
	SiMe <sub>2</sub>	SiPh <sub>2</sub>	SiMes <sub>2</sub>	GeMe <sub>2</sub>	GePh <sub>2</sub>	GeMe <sub>2</sub>
none	465	290, 515	290, 580	325, 560	300, 500	470
Et <sub>2</sub> O	305 <sup>b</sup>	300, 375	310	<i>c,d</i>	360	300
THF	310 <sup>c</sup>	295, 370 <sup>e</sup>	310, 380 (sh) <sup>c</sup>	285, 380 <sup>f</sup>	360 <sup>f</sup>	310 <sup>f</sup>
THT	325 <sup>g</sup>	300, 370 <sup>g</sup>	300, 400	270, 400	350	320
Et <sub>2</sub> NH	280 <sup>h</sup>	300 <sup>h</sup>	320 <sup>h</sup>	280, 340, 430	320 <sup>i</sup>	280
Et <sub>3</sub> N	270 <sup>h</sup>	310 <sup>h</sup>	290 <sup>h</sup>	<i>d</i>	340 <sup>i</sup>	290 <sup>i</sup>
Et <sub>3</sub> P	310	315	320	280, 310	330	290
Cy <sub>3</sub> P <sup>k</sup>	320	320	340	310	340	280

<sup>a</sup>This work unless otherwise noted. <sup>b</sup>Cyclohexane, 20 °C.<sup>27b</sup> <sup>c</sup>In the neat substrate as solvent. <sup>d</sup>Complex not detected. <sup>e</sup>Reference 30a. <sup>f</sup>Reference 31c. <sup>g</sup>Reference 30c. <sup>h</sup>Reference 30d. <sup>i</sup>Reference 31a. <sup>j</sup>Reference 34b. <sup>k</sup>Cyclohexane solution.

containing 1.3 mM Et<sub>3</sub>N showed the germylene and Ge<sub>2</sub>Mes<sub>4</sub> and no distinct additional absorption bands that could be assigned definitively to the corresponding complex. Similar features were observed in spectra recorded in neat Et<sub>2</sub>O, in

**Table 1. Forward Rate ( $k_C$ ) and Equilibrium Constants ( $K_C$ ) for Complexation of Transient Silylenes and Germylenes with Chalcogen and Pnictogen Donors in Hexanes at 25 °C<sup>a</sup>**

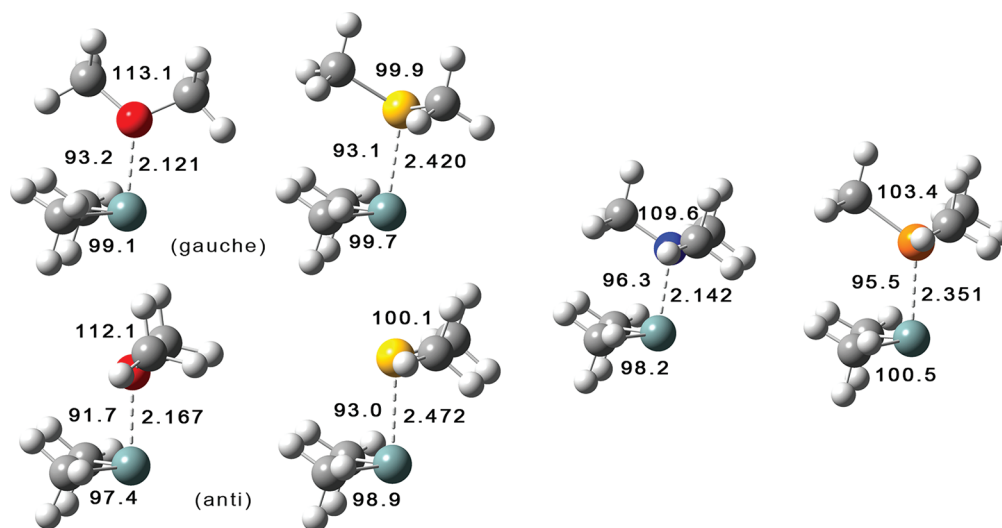
donor	$k_C / 10^9 \text{ M}^{-1} \text{ s}^{-1} [K_C / \text{M}^{-1}]$					
	SiMe <sub>2</sub>	SiPh <sub>2</sub>	SiMes <sub>2</sub>	GeMe <sub>2</sub>	GePh <sub>2</sub>	GeMes <sub>2</sub>
Et <sub>2</sub> O	[1260 ± 50] <sup>b</sup>	15 ± 4 [7100 ± 600]	[0.9 ± 0.1] <sup>b</sup>	[110 ± 10] <sup>b</sup>	[160 ± 10] <sup>b</sup>	[0.09 ± 0.01] <sup>b</sup>
THF	17.3 ± 1.5 <sup>c</sup>	15 ± 1 <sup>c</sup>	[2.4 ± 0.4] <sup>b</sup>	11 ± 2 <sup>d</sup> [9800 ± 3800]	6.3 ± 0.6 <sup>d</sup> [23 000 ± 5000]	[1.1 ± 0.2] <sup>b,d</sup>
THT	21 ± 2 <sup>e</sup>	16 ± 2	7 ± 2 [1500 ± 100]	17 ± 2	9 ± 1	[1000 ± 100] <sup>b</sup>
Et <sub>2</sub> NH	16 ± 3 <sup>f</sup>	8.3 ± 0.7 <sup>f</sup>	3.5 ± 0.5 <sup>f</sup> [6300 ± 600]	12 ± 3	7.3 ± 0.9 <sup>g</sup>	[510 ± 20] <sup>b</sup>
Et <sub>3</sub> N	9.8 ± 0.8 <sup>f</sup>	3.9 ± 0.4 <sup>f</sup>	[130 ± 60] <sup>b</sup>	8.7 ± 0.7 <sup>h</sup>	2.8 ± 0.9 <sup>h</sup>	[≤100] <sup>b</sup>
Et <sub>3</sub> P	16 ± 1	10 ± 1	5.2 ± 0.6	14 ± 2	8.5 ± 0.8	5.3 ± 0.6
Cy <sub>3</sub> P <sup>f</sup>	7.9 ± 0.8	3.5 ± 0.2	1.5 ± 0.1 [25 000 ± 6000]	5.6 ± 0.5	3.1 ± 0.1	1.7 ± 0.4 [3000 ± 1000]

<sup>a</sup>Errors are quoted as twice the standard error from linear least-squares analysis of the data according to eqs 2–4. <sup>b</sup> $k_C$  indeterminable. <sup>c</sup>Reference 30a. <sup>d</sup>Reference 31c. <sup>e</sup>Reference 30c. <sup>f</sup>Reference 30d. <sup>g</sup>Reference 31a. <sup>h</sup>Reference 34b. <sup>i</sup>Cyclohexane solution.

**Table 3.** Electronic Energies, Standard Enthalpies, and Free Energies (298.15 K, in kcal mol<sup>-1</sup>) of Complexation of SiMe<sub>2</sub> and GeMe<sub>2</sub> with Chalcogen and Pnictogen Donors<sup>a</sup> and M–X Distances (Å)<sup>b</sup> in the Corresponding Complexes, Calculated at the Gaussian-4 Level of Theory Relative to the Isolated Reactants

donor	SiMe <sub>2</sub>				GeMe <sub>2</sub>			
	$r_{\text{Si-X}}$	$\Delta E_{\text{el}}$	$\Delta H_{298\text{ K}}$	$\Delta G_{298\text{ K}}$	$r_{\text{Ge-X}}$	$\Delta E_{\text{el}}$	$\Delta H_{298\text{ K}}$	$\Delta G_{298\text{ K}}$
H <sub>2</sub> O	2.156 <sup>d</sup>	-11.1	-9.0	+1.3	2.309 <sup>d</sup>	-10.0	-8.1	+1.5
MeOH <sup>c</sup>	2.081 <sup>d</sup>	-15.1	-13.0	-1.8	2.251 <sup>d</sup>	-13.3	-11.5	-1.8
Me <sub>2</sub> O	2.121 <sup>d</sup>	-15.6	-13.5	-2.5	2.297	-14.8	-12.8	-2.1
Et <sub>2</sub> O	2.092 <sup>d</sup>	-15.6	-13.4	-1.4	2.251 <sup>d</sup>	-13.8	-12.0	-0.9
THF	2.055 <sup>d</sup>	-18.2	-16.0	-4.8	2.236	-17.1	-15.1	-3.6
H <sub>2</sub> S	2.529 <sup>d</sup>	-9.3	-7.3	+2.9	2.728 <sup>d</sup>	-9.2	-7.5	+1.8
Me <sub>2</sub> S	2.472	-19.7	-17.7	-6.0	2.589	-18.5	-16.7	-6.1
Et <sub>2</sub> S	2.477	-19.6	-17.7	-5.9	2.616	-19.2	-17.3	-5.5
THT	2.465	-20.8	-18.9	-7.3	2.588	-19.6	-17.8	-7.0
NH <sub>3</sub> <sup>c</sup>	2.073	-22.1	-19.5	-8.0	2.222	-19.2	-16.9	-6.6
MeNH <sub>2</sub> <sup>c</sup>	2.058	-26.9	-24.2	-12.1	2.198	-23.5	-21.2	-10.2
Me <sub>2</sub> NH <sup>c</sup>	2.067	-29.7	-27.0	-14.1	2.207	-26.4	-24.0	-12.1
Et <sub>2</sub> NH	2.090	-27.7	-24.8	-11.5	2.256	-24.8	-22.3	-9.2
Me <sub>3</sub> N <sup>c</sup>	2.142	-28.6	-25.7	-13.2	2.269	-26.3	-23.9	-12.4
PH <sub>3</sub>	2.400	-14.0	-11.6	-0.4	2.533	-12.6	-10.5	-0.3
Me <sub>2</sub> PH	2.350	-25.2	-23.0	-11.2	2.474	-22.8	-20.8	-9.7
Me <sub>3</sub> P	2.351	-28.5	-26.2	-14.3	2.468	-26.2	-24.2	-13.0

