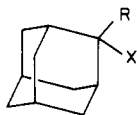


substituted with an  $\alpha$ -Si(CH<sub>3</sub>)<sub>3</sub> or with an  $\alpha$ -CH<sub>3</sub> group solvolyze ( $k_c$  mechanism) at essentially the same rate. Evaluation of ground state effects by ab initio calculations suggests that *in solution an  $\alpha$ -trimethylsilyl group is less effective in stabilizing tertiary carbenium ions than an  $\alpha$ -methyl group, but is more stabilizing than hydrogen.*

To circumvent the problems which did not permit the study of **1** we selected the tertiary 2-adamantyl ester **2a**. Even secondary



- 2, R = Si(CH<sub>3</sub>)<sub>3</sub>; 2a, X = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO = OPNB; 2b, X = +; 2c, X = H; 2d, X = OH  
 3, R = CH<sub>3</sub>; 3a, X = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO = OPNB; 3b, X = +; 3c, X = H  
 4, R = C(CH<sub>3</sub>)<sub>3</sub>; 4a, X = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO = OPNB; 4b, X = +; 4c, X = H  
 5, R = H; 5a, X = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>COO = OPNB; 5b, X = +; 5c, X = H

adamantyl derivatives are known to solvolyse via carbenium ions by a "clean"  $k_c$  process without or with minimal solvent assistance.<sup>8</sup> **2a** was synthesized in 60–70% yield in a "single-pot" reaction of adamantanone with (CH<sub>3</sub>)<sub>3</sub>SiLi followed by the addition of *p*-nitrobenzoyl chloride.<sup>9</sup>

Solvolyse of **2a** in 80% acetone and 97% TFE follow excellent first-order kinetics. Comparison with **3a**<sup>10</sup> and **4a**<sup>10</sup> leads to the following rate ratios: In 80% acetone,  $k(3a)/k(2a) = 2.18$  (at 25 °C), 2.01 (at 100 °C);  $k(4a)/k(2a) = 3.6 \times 10^5$  (at 25 °C),  $2.4 \times 10^4$  (at 100 °C).<sup>11</sup> In 97% TFE,  $k(3a)/k(2a) = 0.93$  (at 25 °C).<sup>12</sup> Thus, 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate (**2a**) and 2-methyl-2-adamantyl *p*-nitrobenzoate (**3a**) solvolyse at essentially the same rate. **2a** solvolyse ca. 10<sup>8</sup> times faster than the secondary adamantyl derivative **5a**,<sup>10</sup> and **4a** solvolyse ca.  $3 \times 10^5$  times faster than **2a**. The practical constancy of  $k(3a)/k(2a)$  in 80% acetone and in 97% TFE strongly supports a limiting  $k_c$  solvolysis for **2a**.<sup>8</sup> Significant rate acceleration of **2a** by neighboring methyl participation is unlikely as **2a** yields only 10% of the rearranged alcohol in 80% acetone.

The relative stabilities of the carbenium ions of interest (**2b–5b**) can be evaluated only if steric and electronic ground-state effects are known. The solvolysis of **4a** is accelerated by a factor of  $4.5 \times 10^5$  relatively to that of **3a** by relief of ground-state strain.<sup>10</sup> Is the solvolysis of **2a** also sterically accelerated? MM2 force-field calculations<sup>13</sup> show this not to be the case. Due to the long C–Si distance the strain in **2c** (or in **2d**) is similar to that in **3c** but much smaller than in **4c**. In contrast to **4a**, **2a** and **3a** solvolyse without significant steric acceleration.

Can electronic effects significantly change the ground-state energy of **2a** as compared to that of **3a**? Since direct experimental data are not available we rely on ab initio calculations.<sup>14</sup> According to eq 1 (in which alcohols model the *p*-nitrobenzoate esters<sup>7b</sup>), the  $\alpha$ -silyl alcohols are destabilized relatively to the corresponding alkyl alcohols by 6–8 kcal mol<sup>-1</sup>.<sup>15</sup>

(8) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.

(9) All new compounds were characterized by elemental analysis and spectroscopic methods.

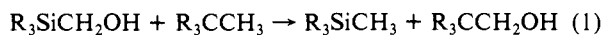
(10) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628.

