

EA, then isobutane would be 10 kcal/mol more acidic than methane;<sup>17</sup> observation of both products from If requires much closer acidities.<sup>14</sup> Coupled with indications that simple aliphatic ketones also have extremely low EA's, this leads to another explanation. If the intermediate for elimination of isobutane, propane, and ethane is actually best described as an anionic cluster where the binding of the electron is weak and dependent on terms other than EA(R $\cdot$ ), then the binding of the electron in II will be small and insensitive to the nature of R. The leaving abilities of these alkyl groups would then be determined by the relative homolytic bond dissociation energies ( $D(C-R)$ ) rather than the relative stabilities of R $\cdot$ . Since methyl anion is bound, we interpret the position of methyl as evidence that methane elimination proceeds through a heterolytic mechanism (by IIa, R = CH<sub>3</sub>). The anomalous order of alkyl leaving group abilities can be explained by a mechanism involving an intermediate in which the electron is bound only by the radical-molecule complex and not specifically by either component of this complex. This mechanism is important only when EA(R $\cdot$ ) approaches zero.

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(17) Based on a thermochemical cycle and the relative C-H bond strengths.<sup>7,8</sup>

## Hydrogen Abstractions by Triplet Methylene and Silylene

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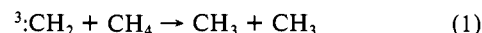
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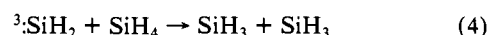
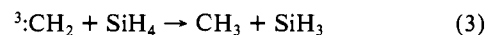
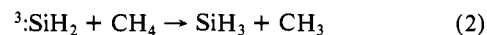
While the most common reactions of singlet methylenes are insertions into Y-H or multiple bonds,<sup>1-3</sup> triplet methylenes tend to abstract hydrogens from Y-H bonds.<sup>1,2</sup> Singlet silylenes are also known to insert,<sup>4-6</sup> while little is known about the corresponding triplets. Several theoretical papers have been devoted to analyses of the insertions of singlet CH<sub>2</sub><sup>7-12</sup> and SiH<sub>2</sub><sup>13-15</sup> into a variety of bonds and the abstractions of hydrogen from H<sub>2</sub><sup>16-20</sup>

and CH<sub>4</sub><sup>17</sup> by triplet methylene. Ab initio calculations including correlation predict that carbenes insert into Y-H<sup>9,11,12,15</sup> bonds with no barrier, in agreement with the prevailing experimental evidence;<sup>1,2</sup> however, silylene insertions may encounter significant energy barriers.<sup>4,5,13-15</sup>

For the reaction



bond energy-bond order (BEBO) calculations predict a 25.6 kcal/mol barrier,<sup>21</sup> whereas MINDO/2 predicts a much smaller barrier of 3.8 kcal/mol.<sup>22</sup> Double- $\zeta$  (DZ) SCF calculations<sup>17</sup> are in qualitative agreement with the BEBO calculations, predicting a barrier of 33 kcal/mol. On the basis of analogous calculations on the abstraction from H<sub>2</sub>,<sup>18</sup> these authors estimate that correlation corrections will drop the barrier for reaction 1 to about 18-23 kcal/mol. This work presents calculations on reaction 1 and the analogous reactions involving silicon:



Whereas the singlet methylene insertions are predicted to occur with no barriers, the triplet abstractions from the same substrates have substantial barriers. Likewise, the insertion of singlet silylene into silane occurs with no barrier,<sup>15</sup> while the corresponding triplet abstraction requires a 15.9 kcal/mol barrier. The insertion of singlet silylene into methane has a substantial barrier,<sup>13-15</sup> but even here the corresponding triplet abstraction barrier is larger by about 5 kcal/mol.