<sup>a</sup>For the chalcogen complexes, unless otherwise noted the anti conformer is the lowest in energy. <sup>b</sup>B3LYP/6-31G(2df,p) distances. <sup>c</sup>Data for the SiMe<sub>2</sub>-derived complexes are from ref 30d. <sup>d</sup>Gauche conformer.



**Figure 2.** Calculated (B3LYP/6-31G(2df,p)) structures of the complexes of SiMe<sub>2</sub> with (from left to right) Me<sub>2</sub>O, Me<sub>2</sub>S, Me<sub>3</sub>N, and Me<sub>3</sub>P, along with the Si–X bond distances (in Å) and the C–X–C (top), X–Si–C (middle), and C–Si–C (bottom) bond angles (in degrees).

addition to a rising absorption at the blue edge of the spectral window that may be assignable to the GeMe<sub>2</sub>–Et<sub>2</sub>O complex.

**Computational Studies.** The complexation of SiMe<sub>2</sub> and GeMe<sub>2</sub> with a selection of representative second- and third-row chalcogen and pnictogen donors was studied computationally at the Gaussian-4 (G4)<sup>33</sup> level of theory. The various donors that were studied are summarized in Table 3, along with the calculated (B3LYP/6-31G(2df,p)) M–X bond distances in the complexes ( $r_{\text{M-X}}$ ) and the G4 electronic energies and standard enthalpies and free energies ( $\Delta E_{\text{el}}$ ,  $\Delta H^\circ$ , and  $\Delta G^\circ$ , respectively) of the complexes relative to the free reactants; the results for the complexes of SiMe<sub>2</sub> with MeOH, NH<sub>3</sub>, and the methylamines were available from an earlier study.<sup>30d</sup> Each of the structures was confirmed to be an energy minimum by inspection of the Hessian matrix, which contained no negative

eigenvalues in any case. Two minimum-energy conformers were located for the Me<sub>2</sub>O and Me<sub>2</sub>S complexes, one (designated gauche) in which one of the chalcogen substituents approximately bisects the C–M–C bond angle in the tetrellylene moiety, and one (designated anti) in which the tetrellylene lone pair approximately bisects the C–X–C bond in the donor moiety. These are shown in Figure 2 for the complexes of SiMe<sub>2</sub> with Me<sub>2</sub>O and Me<sub>2</sub>S; the optimized structures of the complexes with Me<sub>3</sub>N and Me<sub>3</sub>P are also shown along with selected geometric data. The structures suggest that the consistently shorter M–X bond distances in the gauche conformers is due to a larger amount of s character in the bonding orbital at the chalcogen atom compared to that in the anti conformers. This was verified by Natural Bond Orbital (NBO) calculations (vide infra), which showed the O

**Table 4.** Zero-Point Energy Corrected Electronic Energies, Calculated Dative vs Covalent M–X Bond Length Differences ( $\Delta r_{M-X}$ ),<sup>a</sup> Complexation-Induced Changes in Natural Charge at the Heteroatoms ( $\Delta Z_M$ ,  $\Delta Z_X$ ),<sup>b</sup> and Mayer–Wiberg M–X Bond Indices ( $P_{M-X}$ )<sup>b</sup> for the Complexes of SiMe<sub>2</sub> and GeMe<sub>2</sub> with Representative Chalcogen and Pnictogen Donors

donor	SiMe <sub>2</sub>					GeMe <sub>2</sub>				
	$\Delta E_0^c$	$\Delta r_{Si-X}/\text{\AA}$ (%)	$\Delta Z_{Si}$	$\Delta Z_X$	$P_{Si-X}$	$\Delta E_0^c$	$\Delta r_{Ge-X}/\text{\AA}$ (%)	$\Delta Z_{Ge}$	$\Delta Z_X$	$P_{Ge-X}$
MeOH(g)	–12.6	0.43 (26)	–0.08	–0.03	0.198	–11.4	0.47 (26)	–0.06	–0.03	0.156
Me <sub>2</sub> O(g)	–13.4	0.46 (28)	–0.08	–0.05	0.220	–12.5	0.49 (27)	–0.05	–0.04	0.147
Me <sub>2</sub> O(a)	–13.5	0.51 (31)	–0.09	–0.04	0.172	–12.9	0.51 (29)	–0.06	–0.03	0.142
Me <sub>2</sub> S(g)	–17.0	0.25 (12)	–0.27	+0.14	0.478	–16.1	0.33 (15)	–0.22	+0.11	0.382
Me <sub>2</sub> S(a)	–17.5	0.30 (14)	–0.27	+0.14	0.431	–16.9	0.34 (15)	–0.23	+0.11	0.369
Me <sub>2</sub> NH	–26.3	0.33 (19)	–0.14	–0.06	0.284	–23.6	0.37 (20)	–0.12	–0.05	0.250
Me <sub>3</sub> N	–25.1	0.40 (23)	–0.14	–0.07	0.252	–23.6	0.42 (23)	–0.11	–0.05	0.221
Me <sub>2</sub> PH	–22.9	0.07 (3)	–0.41	+0.20	0.709	–20.8	0.15 (6)	–0.37	+0.17	0.614
Me <sub>3</sub> P	–26.1	0.07 (3)	–0.42	+0.21	0.714	–24.3	0.13 (6)	–0.38	+0.19	0.631

<sup>a</sup> $\Delta r_{M-X} = r_{M-X}(\text{complex}) - r_{M-X}(\text{Me}_2\text{RM-XMe}_n)$ , B3LYP/6-31G(2df,p) distances, given in Å; percentages are given in parentheses. <sup>b</sup>From NBO analysis of the HF/6-31G(d) densities; the calculated charges at M in free SiMe<sub>2</sub> and GeMe<sub>2</sub> are  $Z_{Si} = 1.087$  and  $Z_{Ge} = 1.038$ , respectively, while those in the donors are  $Z_O = -0.789$  (MeOH) and  $-0.634$  (Me<sub>2</sub>O),  $Z_S = 0.214$  (Me<sub>2</sub>S),  $Z_N = -0.727$  (Me<sub>2</sub>NH) and  $-0.558$  (Me<sub>3</sub>N), and  $Z_P = 0.656$  (Me<sub>2</sub>PH) and  $0.920$  (Me<sub>3</sub>P). <sup>c</sup>Relative to the isolated donor and acceptor, in kcal mol<sup>–1</sup>.

atoms in the MMe<sub>2</sub>–Me<sub>2</sub>O complexes to be approximately sp<sup>2</sup> hybridized in the gauche conformers, in which the bonding geometry at O is planar, and approximately sp<sup>3</sup> hybridized in the anti conformers. Several conformers were found for the diethyl-substituted systems, which were differentiated by the anti or gauche arrangement with respect to the MMe<sub>2</sub> substituents and also by the conformations of the ethyl groups. In any event, the differences in energy between the various conformers were found to be small, amounting to less than 1.2 kcal mol<sup>–1</sup> in every case. Table 3 contains the calculated data for only the lowest energy conformers of the various structures that were located. The calculated binding energies of the complexes of both SiMe<sub>2</sub> and GeMe<sub>2</sub> with the parent (hydride) donors increase in the order H<sub>2</sub>S < H<sub>2</sub>O < PH<sub>3</sub> < NH<sub>3</sub>, in good general agreement with the results of earlier calculations for SiH<sub>2</sub>,<sup>14,22</sup> GeH<sub>2</sub>,<sup>14</sup> and GeMe<sub>2</sub>.<sup>42</sup> at lower levels of theory. The trends in the calculated M–X bond distances as a function of M and X for the Me<sub>2</sub>X (X = O, S) and Me<sub>2</sub>XH (X = N, P) complexes are also similar to those found in the earlier calculations for the parent hydrides,<sup>14,22</sup> with the bond lengths increasing in the order N < O < P < S for both the silylene and germylene complexes and being systematically longer in the GeMe<sub>2</sub> complexes by roughly 10% for the O and N donors and ca. 5% for the S and P donors.