(11) In 80% acetone,  $k(2a) = (3.82 \pm 0.03) \times 10^{-5} \text{ s}^{-1}$  (125.8 °C),  $\Delta H^\ddagger = 29.4 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -5.0 \text{ eu}$  (temperature range 125–145 °C). Estimated error limits for  $k(3a)/k(2a)$  are 5%.

(12) In 97% TFE  $k(2a) = (7.27 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$  (100.2 °C),  $\Delta H^\ddagger = 22.5 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -12.6 \text{ eu}$  (temperature range 75–100 °C,  $r > 0.9999$ ). The solvolysis rate of **3a** was calculated from that of the corresponding chloride assuming a Cl/OPNB rate ratio of  $9.9 \times 10^4$  (see: McManus, S. P.; Harris, J. M. *J. Org. Chem.* **1977**, *42*, 1422. Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244. Also reference 10 above).

(13) Allinger, N. L.; Yuh, Y. H. *QCPE* **1977**, *12*, 395.

(14) THE GAUSSIAN 80 series of programs were used: Binkley, J. S.; Whiteside, R. M.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1980**, *13*, 406.



$$\text{R} = \text{H} \quad \Delta E = -7.3 \text{ kcal mol}^{-1} \text{ (MP2/6-31G}^*/\text{/3-21G)}$$

$$\text{R} = \text{CH}_3 \quad \Delta E = -6.3 \text{ kcal mol}^{-1} \text{ (6-31G}^*/\text{/3-21G)}$$

Combining these ground-state energy differences with the similar solvolysis rates of **2a** and **3a** we conclude that *in solution an  $\alpha$ -Si(CH<sub>3</sub>)<sub>3</sub> substituent destabilizes the 2-adamantyl cation by several kilocalories per mole compared to methyl (i.e., by 6–8 kcal mol<sup>-1</sup> if the gas-phase ground-state differences pertain in solution).* However, in contrast to previous conclusions,<sup>5a</sup> an  $\alpha$ -Si(CH<sub>3</sub>)<sub>3</sub> is by ca. 12–14 kcal mol<sup>-1</sup> more stabilizing than hydrogen.<sup>16</sup>

In the gas phase, we calculate that relatively to the corresponding hydrocarbons H<sub>3</sub>SiC<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub> is less stable than (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> by 8.6 kcal mol<sup>-1</sup> (at 6-31G<sup>\*</sup>//3-21G). The  $\alpha$ -silyl destabilization is even larger in secondary and primary carbenium ions; i.e., (CH<sub>3</sub>)<sub>2</sub>CH<sup>+</sup> and CH<sub>3</sub>CH<sub>2</sub><sup>+</sup> are more stable than CH<sub>3</sub>(SiH<sub>3</sub>)CH<sup>+</sup> and H<sub>3</sub>SiCH<sub>2</sub><sup>+</sup>, respectively, by 14.3 and 18.3 kcal mol<sup>-1</sup>, respectively (at MP2/6-31G<sup>\*</sup>//3-21G). The (SiH<sub>3</sub>)C(CH<sub>3</sub>)<sub>2-n</sub>H<sub>n</sub><sup>+</sup> cations are, however, significantly more stable than the corresponding HC(CH<sub>3</sub>)<sub>2-n</sub>H<sub>n</sub><sup>+</sup> cations. Thus, *both in solution and in the gas phase,  $\alpha$ -silyl substitution at a carbenium ion center is destabilizing relatively to methyl but stabilizing relatively to hydrogen.* Further experimental and theoretical studies on the stabilities of other  $\alpha$ - and  $\beta$ -silyl carbenium ions are in progress.

**Acknowledgment.** We thank the Computer Center of the Technion for generous allocation of computer time and J. Arnon for technical assistance with the calculations. This research was partially supported by the Fund for the Promotion of Research at the Technion.

(15) This conclusion is supported by indirect experimental evidence. See: Peterson, P. E. *Tetrahedron Lett.* **1981**, 1295. Further discussion is given in ref 6 and 7b.