All structures were calculated at the UHF/SCF level with the 3-21G basis set<sup>23</sup> using GAUSSIAN80.<sup>24</sup> For the prediction of the energetics of the reactions single-point calculations were carried out with 6-31G\*\*<sup>25</sup> and third-order Møller-Plesset perturbation theory (UMP3<sup>26</sup>). The reliability of the unrestricted wave functions for the species treated here is indicated by the S<sup>2</sup>p expectation values. These range from 2.0 to 2.05 for the triplets and from 0.75 to 0.80 for the doublets. The exact values are 2.0 and 0.75, respectively. Force fields at the transition-state structures were calculated by using GAMESS.<sup>27</sup>

The 3-21G geometries for all reactants and products except methylene and silylene have been published previously.<sup>28</sup> For CH<sub>2</sub>, we find  $R = 1.071 \text{ \AA}$  and  $\alpha = 131.3^\circ$ , in good agreement with experiment.<sup>1,2</sup> The corresponding parameters for silylene (1.482 Å and 118.7°) are very close to those of Schaefer et al.<sup>29</sup>

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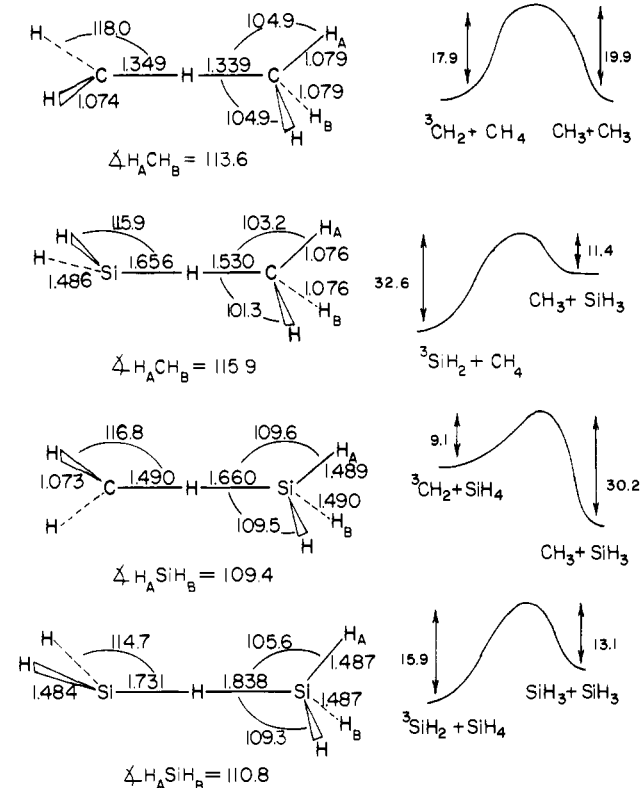
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**Figure 1.** Transition-state structures (bond lengths in Å, angles in deg) and energetics (kcal/mol) for abstraction reactions.

The saddle-point structures for reactions 1-4 are shown in Figure 1, together with schematics of the potential energy curves. All four structures are found to be linear in X-H-Y. When CH<sub>2</sub> is the attacking group, it is coplanar with the substrate H, while the analogous silicon is pyramidal. This is consistent with the structures of the methyl and silyl radicals.<sup>28</sup> The imaginary frequencies for reactions 1-4 are 2369, 1657, 1729, and 1487 cm<sup>-1</sup>, respectively. For comparison, the 3-21G C-H and Si-H reactant and product frequencies are about 3200 and 2200 cm<sup>-1</sup>.<sup>28</sup>

Reaction 1 is predicted to be nearly thermoneutral, with an exothermicity of only 2 kcal/mol, compared with an experimental value of 5 kcal/mol.<sup>30</sup> The predicted abstraction barrier is 17.9 kcal/mol, at the lower end of the range predicted by Bauschlicher et al.<sup>17</sup> but much higher than the MINDO/2 result.<sup>22</sup> When the attacking group is SiH<sub>2</sub> (reaction 2), the transition state moves deeper into the exit channel, and the reaction is endothermic. The larger forward barrier in reaction 2 relative to (1) reflects the weaker Si-H vs. C-H bond.<sup>31</sup>