Table 4 gives, for selected MMe<sub>2</sub>–donor Lewis pairs in the series, the differences between the M–X bond distances ( $r_{M-X}$ ) in the complexes and those in the corresponding Me<sub>2</sub>RM–XMe<sub>n</sub> (R = H, Me) compounds, which were optimized at the same (B3LYP/6-31G(2df,p)) level of theory as employed in the G4 compound method. The table also gives the differences between the natural (NPA) charges at M and X in the complexes and those in the free reactants and the Mayer–Wiberg M–X bond indices ( $P_{M-X}$ ), obtained from natural bond orbital (NBO) analysis of the HF/6-31G(d) densities that were generated as part of the G4 calculations.

More complete details of the computational results for representative complexes in the series are given in the Supporting Information.

## DISCUSSION

The successful determination of equilibrium constants for complexation of the six transient silylenes and germylens with Et<sub>2</sub>O allows the first quantitative experimental assessment to be

made of the differences in Lewis acidity of silylenes and germylens of homologous structures and of its response to changes in substitution at the tetrel center, as they apply to complexation with a common Lewis base. As can be seen from Table 1, the  $K_C$  values for complexation with Et<sub>2</sub>O span a range of roughly 5 orders of magnitude between that of the weakest Lewis acid in the series (GeMe<sub>2</sub>) to the strongest (SiPh<sub>2</sub>), corresponding to a range in binding free energies of  $-5.2$  to  $+1.7$  kcal mol<sup>–1</sup>, where the standard state is a hexanes solution containing 1 M concentrations of each of the reactants at 25 °C. For both sets of compounds the trend in Lewis acidities follows the order MPh<sub>2</sub> > MMe<sub>2</sub> ≫ MMe<sub>2</sub>, reflecting the  $\sigma$ - and  $\pi$ -electron-withdrawing effects of the phenyl substituent relative to methyl, which leads to enhanced acidity, and the (much larger) destabilizing effect of steric hindrance on the complexation equilibria in the cases of the diaryltetrellylenes. The electronic effect associated with phenyl for methyl substitution appears to be somewhat larger for the silylenes ( $K_C^{\text{SiPh}_2}/K_C^{\text{SiMe}_2} = 5.6 \pm 0.6$ ) than for the germylens ( $K_C^{\text{GePh}_2}/K_C^{\text{GeMe}_2} = 1.5 \pm 0.3$ ), which we attribute tentatively to preferential enhancement of the Lewis acidity of SiPh<sub>2</sub> compared to GePh<sub>2</sub>, owing to the somewhat more effective  $\pi$  overlap that is possible between the phenyl substituents and the 3p orbital on Si, compared to that involving the 4p orbital on Ge. We note in passing that the  $K_C^{\text{GePh}_2}/K_C^{\text{GeMe}_2}$  ratio for complexation with Et<sub>2</sub>O is somewhat smaller than those for complexation with MeOH, *t*-BuOH, and THF,<sup>31c</sup> which together indicate that GePh<sub>2</sub> is the stronger Lewis acid by an average factor of  $3 \pm 1$ . In any event, the difference disappears in the MMe<sub>2</sub> derivatives (i.e.,  $K_C^{\text{SiMe}_2}/K_C^{\text{SiMe}_2} \approx K_C^{\text{GeMe}_2}/K_C^{\text{GeMe}_2}$ ), in which  $\pi$  overlap is reduced by steric-induced twisting of the aryl rings out of the (near) coplanar arrangement that is possible in the phenylated derivatives. Mesityl for phenyl substitution gives rise to reductions in  $K_C$  of  $10^3$ – $10^4$ , indicating differences in binding free energies of 5–6 kcal mol<sup>–1</sup> between the corresponding MMe<sub>2</sub> and MPh<sub>2</sub> complexes with Et<sub>2</sub>O. The  $K_C^{\text{GePh}_2}/K_C^{\text{GeMe}_2}$  ratio varies with steric factors in the Lewis base, from values of ca. 220–250 for MeOH and *t*-BuOH,<sup>31c</sup> through ca. 2000 for Et<sub>2</sub>O, to ca. 20 000 for THF.<sup>31c</sup> Similar trends can be expected to hold for the silylenes, though the actual numbers for MeOH and THF cannot be measured for one reason or another (vide infra).

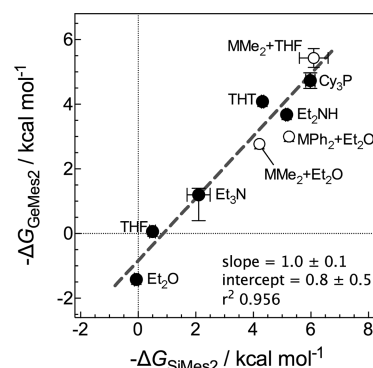
The results for each of the three silylene–germylene pairs show the silylene to be the consistently stronger Lewis acid by roughly an order of magnitude in  $K_C$ , corresponding to differences in binding free energies of 1.4–2.2 kcal mol<sup>-1</sup>. This is in good agreement with theoretical predictions for other silylene– and germylene–O-donor systems.<sup>14,25a,43</sup> The difference is somewhat larger for the MPh<sub>2</sub>–Et<sub>2</sub>O pairs ( $K_C^{\text{Si}}/K_C^{\text{Ge}} = 44 \pm 7$ ) than for the MMe<sub>2</sub>–Et<sub>2</sub>O ( $K_C^{\text{Si}}/K_C^{\text{Ge}} = 12 \pm 2$ ) and MMe<sub>2</sub>–Et<sub>2</sub>O ( $K_C^{\text{Si}}/K_C^{\text{Ge}} = 10 \pm 2$ ) systems, presumably reflecting the more effective  $\pi$  overlap that is possible in SiPh<sub>2</sub> in comparison to the germanium homologue, as discussed above.

Equilibrium constant measurements are not possible for complexation of the three silylenes with MeOH, owing to the rapidity with which the complexes react to yield the net O–H insertion products via (catalytic) H transfer.<sup>30b</sup> This is not the case for the corresponding germylenes, whose complexes with MeOH are sufficiently stable that they can be detected even in the neat alcohol as solvent.<sup>44</sup> On the basis of the differences observed for the Et<sub>2</sub>O complexations and the experimental  $K_C$  values for complexation of MeOH with the germylenes,<sup>44</sup> it is possible to derive estimates of  $K_C \approx 10^4$ ,  $1.5 \times 10^5$ , and  $150 \text{ M}^{-1}$  for complexation of MeOH with SiMe<sub>2</sub>, SiPh<sub>2</sub>, and SiMes<sub>2</sub>, respectively, in hexanes at 25 °C. Estimates of  $K_C \approx 10^5$  and  $10^6 \text{ M}^{-1}$  can be similarly derived for the equilibrium constants for complexation of THF with SiMe<sub>2</sub> and SiPh<sub>2</sub>, respectively. These are both larger than the upper measurable limit that is accessible with our experimental method, as we concluded in our earlier reported studies of these species in solution.<sup>30a</sup> Given the uncertainties, the predicted value of  $K_C$  for SiMe<sub>2</sub>–THF in hexanes is in reasonable agreement with the value (of  $K_C \approx 30\,000 \text{ M}^{-1}$ ) estimated from the gas-phase data of Baggott et al. (vide supra).<sup>29,40</sup> This, along with the reasonably close agreement between the estimated  $K_C$  value for complexation of SiMe<sub>2</sub> with Me<sub>2</sub>O in the gas phase and that measured in the present work for complexation with Et<sub>2</sub>O in hexanes, shows that solvation effects on the complexation equilibria are minimal, at least for the more weakly bound Lewis pairs in the series.