(16) The **3a/5a** (or the **2a/5a**) solvolysis rate ratios of 10<sup>8</sup> correspond to an energy difference of 11 kcal mol<sup>-1</sup> at 25 °C.<sup>8</sup>

## Conformation, Configuration, and Reactivity of Thiosulfonium Ions Derived from 1,2-Dithianes and 1,2-Dithiolanes. Stereoelectronic Effects

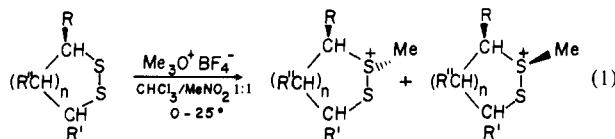
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Received August 13, 1984

Revised Manuscript Received February 15, 1985

Thiosulfonium ions can be prepared by alkylation of cyclic disulfides and, in this manner, S-methylated 1,2-dithianes **1–4** and dithiolanes **5–9** have been prepared as fluoroborate salts (eq 1).<sup>1</sup> Their conformational and configurational preferences, and



11, R = R' = R'' = H; n = 2	1	
12, R = R' = Me(trans), R'' = H; n = 2	2	(100%)
13, R = R' = Me(cis), R'' = H; n = 2	3	(100%)
14, R = R' = H, R'' = (CH <sub>2</sub> ) <sub>2</sub> (trans); n = 2	4	(100%)
15, R = R' = R'' = H; n = 1 (polymer)	5	
16, R = R' = Me(trans), R'' = H; n = 1	6a	(65%)
17, R = R' = Me(cis), R'' = H; n = 1	7a	(52%)
18, R = (CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> Me, R' = R'' = H; n = 1	8a	(26%)
18, R = R'' = H, R' = (CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> Me; n = 1	9a	(33%)
	6b	(35%)
	7b	(48%)
	8b	(11%)
	9b	(30%)
	(trans)	(cis)

**Table I.** NMR Chemical Shifts in 1-Methyl-1,2-dithianium and -1,2-dithiolanium Tetrafluoroborates in CD<sub>3</sub>NO<sub>2</sub> at 25 °C

structure <sup>a</sup>		<sup>13</sup> C chemical shifts <sup>b,c</sup>					<sup>1</sup> H chemical shifts (500 MHz) <sup>d</sup>					
		C3	C4	C5	C6	MeS	H1	H2	H3	H4	MeS	
<b>1</b>	found	26.7	23.5	17.5	40.1	25.5	found	3.75	3.53	3.68	3.12	3.38
100%	calcd		24.8	18.9	40.6	25.0	+Me <sub>2</sub> S	3.64	3.64	3.40	3.40	3.37
<b>2</b>	found	36.1	34.7	27.4	50.2	20.7	found	3.91		3.75		3.25
100%	calcd		33.7	27.8	46.8	20.9	+Me <sub>2</sub> S	3.87		3.73		3.24
<b>3</b>	found	37.7	(27.5)	(26.1) <sup>e</sup>	47.0	28.2	found		3.80	3.75		3.38
100%	calcd		26.5	23.8	48.3	27.9	+Me <sub>2</sub> S		3.80	3.75		3.37
<b>4</b>	found	31.0	40.6	33.5	44.8	25.2	found	3.45	3.43	3.44	2.95	3.37
100%	calcd		40.8	34.9	45.3	25.4	+Me <sub>2</sub> S	3.45	3.43	3.44	2.95	3.37
<b>5</b>	found	42.7	33.7	54.0		33.3	found	4.06	4.06	(3.80)	(3.96) <sup>e</sup>	3.09
100%							+Me <sub>2</sub> S	4.06	4.06	3.88	3.88	3.09
<b>6a</b>	found	56.4	45.6	68.3		34.7	found		4.67		4.80	3.18
65%	calcd <sup>f</sup>					33.3						
<b>6b</b>	found	54.3	44.9	63.5		26.4	found	4.80		4.67		2.97
35%	calcd <sup>f</sup>					26.4						
<b>6a + 6b</b>							+Me <sub>2</sub> S	4.70	4.70	4.79	4.79	3.11
<b>7a</b>	found	56.0	50.0	72.0		33.4	found		4.55	4.56		3.22
52%	calcd <sup>f</sup>					33.3						
<b>7b</b>	found	55.5	45.3	65.6		27.6	found	4.61			4.43	3.03
48%	calcd <sup>f</sup>					26.4						
<b>7a + 7b</b>							Me <sub>2</sub> S	4.58	4.58	4.50	4.50	3.12
<b>8a</b>	found	40.8	37.4	73.9		32.7						3.13
26%	calcd <sup>f</sup>					33.3						
<b>8b</b>	found	39.5	35.0	70.6		26.0						2.97
11%	calcd <sup>f</sup>					26.4						
<b>8a + 8b</b>	+Me <sub>2</sub> S	40.4	36.7	72.9		30.7						3.08
<b>9a</b>	found	52.0	37.8	60.7		32.8						3.14
33%	calcd <sup>g</sup>					33.3						
<b>9b</b>	found	52.9	36.8	62.4		32.9						3.15
30%	calcd <sup>f</sup>					33.3						
<b>9a + 9b</b>	+Me <sub>2</sub> S	52.0	37.3	61.4		32.9						3.15