For reaction 3 the saddle point lies much closer to reactants than products. The smaller barrier relative to reaction 1 reflects the greater ease of abstracting a hydrogen from silane than from methane. Reaction 4 has its transition state more toward the center of the reaction path and is nearly thermoneutral, with a 2.8 kcal/mol endothermicity. The relative ease of abstracting a hydrogen from silane results in a forward barrier half the size of reaction 2. Triplet silylene is less effective than methylene as a hydrogen abstractor, as may be seen by comparing the forward barriers for reaction 4 vs. 3 and reaction 2 vs. 1. Finally, from the parent XH<sub>3</sub>YH<sub>3</sub> energies obtained previously,<sup>15</sup> the CC, CSi, and SiSi single-bond energies are calculated to be 95.0, 84.6, and 73.0 kcal/mol, respectively, in good agreement with the experimental values of 88.0, 85.0, and 74.0.<sup>31</sup>

**Registry No.** H<sub>2</sub>, 13333-74-0; CH<sub>4</sub>, 74-82-8; SiH<sub>4</sub>, 7803-62-5; :CH<sub>2</sub>, 2465-56-7; :SiH<sub>2</sub>, 13825-90-6.

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## Electron-Transfer Quenching and Outer-Sphere Charge-Transfer Transitions in Mixed-Metal Ion Pairs. The [EuC2.2.1]<sup>3+</sup>-M(CN)<sub>6</sub><sup>4-</sup> Systems<sup>1</sup>

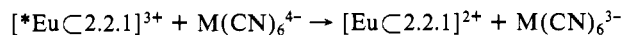
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Electron-transfer quenching (ETQ) of excited states<sup>4</sup> and outer-sphere charge-transfer (OSCT) transitions in ion pairs<sup>5</sup> are playing important roles in the development of electron-transfer theories.<sup>6</sup> A great number of ETQ studies have been performed in the last few years, but with a few exceptions,<sup>7</sup> they have concerned systems where ion pairs are not present. On the other hand, OSCT transitions have only been reported to occur for a few ion pairs,<sup>5</sup> none of which involves complexes having long-lived, luminescent excited states. We report here results concerning systems in which both OSCT transitions and ETQ can be observed.

Encapsulation of Eu<sup>3+</sup> ion into the 4, 7, 13, 16, 21-pentaoxo-1,10-diazabicyclo[8.8.5]tricosane ligand (Lehn's<sup>8</sup> [2.2.1]cryptand) yields a stable cryptate complex, [EuC2.2.1]<sup>3+</sup>.<sup>9,10</sup> The photo-physical properties of this complex have recently been studied.<sup>11</sup> Its lowest excited state, which is the <sup>5</sup>D<sub>0</sub> metal centered (f → f) excited state, lies 2.1 eV above the <sup>7</sup>F<sub>0</sub> ground state, exhibits a bright luminescence emission, and has a lifetime of 215 μs in aqueous solution at room temperature. We have found that the luminescence emission of [EuC2.2.1]<sup>3+</sup> is quenched by M(CN)<sub>6</sub><sup>4-</sup> (M = Fe, Ru, or Os) complexes. At low quencher concentrations the quenching process is *dynamic* in nature and is due to an *electron-transfer mechanism*:<sup>12</sup>



The bimolecular quenching constants (aqueous solutions, 1 M KCl, 295 K) are 7.5 × 10<sup>8</sup>, 2.2 × 10<sup>8</sup>, and 7.8 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> for the Fe, Ru, and Os cyanides, respectively.

When relatively concentrated aqueous solutions of [EuC2.2.1]<sup>3+</sup> and M(CN)<sub>6</sub><sup>4-</sup> were used, formation of ion pairs was clearly observed. Addition of 5-500 μL of a 0.5 M Fe(CN)<sub>6</sub><sup>4-</sup>

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