We knew from previous work that the equilibrium constants for complexation of MMe<sub>2</sub> and MPh<sub>2</sub> with the amines<sup>30d,31a,d,34b</sup> are also larger than can be measured by our experimental method; thus, it was not particularly surprising to find that the same is also true for complexation with THT<sup>30c</sup> and the trialkylphosphines. On the other hand, the increased steric interactions afforded by mesityl for phenyl substitution results in measurable  $K_C$  values for all the SiMes<sub>2</sub>– and GeMes<sub>2</sub>–donor pairs except those with Et<sub>3</sub>P, which are again larger than the measurable limit. Remarkably, the variation in the equilibrium constants with Lewis base for SiMes<sub>2</sub> coincides nearly perfectly with that observed for GeMes<sub>2</sub>, the  $K_C$  values increasing in the order Et<sub>2</sub>O < THF < Et<sub>3</sub>N < THT < Et<sub>2</sub>NH < Cy<sub>3</sub>P < Et<sub>3</sub>P for SiMes<sub>2</sub> and in the same order but with THT and Et<sub>2</sub>NH reversed for GeMes<sub>2</sub>. As we found for the complexations with Et<sub>2</sub>O, the silylene displays a significantly higher Lewis acidity than the germylene toward all the donors in the series; the difference in  $K_C$  is roughly a factor of 10 for Et<sub>2</sub>O, Et<sub>2</sub>NH, and Cy<sub>3</sub>P but reduces to a factor of 1.5–2 for THF and THT. The reasons for the different behavior of the last two Lewis bases are not clear but may be due to entropic effects, owing to the rigidity of their cyclic structures. In contradiction with the general classification of silylenes and germylenes as hard electrophiles,<sup>25a</sup> the results indicate that

trialkylphosphines (even the relatively hindered derivative, Cy<sub>3</sub>P) are significantly stronger donors than the secondary and tertiary amines toward both SiMes<sub>2</sub> and GeMes<sub>2</sub> in solution at ambient temperatures. The same is true of the sulfide (THT) compared to its second-row homologue, THF.

The data for all nine of the experimentally characterized MR<sub>2</sub>–donor Lewis pairs are shown in Figure 3, in the form of a



**Figure 3.** Plot of experimental free energies of complexation of GeMes<sub>2</sub> vs those of SiMes<sub>2</sub> with the same donor in hexanes at 25 °C (●); the dashed line is the least-squares fit of the six data points. The points for the MPh<sub>2</sub>–Et<sub>2</sub>O, MMe<sub>2</sub>–Et<sub>2</sub>O, and MMe<sub>2</sub>–THF systems are also included in the plot (○) (reference state: 1 M solution, 25 °C).

plot of the binding free energies of the germylene complexes versus the corresponding values for the homologous silylene complexes, where the reference state is a 1 M solution in hexanes at 25 °C. The plot accentuates the parallels between the Lewis acid–base complexation behavior of the silylene and germylene systems; least-squares analysis of the six data points for the MMe<sub>2</sub>–donor Lewis pairs affords a slope of  $1.0 \pm 0.1$ , indicating that the difference in Lewis acidity between SiMes<sub>2</sub> and GeMes<sub>2</sub> is more or less independent of the donor and the strength of the Lewis acid–base interaction, over a 6–7 kcal mol<sup>-1</sup> range in binding energy. The intercept corresponds to the average difference in the binding energies of the complexes of SiMes<sub>2</sub> and GeMes<sub>2</sub> with a given donor, which is  $0.8 \pm 0.5$  kcal mol<sup>-1</sup> in favor of (i.e.,  $\Delta G$  is more negative for) the silylene.

**Comparisons with Theory.** Since experimental limitations prevent the measurement of equilibrium constants for complexation of the less hindered tetrilylenes with the S, N, and P donors, we turned to theoretical calculations in order to expand the comparison of the binding thermodynamics of SiMe<sub>2</sub>–donor and GeMe<sub>2</sub>–donor complexes to cover a broader range in donor strength, using the Gaussian-4 (G4) compound method of Curtiss and co-workers.<sup>33</sup> The G4 method has been shown to reproduce experimental thermochemical data for a wide variety of organic and main-group systems with an average chemical accuracy of ca. 1 kcal mol<sup>-1</sup>,<sup>33</sup> and indeed the calculated binding free energies of the SiMe<sub>2</sub>–Et<sub>2</sub>O, SiMe<sub>2</sub>–Me<sub>2</sub>O,<sup>29,40</sup> SiMe<sub>2</sub>–THF,<sup>29,40</sup> GeMe<sub>2</sub>–Et<sub>2</sub>O, GeMe<sub>2</sub>–MeOH,<sup>31c</sup> and GeMe<sub>2</sub>–THF complexes (see Table 3) match the experimentally determined values (after conversion to the gas-phase reference state; see Table 5) within this limit of uncertainty in all cases. It should be noted that the calculations predict the same ordering of stability of the SiMe<sub>2</sub>– and GeMe<sub>2</sub>–O-donor complexes as a function of donor as was found experimentally, and they successfully reproduce the small

**Table 5.** Experimental Gibbs Free Energies (Reference State, Gas Phase, 1 atm, 25 °C) for Lewis Acid–Base Complexation of Silylenes and Germynes with Chalcogen and Pnictogen Donors in Hexanes at 25 °C (in kcal mol<sup>-1</sup>)

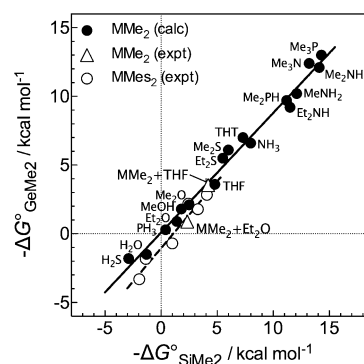
	$\Delta G$					
	SiMe <sub>2</sub>	SiPh <sub>2</sub>	SiMes <sub>2</sub>	GeMe <sub>2</sub>	GePh <sub>2</sub>	GeMes <sub>2</sub>
MeOH	<i>a</i>	<i>a</i>	<i>a</i>	-2.1 ± 0.1	-2.9 ± 0.2	+0.3 ± 0.3
Et <sub>2</sub> O	-2.3 ± 0.1	-3.4 ± 0.1	+2.0 ± 0.1	-0.9 ± 0.1	-1.1 ± 0.1	+3.3 ± 0.4
THF	-4.2 ± 0.1 <sup>b</sup>	<i>a, c</i>	+1.4 ± 0.1	-3.5 ± 0.3	-4.0 ± 0.1	+1.8 ± 0.1
THT	<i>a, c</i>	<i>a, c</i>	-2.4 ± 0.1	<i>a, c</i>	<i>a, c</i>	-2.2 ± 0.1
Et <sub>2</sub> NH	<i>a, c</i>	<i>a, c</i>	-3.3 ± 0.1	<i>a, c</i>	<i>a, c</i>	-1.8 ± 0.1
Et <sub>3</sub> N	<i>a, c</i>	<i>a, c</i>	-1.0 ± 0.4	<i>a, c</i>	<i>a, c</i>	≥ -0.8 <sup>a,d</sup>
Et <sub>3</sub> P	<i>a, c</i>	<i>a, c</i>	<i>a, b</i>	<i>a, c</i>	<i>a, c</i>	<i>a, c</i>
Cy <sub>3</sub> P <sup>i</sup>	<i>a, c</i>	<i>a, c</i>	-4.1 ± 0.1	<i>a, c</i>	<i>a, c</i>	-2.8 ± 0.2

<sup>a</sup> $K_C$  indeterminable. <sup>b</sup>Gas phase; see ref 39. <sup>c</sup>Upper limit is -6.0 kcal mol<sup>-1</sup>. <sup>d</sup>Lower limit.

differences in the experimental binding energies of the SiMe<sub>2</sub> and GeMe<sub>2</sub> complexes with a common O donor. The calculations also predict nearly equal binding free energies for the SiMe<sub>2</sub> and GeMe<sub>2</sub> complexes with each of the three sulfides (Me<sub>2</sub>S, Et<sub>2</sub>S, and THT; see Table 3), as was found experimentally for the MMe<sub>2</sub>-THT complexes. The calculated values of  $\Delta G^\circ$  for the MMe<sub>2</sub>-THT complexes ( $\Delta G \approx -7$  kcal mol<sup>-1</sup>; 1 atm gas phase at 25 °C as reference state) correspond to  $K_C$  values on the order of  $5 \times 10^6$  M<sup>-1</sup>, which is consistent with the indication from experiment that they are greater than the measurable upper limit of our experimental method. Again, solvation effects appear to have a minimal effect on the complexation equilibria in comparison to the gas phase, for the weaker Lewis bases in the series at least.

The calculated binding energies of the complexes of both SiMe<sub>2</sub> and GeMe<sub>2</sub> with the parent chalcogen and pnictogen hydrides increase in the order H<sub>2</sub>S < H<sub>2</sub>O < PH<sub>3</sub> < NH<sub>3</sub>, in agreement with previous theoretical results for SiH<sub>2</sub><sup>14,22</sup> and GeH<sub>2</sub>.<sup>14</sup> The ordering differs from that found by Su and Chu for the complexes with GeMe<sub>2</sub> (H<sub>2</sub>S < PH<sub>3</sub> < H<sub>2</sub>O < NH<sub>3</sub>) at the B3LYP/6-311G(d) and MP2/6-311G(d) levels of theory,<sup>42</sup> which appear to predict anomalously high values of the binding energy for the GeMe<sub>2</sub>-H<sub>2</sub>O complex. Alkyl substitution in the donor leads to marked increases in basicity, more so for the third-row donors than the second,<sup>45</sup> and together with steric effects (which are greater for the second-row donors than the third) produces a complete change in the order of stabilities of the corresponding complexes in comparison to those found for the parent chalcogen and pnictogen hydrides.