<sup>a</sup> See eq 1. <sup>b</sup> MeS shifts were estimated from shielding effects of ring methyls on the base value of MeS(ax) as 25.0 ppm. To the value of 25.0 ppm was added 2.26 for 6-Me(ax), -4.72 for 6-Me(eq), 0.63 for 3-Me(eq) or 5-CH<sub>2</sub>(eq), -0.18 for 4-CH<sub>2</sub>(eq). Base value for MeS(eq) is estimated to be 34.0 ppm<sup>5a</sup> and shifts for MeS(eq) in 2-4 follow by adding -4.28 for 6-Me(ax), -2.02 for 6-Me(eq), 0.11 for 3-Me(eq) or 5-CH<sub>2</sub>(eq), and 0.03 for 4-CH<sub>2</sub>(eq). <sup>c</sup> Ring carbon shifts were estimated from <sup>13</sup>C spectra of the parent 1,2-dithianes by adding 11.1, -4.4, and -2.9 ppm to C6, C5, and C4 shifts for MeS(eq), and 5.8, -10.0, and -4.1 for C6, C5, and C4 shifts for MeS(ax). <sup>d</sup> H1, H2 next to S<sup>+</sup>; H3, H4 next to S; H2, H3 cis to SMe; H1, H4 trans to SMe. <sup>e</sup> Assignments in parentheses could be reversed. <sup>f</sup> Calculated by assuming MeS shift in 5 (33.3 ppm) is shielded by an adjacent cis methyl by 6.9 ppm.<sup>5d</sup>

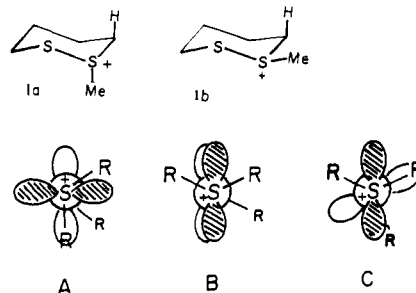
their reactions with sulfide nucleophiles, are remarkable, as we now report.

At 500 MHz, the <sup>1</sup>H NMR of **1** in CD<sub>3</sub>NO<sub>2</sub> was temperature independent from -35 to 25 °C with  $\delta$  and  $J$  values indicative of a homogeneous undistorted chair conformation with the methyl group axial (**1a**).<sup>2</sup> In particular, the MeS<sup>+</sup> resonance appeared as a doublet due to spin coupling with the axial proton at C6 ( $^4J = 0.3$  Hz). For optimum long-range spin interaction, the intervening bonds must be coplanar, which can only be achieved when the MeS<sup>+</sup> is axial, methyl rotation notwithstanding.<sup>3</sup>

Methylation of dithianes **12-14** gave a single diastereomer in each case—although two are possible. Each was conformationally homogeneous with MeS<sup>+</sup> axial.<sup>4</sup> This behavior contrasts with related thianes, which show little stereoselectivity on methylation and form conformationally mobile thianium ions.<sup>5,6a</sup> Replacing the C-S<sup>+</sup> functionality with S-S<sup>+</sup> clearly has a pronounced effect

on conformational preference and ring mobility.<sup>6b</sup>

Ab initio MO calculations provide insight into the origin of the observed stereoelectronic or anomeric effect. Geometry optimization at the 3-21G\* level<sup>7</sup> for model compounds H<sub>2</sub>S<sup>+</sup>SH and Me<sub>2</sub>S<sup>+</sup>SMe yielded local minima A and C. Structure A corre-



sponds to **1a**, but C has no counterpart in a six-membered ring. Structure B, equivalent to **1b**, was not a local minimum and relaxed without activation to C. However, at the STO-3G\*\*//STO-3G level,<sup>8</sup> S-protonated 1,2-dithiane showed axial and equatorial forms to be stable, the axial form being favored by 3.1 kcal mol<sup>-1</sup>. Fourier analysis of the conformational profile of H<sub>2</sub>S<sup>+</sup>SH and Me<sub>2</sub>S<sup>+</sup>SMe indicated the 2-fold (180°) term to be dominant.<sup>9</sup> Possibly this means that electron repulsion is min-