The overall trends are illustrated in Figure 4, a plot of the calculated binding free energies of the 17 GeMe<sub>2</sub>-donor complexes versus those of the corresponding SiMe<sub>2</sub> complexes. The experimental data from Figure 3 are also included in the plot (after conversion to the gas-phase reference state; see Table 5), in order to illustrate the level of agreement between theory and experiment for the MMe<sub>2</sub>-Et<sub>2</sub>O and MMe<sub>2</sub>-THF Lewis pairs and the relationship between the theoretical estimates for the MMe<sub>2</sub>-donor systems and the experimentally determined  $\Delta G$  values for the sterically encumbered MMe<sub>2</sub>-donor systems. As can be seen in the figure, theory predicts a similar overall trend in the binding energies of the MMe<sub>2</sub>-donor systems as a function of the donor as is observed experimentally for the MMe<sub>2</sub> systems, with the trialkylphosphine (Me<sub>3</sub>P) forming the strongest complexes and the acyclic ethers and MeOH the weakest, stronger only than those with H<sub>2</sub>S, H<sub>2</sub>O, and PH<sub>3</sub>. The calculations suggest that the difference in Lewis acidities of SiMe<sub>2</sub> and GeMe<sub>2</sub> increases very modestly as the Lewis base strength of the donor increases

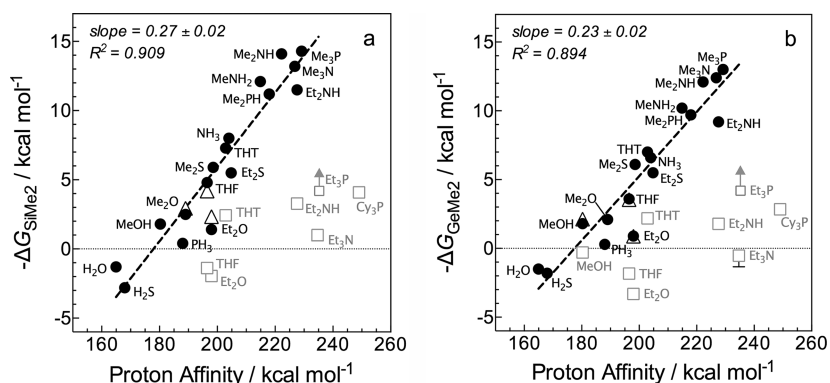


**Figure 4.** Plot of calculated (G4) binding free energies of GeMe<sub>2</sub>-donor complexes vs those of the corresponding SiMe<sub>2</sub>-donor complexes (●). The experimental data points for the MMe<sub>2</sub>-O-donor (△) and MMe<sub>2</sub>-donor (○) Lewis pairs (see Figure 3) are also included in the figure (standard state gas phase, 1 atm, and 25 °C).

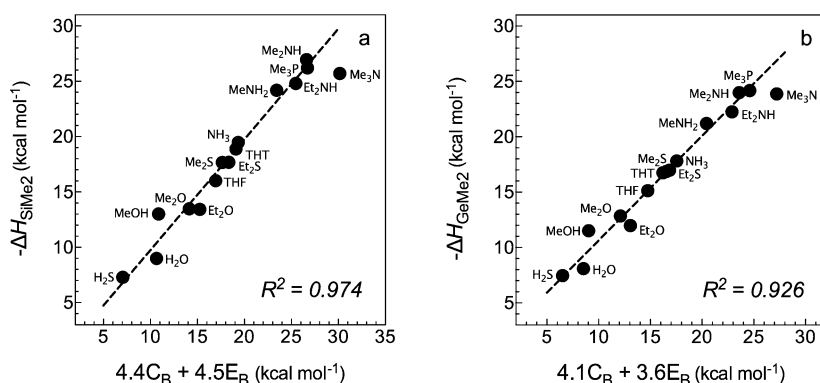
over a 20 kcal mol<sup>-1</sup> range in binding free energy, as revealed by the nonunit slope of the plot (0.87 ± 0.03).

As individual data sets, the calculated binding energies of the SiMe<sub>2</sub> and GeMe<sub>2</sub> complexes correlate with the (experimental) proton affinity (PA) values of the donors,<sup>45,46</sup> albeit fairly roughly. This is illustrated in Figure 5, again with the available experimental data for the corresponding MMe<sub>2</sub>-donor and MMe<sub>2</sub>-donor systems included for comparison; the data points for the MMe<sub>2</sub>-Et<sub>3</sub>P complexes are shown in the plots as upward-pointing arrows, to signify the fact that only lower limits of the binding energies could be established experimentally for these two systems. Both correlations improve quite significantly ( $R^2 \geq 0.947$ ) if the data points for Et<sub>2</sub>O and Et<sub>2</sub>NH are excluded from the analyses. This is justifiable, considering that these are the only systems for which the favored conformation of the donor moiety in the complexes is different from the all-trans conformation favored by the free donor; torsional strain effects thus decrease the stabilities of these MMe<sub>2</sub>-donor complexes by a small (2–3 kcal mol<sup>-1</sup>) increment which is not accounted for by the PA values of the two donors. Similar-quality correlations are also observed with the experimental donor gas basicities,<sup>45</sup> not surprisingly, given that the proton affinities and gas basicities of the series of Lewis bases studied in this work are strongly correlated<sup>45</sup> (so too are the calculated  $\Delta H$  and  $\Delta G$  values for the MMe<sub>2</sub>-donor complexes; see Figure S29, Supporting Information); we have employed proton affinities to illustrate the correlation with Brønsted basicity for the simple reason that it is the only experimental measure of gas-phase basicity that is available for





**Figure 5.** Plots of calculated (G4; ●) and experimental (hexanes; △) standard free energies of complexation of chalcogen and pnictogen donors with (a) SiMe<sub>2</sub> and (b) GeMe<sub>2</sub> vs the (experimental) proton affinities of the donors. The experimental values for the SiMe<sub>2</sub>– and GeMe<sub>2</sub>–donor complexes (□; hexanes) are also shown in the plots. The reference state is the gas phase at 1 atm and 25 °C in all cases.



**Figure 6.** Plots of calculated (G4) gas-phase binding enthalpies of (a) SiMe<sub>2</sub> and (b) GeMe<sub>2</sub> with chalcogen and pnictogen donors, vs the two-parameter functions defined by least-squares fitting of the data to eq 5.

Cy<sub>3</sub>P.<sup>46</sup> Not unexpectedly given the increased steric interactions, the MMe<sub>2</sub>–donor systems show only a trend of increasing binding free energy with increasing donor PA, but no significant correlation. The calculations predict nearly equal binding energies for the complexes of SiMe<sub>2</sub> with Me<sub>2</sub>NH, Me<sub>3</sub>N, and Me<sub>3</sub>P and the same as well for the corresponding GeMe<sub>2</sub> complexes. This is due at least in part to a much greater sensitivity of the binding energies of the tertiary amine complexes to steric destabilization; the fact that the MMe<sub>2</sub>–Et<sub>3</sub>N complexes are at least 5 kcal mol<sup>−1</sup> less stable than the MMe<sub>2</sub>–Et<sub>3</sub>P complexes shows that the preferential destabilization of the tertiary amine complexes increases even further as steric bulk is built into the tetrellylene.

Plots of the calculated binding enthalpies of the MMe<sub>2</sub>–donor complexes against BF<sub>3</sub> affinity values (CH<sub>2</sub>Cl<sub>2</sub> solution, 298 K)<sup>41</sup> for the six donors for which parameters are available are suggestive of two-family correlations. Those for the complexes with Et<sub>2</sub>O, Me<sub>2</sub>O, THF, and Me<sub>3</sub>N correlate strongly with BF<sub>3</sub> affinities ( $R^2 \geq 0.990$ ), while the  $-\Delta H$  values for the THT and Me<sub>3</sub>P complexes are 8–9 kcal mol<sup>−1</sup> larger than the correlations for the second-row donors would predict. The Lewis acid properties of SiMe<sub>2</sub> and GeMe<sub>2</sub> are clearly remarkably similar to one another, but they do not exhibit behavior typical of hard Lewis acids such as BF<sub>3</sub>.

Significantly better correlations are observed between the calculated binding enthalpies of the SiMe<sub>2</sub>–donor and GeMe<sub>2</sub>–donor complexes and the donor  $E_B$  and  $C_B$  constants of Drago and co-workers.<sup>47</sup> The analysis employs eq 5, an empirical relationship that separates the binding enthalpy of a given

Lewis acid–base (AB) pair into individual contributions from electrostatic ( $E$ ) and covalent ( $C$ ) bonding components.<sup>48</sup> Figure 6 shows the least-squares fits of the calculated binding enthalpies to eq 5, incorporating all the systems for which donor  $E_B$  and  $C_B$  constants have been assigned except the MMe<sub>2</sub>–Me<sub>3</sub>N pairs (vide infra). The analyses afford values of  $C_A = 4.4 \pm 0.2$  and  $E_A = 4.5 \pm 0.4$  (kcal mol<sup>−1</sup>)<sup>1/2</sup> for SiMe<sub>2</sub> ( $R^2 = 0.974$ ) and  $C_A = 4.1 \pm 0.3$  and  $E_A = 3.6 \pm 0.6$  (kcal mol<sup>−1</sup>)<sup>1/2</sup> for GeMe<sub>2</sub> ( $R^2 = 0.926$ ), where the errors are quoted as the standard errors from the two-parameter least-squares fits. We note that the bases in the series span a range of ca. 750 in  $E_B/C_B$  ratio, which helps to maximize the accuracy of the  $E_A$  and  $C_A$  values determined from such analyses.<sup>48</sup>

$$-\Delta H = E_A E_B + C_A C_B \quad (5)$$

The results of the EC analysis suggest that SiMe<sub>2</sub> and GeMe<sub>2</sub> are of *borderline* hardness, significantly softer and more acidic than (for example) BMe<sub>3</sub> ( $E_A = 2.90$ ;  $C_A = 3.60$ )<sup>47</sup> but qualitatively similar to it in terms of the tendency to engage in covalent vs electrostatic binding with Lewis bases. The roughly equal  $C_A$  and  $E_A$  values implies, in essence, that the nature of the Lewis base alone (as defined by its  $E_B/C_B$  ratio) defines the nature of the bonding interaction in a given complex, whether predominantly electrostatic (e.g., water and alcohols;  $E_B/C_B > 2.5$ ), predominantly covalent (e.g., sulfides and phosphines;  $E_B/C_B < 0.1$ ), or a mixture of both (e.g., ethers and amines;  $E_B/C_B \approx 1$  and 0.2–1, respectively). The only outliers in the correlations are the MMe<sub>2</sub>–Me<sub>3</sub>N Lewis pairs, for which the calculated binding enthalpies are in both cases ca. 3 kcal mol<sup>−1</sup>

smaller than the correlations predict they should be. The discrepancy can be attributed to a steric effect on the binding enthalpy, which is not accounted for in the *E* and *C* parameters.<sup>48</sup> The effect is absent in the complexes with the primary and secondary amines, whose favored conformations have an N–H bond bisecting the two methyl groups in the tetrellylene moiety. On the other hand, the fact that the binding enthalpies of the  $\text{MMe}_2\text{--Me}_3\text{P}$  complexes obey the correlations defined by the other  $\text{MMe}_2$ -donor pairs indicates that steric factors are much less important than in the amine complexes, and that there is no detectable stabilization from  $\pi$  back-bonding (which the *E* and *C* parameters also do not account for). The latter conclusion is consistent with a recent theoretical evaluation of the bonding in the parent  $\text{SiH}_2\text{--PH}_3$  complex.<sup>23</sup>

The variations in the calculated structures, charge distributions, and M–X bond orders of the complexes tell a similar story, more or less. The data for selected complexes in the series are shown in Table 4, the structural information in the form of the percent differences between the M–X bond lengths in the complexes and in the corresponding covalent compounds  $\text{Me}_2\text{RM--XMe}_n$ , which decrease in the order  $\text{O} > \text{N} > \text{S} > \text{P}$ , and the charge distributions in the form of the differences between the NPA charges at M and X in the complexes and those in the free donors and acceptors, which increase along with the M–X bond orders in the same order as the bond length differences decrease. In partial contrast to the conclusions derived from the EC analysis, the NPA charge analysis indicates a clear difference between the bonding characteristics of the complexes with the second- and third-row donors, the data for the former being consistent with predominantly electrostatic binding and the latter with predominantly covalent binding, especially for the phosphine complexes. The role of steric effects in the binding to amines is clearly evident in the data for the complexes with  $\text{Me}_2\text{NH}$  and  $\text{Me}_3\text{N}$ , where the latter complexes possess longer bonds and smaller bond orders compared to the complexes with the former. In contrast, the bond distances, charge polarizations, and bond orders of the  $\text{Me}_2\text{PH}$  and  $\text{Me}_3\text{P}$  complexes are identical; steric effects are absent (more or less) because the bonds to phosphorus are longer than those to nitrogen. Differences in steric factors may also be partly responsible for the inversion in the relative stabilities of the ether and sulfide complexes relative to those of the complexes with the parent hydrides,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .

**Electronic Spectra of Silylene- and Germylene-Donor Complexes in Solution.** For each of the three silylene–germylene pairs, the UV–vis spectra of the corresponding  $\text{Et}_2\text{O}$  complexes are quite similar to one another, with the absorption maximum of the germylene– $\text{Et}_2\text{O}$  complex appearing at slightly shorter wavelength than that of the corresponding silylene– $\text{Et}_2\text{O}$  complex. For the diaryltetrellylenes the relative positions of  $\lambda_{\text{max}}$  for the complexes are the same as those for the uncomplexed (free) species (i.e., with the  $\text{GeAr}_2\text{--Et}_2\text{O}$  complexes absorbing at shorter wavelengths than the corresponding  $\text{SiAr}_2\text{--Et}_2\text{O}$  complexes), while the opposite is true of the dimethyl systems. In any event, it is clear that the magnitude of the spectral shift that occurs upon complexation does not correlate with the relative magnitudes of the binding energies; the spectral shift is generally somewhat greater for the germylene than the silylene, regardless of the fact that the germylene–ether complex is the more weakly bound of the two. The same trend holds for the tetrellylene–THF

complexes, for which the equilibrium constants and underlying binding energies are larger owing to the higher Lewis basicity of THF compared to  $\text{Et}_2\text{O}$ .<sup>41</sup> For most of the donors that have been studied, the trends in the UV–vis absorption characteristics of the various complexes are somewhat different in solution than in low-temperature matrices.<sup>20b,21b</sup> Nevertheless, as they do under low-temperature matrix conditions, in fluid solution silylene– and germylene–chalcogen complexes consistently absorb at significantly longer wavelengths than the corresponding pnictogen complexes, perhaps reflecting the generally weaker binding that characterizes the former complexes compared to the latter ones. However, there is no consistent variation in  $\lambda_{\text{max}}$  with the donor atoms within the same group, the direction and magnitude of the spectral shift appearing to vary from (tetrellylene) system to system.

**Kinetics of Lewis Acid–Base Complexation.** The kinetic data show complexation to be invariably fast, proceeding in all cases with rate constants within a factor of 20 of the diffusion limit in hexanes solution ( $k_{\text{diff}} \approx 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C), with only modest variations with substituents in either the tetrellylene or the donor, or with the overall reaction thermochemistry. This is consistent with complexation being an essentially barrierless process enthalpically. Both  $\text{SiPh}_2$  and  $\text{GePh}_2$  react roughly half as fast as their methyl homologues with the pnictogen donors, despite the fact that complexation with the phenyl-substituted systems is thermodynamically more favorable; similar differences in rate are observed for the reactions of  $\text{GePh}_2$  with the chalcogen donors compared to  $\text{GeMe}_2$ , but not for  $\text{SiPh}_2$ . The small rate retardation may be a reflection of the greater steric demand of the phenyl substituent compared to methyl, since  $\text{SiMe}_2$  reacts 2–4 times slower than  $\text{SiPh}_2$  with each of the S, N, and P donors for which rate constant measurements are possible. There is a general trend of marginally faster complexation rates with the heavier donor element within a group, all else being equal; for example,  $\text{GeMe}_2$  and  $\text{GePh}_2$  react slightly faster with THT than with THF, and both the germylens and silylenes react roughly twice as fast with  $\text{Et}_3\text{P}$  than with  $\text{Et}_3\text{N}$ . This is undoubtedly a reflection of the longer equilibrium bond distances in the complexes with third-row donors compared to those with second-row donors (vide supra and refs 14, 22, 25a, and 42) and thus a lower sensitivity in the transition state to steric factors associated with the donor substituents. Interestingly, there is essentially no dependence of the rate constant on the tetrel element except for the complexations with THF, for which the silylenes ( $\text{SiMe}_2$  and  $\text{SiPh}_2$ ) are faster by a factor of about 2. This is also the case for complexation of the  $\text{MMe}_2$  and  $\text{MPh}_2$  systems with alcohols;<sup>30b,31c</sup> thus, the trend appears to be general for O-donor systems.