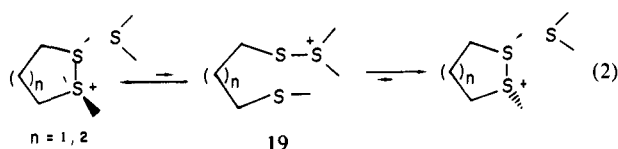
- (1) Caserio, M. C.; Kim, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3231.
- (2)  $R = 2.2$ ,  $\psi_{5,6} = 58^\circ$ . Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87.
- (3) For related  $^4J$  coupling between angular methyl groups and axial protons in steroids and terpenes, see: Williamson, K. L.; Howell, T.; Spencer, T. A. *J. Am. Chem. Soc.* **1966**, *88*, 325.
- (4) Deduced from <sup>13</sup>C and <sup>1</sup>H NMR spectra using chemical shift correlations established for related 1-methylthianium and thiolanium ions. See Table I and ref 5.
- (5) (a) Willer, R. L.; Eliel, E. L. *Org. Magn. Reson.* **1977**, *9*, 285. (b) Eliel, E. L.; Willer, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 1936. (c) Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 108, 469. (d) Barbarella, G.; Dembech, P. *Ibid.* **1980**, *13*, 282; **1981**, *15*, 72.
- (6) (a) The conformational free energy of MeS<sup>+</sup> in 1-methylthianium ions is small (0-0.6 kcal mol<sup>-1</sup> compared to methylcyclohexane 1.7 kcal mol<sup>-1</sup>) in favor of the equatorial form.<sup>5</sup> In 1,2-dithianium ions, the minimum  $\Delta G^\circ$  for **1<sub>ax</sub>**  $\rightleftharpoons$  **1<sub>eq</sub>** at the detection limit of 94:6 is 1.6 kcal mol<sup>-1</sup> in favor of **1<sub>ax</sub>**. (b) 1,2-Dithiane monoxide also prefers the axial form. See: Woody Bass, S.; Evan, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 710.

- (7) (a) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *Ibid.* **1980**, *102*, 3334.
- (8) (a) STO-3G\* basis set: Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142. (b) STO-3G basis set: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *Ibid.* **1969**, *51*, 2657 and later papers.

imized when adjacent  $\pi$ -type lone pairs are orthogonal (A) rather than parallel (B) and/or that stability is maximized when the  $\pi$  lone pair at neutral sulfur can donate electrons to the  $\sigma^*$  orbital of the adjacent Me-S<sup>+</sup> bond, as in A (or **1a**).<sup>10</sup>

Evidence of  $n$ - $\sigma^*$  donation is also seen in the <sup>1</sup>H NMR spectra of **1-4** (Table I); the axial C3 proton is almost as deshielded as the axial C6 proton, consistent with extensive charge delocalization, —CHSS<sup>+</sup>CH— ↔ —CHS<sup>+</sup>=SCH—.

Unlike 1,2-dithianes, methylation of 1,2-dithiolanes **15-18** was nonselective. Methyl lipoate **18** gave the four possible regio- and stereoisomers **8a,b** and **9a,b** in the ratio 26:11:33:30. A remarkable dynamic NMR effect was observed whereby <sup>1</sup>H and <sup>13</sup>C resonances for pairs of diastereomers **6a,b**, **7a,b**, **8a,b**, and **9a,b** became indistinguishable on addition of traces of sulfide (e.g., Me<sub>2</sub>S). The <sup>1</sup>H spectrum of the chiral ion **5** (six nonequivalent ring protons) collapsed to one with planar symmetry (three pairs of nonequivalent ring protons) on adding Me<sub>2</sub>S, indicating rapid interconversion of enantiomers. No net change occurred as the salts could be recovered unchanged. We attribute these results to a rapid and reversible ring opening by the sulfide nucleophile whereby chirality at pyramidal sulfur is destroyed.<sup>11</sup> Reclosure to either of two configurations results in the interconversion of enantiomers for **5** and diastereomers for **6-9** (eq 2).