## SUMMARY AND CONCLUSIONS

The scattered handful of thermodynamic data for Lewis acid–base complexation of simple dialkyl- and diarylsilylenes and dialkyl- and diarylgermylenes in solution that existed at the onset of this work has been expanded quite substantially, through the determination of equilibrium constants for complexation of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  with two ethers, a sulfide, a secondary and tertiary amine, and two trialkylphosphines and of those for complexation of the homologous  $\text{MMe}_2$  and  $\text{MPh}_2$  pairs with  $\text{Et}_2\text{O}$ , all in hydrocarbon solvents at 25 °C. The results reveal a systematically higher Lewis acidity for the silylene compared to the germylene homologue by roughly 1 pK unit, which is more or less independent of substitution in

the tetrellylene or the identity of the donor over a range of ca.  $10^5 \text{ M}^{-1}$  in the binding constant, or ca.  $7 \text{ kcal mol}^{-1}$  in binding free energy. For both series of tetrellylenes, the Lewis acidity decreases in the order  $\text{MPh}_2 > \text{MMe}_2 \gg \text{MMes}_2$ , reflecting the  $\sigma$ - and  $\pi$ -electron-withdrawing effects of the phenyl substituent relative to methyl, which leads to enhanced Lewis acidity, and the (much larger) destabilizing effect of steric hindrance on the complexation equilibria. The data for the  $\text{MMes}_2$  systems show that third-row chalcogen and pnictogen donors complex significantly more strongly than their second-row homologues with both silylenes and germlyenes, O donors binding the weakest, trialkylphosphines the strongest, and sulfides and amines jostling for the middle positions according to steric factors, to which complexation with amines is particularly sensitive. They thus exhibit behavior that is characteristic of "borderline soft" Lewis acids. Complexation is accompanied by characteristic blue shifts of the UV-vis absorption spectra of the tetrellylenes, but while they are generally larger for pnictogen than chalcogen donors, there is no systematic variation with the binding energy of the complex. The forward rate constants for complexation are typically close to diffusion controlled and exhibit only slight systematic variations with structure in either the tetrellylene or the donor or with the overall thermodynamics of the process.

These conclusions are corroborated and extended by computational chemistry, using the chemically accurate Gaussian-4 compound method to calculate binding enthalpies and free energies of the complexes of  $\text{SiMe}_2$  and  $\text{GeMe}_2$  with 17 representative chalcogen and pnictogen donors in the gas phase, several from the same group of donors that has been studied experimentally in solution. For six of the  $\text{MMe}_2$ -O-donor systems, the theoretical binding free energies match the experimental gas- or solution-phase values to within  $1 \text{ kcal mol}^{-1}$ , giving some confidence in the accuracy of the computational method as applied to the other donors in the series. The calculated data reveal a difference in Lewis acidity between  $\text{SiMe}_2$  and  $\text{GeMe}_2$  similar to that obtained experimentally, though they suggest that the difference increases (modestly) with increasing donor basicity over a ca.  $20 \text{ kcal mol}^{-1}$  range in binding energy. The calculations indicate that both  $\text{SiMe}_2$  and  $\text{GeMe}_2$  coordinate with  $\text{Me}_3\text{P}$  and  $\text{Me}_3\text{N}$  to afford complexes of nearly equal binding energies, in contrast to the experimental data for the dimesityl systems, which indicate stronger binding to  $\text{Et}_3\text{P}$  by at least  $5 \text{ kcal mol}^{-1}$  relative to  $\text{Et}_3\text{N}$ . The differences reflect the much greater sensitivity of the binding energy to steric effects in the case of the amines relative to trialkylphosphines. The calculated binding enthalpies correlate remarkably well with the empirical two-parameter donor basicity scale of Drago and co-workers. The correlations verify the conclusion that  $\text{SiMe}_2$  and  $\text{GeMe}_2$  are borderline soft Lewis acids, stronger and softer than unhindered trialkylboranes such as  $\text{BMe}_3$ .

Further studies of the Lewis acid-base chemistry of heavy group 14 carbene analogues, and its effects on their reactivity, are in progress.

## ■ EXPERIMENTAL SECTION

$^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AV600 spectrometer in  $\text{CDCl}_3$  solution. GC/MS analyses were carried out on a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5 ms capillary column (30 m  $\times$  0.25 mm; 0.25 mm; Varian, Inc.).

Dodecamethylcyclohexasilane (1) was synthesized using literature procedures<sup>49</sup> followed by several recrystallizations from 7/1 ethanol/

THF. 1,1,3,3-Tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (2)<sup>34c</sup> and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (3)<sup>36</sup> were synthesized as reported previously and were purified by column chromatography on silica gel with hexanes as eluent, followed by recrystallization from methanol (2) or hexanes (3). The germacyclopent-3-enes 4–6 were synthesized and purified according to previously reported procedures.<sup>31d,34a,b</sup> All six compounds were judged to be >97% pure by GC/MS analysis and  $^1\text{H}$  NMR spectroscopy. Tetrahydrofuran (THF, Caledon Reagent) was refluxed over  $\text{CaH}_2$  for 2 h, distilled into a flask containing sodium, refluxed over sodium for 5 days, and finally distilled immediately prior to use. Cyclohexane (Caledon Reagent) was refluxed over sodium for several days and distilled immediately prior to use. Tetrahydrothiophene (THT, 99% Sigma-Aldrich) was purified by distillation from anhydrous sodium sulfate.<sup>50</sup> Diethylamine ( $\text{Et}_2\text{NH}$ , 99.5% Sigma-Aldrich) and triethylamine ( $\text{Et}_3\text{N}$ ,  $\geq 99\%$  Sigma-Aldrich) were refluxed over solid NaOH for several hours and then distilled under nitrogen. Triethylphosphine ( $\text{PEt}_3$ , 99% Sigma-Aldrich) was distilled under argon prior to use, while tricyclohexylphosphine ( $\text{PCy}_3$ ,  $\geq 94\%$  Sigma-Aldrich) was recrystallized from hexane; all manipulations of the phosphines were carried out in a glovebox under a dry argon atmosphere, and purity was checked by  $^{31}\text{P}$  NMR spectroscopy. Hexanes (EMD OmniSolv) and  $\text{Et}_2\text{O}$  (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc.).

Laser flash photolysis experiments were carried out using a Lambda Physik Compex 120 excimer laser filled with  $\text{F}_2/\text{Kr}/\text{Ne}$  (248 nm, 20 ns, 98–110 mJ/pulse) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.<sup>34a</sup> The solutions were prepared in deoxygenated anhydrous hexanes such that the absorbance at 248 nm was between 0.4 and 0.7. The solutions were flowed rapidly through a  $7 \times 7$  mm Suprasil flow cell connected to calibrated 100 or 250 mL reservoirs, which contain a glass frit to allow bubbling of argon gas through the solution for 40 min prior to and throughout the experiment. The flow cell was connected to a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.), which pulls the solution through the cell at a constant rate of 2–3 mL/min. The glassware, sample cell, and transfer lines were dried in a vacuum oven (65–85 °C) before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell. Substrates were added directly to the reservoir by microliter syringe as aliquots of standard solutions.

The  $\text{Et}_3\text{P}$  and  $\text{Cy}_3\text{P}$  stock solutions were prepared in a glovebox in volumetric flasks, transferred to a 25 mL Schlenk bomb, and attached to a Schlenk line under a dry Ar atmosphere. The stopcock on the bomb was replaced with a rubber septum, and the solution was then withdrawn using a 1 or 2.5 mL gastight syringe, which was inserted through the septum on the reservoir containing the precursor solution to allow the addition of the desired amounts of the substrate to the reservoir solution. The syringe was left attached to the reservoir until the end of the experiment to avoid contact with air and moisture.

Transient absorbance-time profiles were recorded by signal averaging of data obtained from 10–40 individual laser shots. Decay rate constants were calculated by nonlinear least-squares analysis of the transient absorbance-time profiles using the Prism 5.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate and equilibrium constants were calculated by linear least-squares analysis of transient absorbance data that spanned as large a range in transient decay rate or initial signal intensity as possible. Errors are quoted in all cases as twice the standard error obtained from the least-squares analyses.

## ■ ASSOCIATED CONTENT

### Supporting Information

Tables and figures giving additional kinetic data determined in laser flash photolysis experiments, details of the computational studies, and calculated Cartesian coordinates and energies for

selected complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.
- (2) (a) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, pp 2463–2568. (b) Tokitoh, N.; Ando, W. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; pp 651–715.
- (3) Maier, G.; Meudt, A.; Jung, J.; Pacl, H.; Rappoport, Z.; Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1998; pp 1143–1185.
- (4) (a) Becerra, R.; Walsh, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2817. (b) Becerra, R.; Walsh, R. *Dalton Trans.* **2010**, *39*, 9217.
- (5) (a) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.
- (6) Jasinski, J. M.; Becerra, R.; Walsh, R. *Chem. Rev.* **1995**, *95*, 1203.
- (7) (a) Driess, M.; Grutzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (b) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165.
- (8) (a) Kira, M.; Ishida, S.; Iwamoto, T. *Chem. Rec.* **2004**, *4*, 243. (b) Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258.
- (9) (a) Belzner, J.; Ihmels, H. *Adv. Organomet. Chem.* **1999**, *43*, 1. (b) Boganov, S. E.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M. *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 960.
- (10) Kolesnikov, S. P.; Perl'mutter, B. L.; Nefedov, O. M. *Dokl. Akad. Nauk SSSR* **1971**, *196*, 85.
- (11) (a) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. Eur. J.* **2003**, *9*, 3530. (b) Toshimitsu, A.; Saeki, T.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 9210. (c) Gau, D.; Kato, T.; Saffon-Merceron, N.; Cossio, F. P.; Baceiredo, A. *J. Am. Chem. Soc.* **2009**, *131*, 8762.
- (12) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Organometallics* **2010**, *29*, 4871.
- (13) (a) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466. (b) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748.
- (14) Schoeller, W. W.; Schneider, R. *Chem. Ber.* **1997**, *130*, 1013.
- (15) Tamao, K.; Asahara, M.; Saeki, T.; Toshimitsu, A. *J. Organomet. Chem.* **2000**, *600*, 118.
- (16) Gau, D.; Rodriguez, R.; Kato, T.; Saffon-Merceron, N.; Cossio, F. P.; Baceiredo, A. *Chem. Eur. J.* **2010**, *16*, 8255.
- (17) (a) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683. (b) Ghadwal, R. S.; Roesky, H. W.; Granitzka, M.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 10018.
- (18) (a) Xiong, Y.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7562. (b) Jana, A.; Tavcar, G.; Roesky, H. W.; Schulzke, C. *Dalton Trans.* **2010**, *39*, 6217. (c) Yao, S.; Xiong, Y.; Driess, M. *Chem. Eur. J.* **2010**, *16*, 1281. (d) Al-Rafia, S. M. I.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. Commun.* **2012**, *48*, 1308.
- (19) (a) Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Dalton Trans.* **2000**, *2000*, 3094. (c) Rupar, P. A.; Jennings, M. C.; Ragnogna, P. J.; Baines, K. M. *Organometallics* **2007**, *26*, 4109. (d) Rupar, P. A.; Staroverov, V. N.; Ragnogna, P. J.; Baines, K. M. *J. Am. Chem. Soc.* **2007**, *129*, 15138. (e) Rupar, P. A.; Jennings, M. C.; Baines, K. M. *Organometallics* **2008**, *27*, 5043. (f) Ruddy, A. J.; Rupar, P. A.; Bladec, K. J.; Allan, C. J.; Avery, J. C.; Baines, K. M. *Organometallics* **2010**, *29*, 1362. (g) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (h) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119. (i) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E. *J. Am. Chem. Soc.* **2011**, *133*, 777. (j) Yao, S.; Zhang, X.; Xiong, Y.; Schwarz, H.; Driess, M. *Organometallics* **2010**, *29*, 5353.
- (20) (a) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558. (b) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487.
- (21) (a) Ando, W.; Itoh, H.; Tsumuraya, T.; Yoshida, H. *Organometallics* **1988**, *7*, 1880. (b) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.
- (22) Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. *J. J. Am. Chem. Soc.* **1984**, *106*, 5853.
- (23) Calhorda, M. J.; Krapp, A.; Frenking, G. *J. Phys. Chem. A* **2007**, *111*, 2859.
- (24) Liao, H.-Y.; Yen, M.-Y. *New J. Chem.* **2008**, *32*, 511.
- (25) (a) Oláh, J.; De Proft, F.; Veszprémi, T.; Geerlings, P. *J. Phys. Chem. A* **2005**, *109*, 1608. (b) Oláh, J.; Veszprémi, T.; De Proft, F.; Geerlings, P. *J. Phys. Chem. A* **2007**, *111*, 10815.
- (26) Broeckeaert, L.; Geerlings, P.; Ruzicka, A.; Willem, R.; De Proft, F. *Organometallics* **2012**, *31*, 1605.
- (27) (a) Levin, G.; Das, P. K.; Lee, C. L. *Organometallics* **1988**, *7*, 1231. (b) Levin, G.; Das, P. K.; Bilgrien, C.; Lee, C. L. *Organometallics* **1989**, *8*, 1206.
- (28) Yamaji, M.; Hamanishi, K.; Takahashi, T.; Shizuka, H. *J. Photochem. Photobiol. A: Chem.* **1994**, *81*, 1.
- (29) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Int. J. Chem. Kinet.* **1992**, *24*, 127.
- (30) (a) Moiseev, A. G.; Leigh, W. J. *Organometallics* **2007**, *26*, 6277. (b) Leigh, W. J.; Kostina, S. S.; Bhattacharya, A.; Moiseev, A. G. *Organometallics* **2010**, *29*, 662. (c) Kostina, S. S.; Leigh, W. J. *J. Am. Chem. Soc.* **2011**, *133*, 4377. (d) Kostina, S. S.; Singh, T.; Leigh, W. J. *J. Phys. Org. Chem.* **2011**, *24*, 937.
- (31) (a) Leigh, W. J.; Harrington, C. R. *J. Am. Chem. Soc.* **2005**, *127*, 5084. (b) Leigh, W. J.; Dumbra, I. G.; Lollmahomed, F. *Can. J. Chem.* **2006**, *84*, 934. (c) Leigh, W. J.; Lollmahomed, F.; Harrington, C. R.; McDonald, J. M. *Organometallics* **2006**, *25*, 5424. (d) Huck, L. A.; Leigh, W. J. *Organometallics* **2007**, *26*, 1339.
- (32) Equilibrium constants have also been reported for the complexation of SiH<sub>2</sub> with Me<sub>2</sub>O and CD<sub>3</sub>OD in the gas phase at 150–170 °C; see: Alexander, U. N.; King, K. D.; Lawrance, W. D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3085; *J. Phys. Chem. A* **2002**, *106*, 973.
- (33) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, 084108.
- (34) (a) Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2004**, *126*, 16105. (b) Leigh, W. J.; Lollmahomed, F.; Harrington, C. R. *Organometallics* **2006**, *25*, 2055. (c) Moiseev, A. G.; Leigh, W. J. *Organometallics* **2007**, *26*, 6268.
- (35) Shizuka, H.; Tanaka, H.; Tonokura, K.; Murata, K.; Hiratsuka, H.; Ohshita, J.; Ishikawa, M. *Chem. Phys. Lett.* **1988**, *143*, 225.
- (36) Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.
- (37) Lollmahomed, F.; Leigh, W. J. *Organometallics* **2009**, *28*, 3239.
- (38) Toldt, N. P.; Leigh, W. J.; Kollegger, G. M.; Stibbs, W. G.; Baines, K. M. *Organometallics* **1996**, *15*, 3732.

(39) Leigh, W. J.; Moiseev, A. G.; Coulais, E.; Lollmahomed, F.; Askari, M. S. *Can. J. Chem.* **2008**, *86*, 1105.

(40) Baggott et al. estimated equilibrium constants of 400 and 12 000 atm<sup>-1</sup> for the complexation of SiMe<sub>2</sub> in the gas phase with dimethyl ether and THF, respectively, using rate coefficients extracted from biexponential analyses of SiMe<sub>2</sub> decay data.<sup>29</sup> Reanalysis of the data shown in Figure 6 of ref 29 according to eq 2 yields estimates of 145 and 1200 atm<sup>-1</sup>, respectively. These correspond to ΔG values of -2.94 and -4.19 kcal mol<sup>-1</sup>, respectively, in good agreement with the computed (G4) values and with the experimental value reported in the present work for SiMe<sub>2</sub>-Et<sub>2</sub>O in solution.

(41) Laurence, C.; Gal, J.-F. *Lewis Basicity and Affinity Scales: Data and Measurement*; Wiley: Chichester, U.K., 2010.

(42) Su, M. D.; Chu, S. Y. *J. Phys. Chem. A* **1999**, *103*, 11011.

(43) (a) Heaven, M. W.; Metha, G. F.; Buntine, M. A. *J. Phys. Chem. A* **2001**, *105*, 1185. (b) Su, M. D. *Chem. Eur. J.* **2004**, *10*, 6073.

(44) Lollmahomed, F.; Huck, L. A.; Harrington, C. R.; Chitnis, S. S.; Leigh, W. J. *Organometallics* **2009**, *28*, 1484.

(45) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(46) Liu, M.; Yang, I.; Buckley, B.; Lee, J. K. *Org. Lett.* **2010**, *12*, 4764.

(47) (a) Drago, R. S.; Dadmun, A. P.; Vogel, G. C. *Inorg. Chem.* **1993**, *32*, 2473. (b) Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654.

(48) (a) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1975**, *93*, 6014. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251. (c) Vogel, G. C.; Drago, R. S. *J. Chem. Educ.* **1996**, *73*, 701.

(49) Chen, S.-M.; Katti, A.; Blinka, T. A.; West, R. *Synthesis* **1985**, 1985, 684.

(50) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, New York, 1980.