The <sup>1</sup>H spectrum of the chiral dithianium ion **1a** also collapsed to that of a symmetrical ring on addition of Me<sub>2</sub>S—consistent with rapid equilibration of enantiomers through an achiral acyclic intermediate (**19**). Reclosure to an equatorial MeS<sup>+</sup> orientation does not occur. Similar sulfide-induced ring opening may be expected of ions **2-4** but there was no change in the <sup>1</sup>H or <sup>13</sup>C spectra on addition of Me<sub>2</sub>S, and no interconversion of diastereomers of **2-4** could be detected. We regard this as evidence that reclosure of **19** to a configuration in which MeS<sup>+</sup> is equatorial is energetically disfavored over reclosure to the axial form.

In comparison, 1,2-dithiolanium diastereomers are comparable in energy, which suggests that the five-membered ring is torsionally flexible and can adopt twist conformations that avoid destabilizing interactions<sup>12</sup> while retaining the stereoelectronic advantage of a pseudoaxial MeS<sup>+</sup>. Most importantly, ring-opening equilibria (eq 2) strongly favor ring closure, which means that ring strain is not the source of reactivity in 1,2-dithiolanium ions, as has been suggested for 1,2-dithiolanes.<sup>13</sup> Rather, reactivity is best attributed to the rapid cleavage of S-S<sup>+</sup> bonds by nucleophiles. The ready polymerization of 1,2-dithiolanes<sup>14</sup> can likewise be attributed to initial thiolanium ion formation followed by monomer-induced ring cleavage. The process can be reversed, as we have shown by the successful preparation of **5** (eq 1) by methylation of 1,2-dithiolane polymer.

**Acknowledgment.** We are indebted to the NSF-supported Southern California NMR facility at Caltech for the high-field spectra and to partial support from General Medical Sciences, GM 27319.

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(10)  $n$ - $\sigma^*$  donation in B (or **1b**) is not a factor since it could occur only from a less accessible  $\sigma$ -type lone pair at neutral sulfur. See also: Andretti, G. D.; Bernadi, F.; Bottoni, A.; Fava, A. *J. Am. Chem. Soc.* **1982**, *104*, 2176.

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## Electron-Rich, Hydrocarbon-Metal Complexes: Synthesis and Reversible One-Electron Oxidation. X-ray Structure of a 17-Electron Iron Cation

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Received December 7, 1984

Electron-rich metal complexes containing hydrocarbon fragments have recently attracted interest, because they offer evidence for new organometallic processes such as C-H-M intramolecular interaction,<sup>2</sup> C-H activation,<sup>3</sup> or radical-promoted reactions.<sup>4</sup> Among unstable conjugated hydrocarbon fragments, the trapping by an electron-rich metal center of the formally cross-conjugated trimethylenemethane (TMM) dianion<sup>5</sup> is of special interest. Although electron-poor metal-TMM complexes have been characterized,<sup>6</sup> electron-rich metal-TMM complexes have never been isolated even though they have been found to be key intermediates as sources of the trimethylenemethane group in carbon-carbon bond formation reactions.<sup>7</sup> We now wish to describe a simple route to electron-rich metal-TMM complexes, starting directly from FeCl<sub>2</sub>, and to show their facile oxidation by a reversible one-electron process to produce 17-electron species; the X-ray structure of one of these, the paramagnetic piano-stool complex Fe( $\eta^4$ -C<sub>4</sub>H<sub>6</sub>)(PMe<sub>3</sub>)<sub>3</sub><sup>+</sup>(CF<sub>3</sub>SO<sub>3</sub>)<sup>-</sup>, is reported.

To a THF solution containing 1 equiv of FeCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub><sup>8</sup> and of PMe<sub>2</sub>Ph were added successively, under inert atmosphere, an excess of magnesium and of CH<sub>2</sub>=C(CH<sub>2</sub>Cl)CH<sub>2</sub>Cl (**1**) to give an orange complex **2**, isolated to a 40% yield<sup>9</sup> (Scheme I). A similar reaction using FeCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub><sup>8</sup> and 1 equiv of PMe<sub>3</sub> in THF yielded an orange oil **3** in 47% yield.<sup>10</sup> By direct addition of the

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(9) Complex **2**. Anal. Calcd for C<sub>28</sub>H<sub>39</sub>P<sub>3</sub>Fe: C, 64.12; H, 7.44; P, 17.74; Fe, 10.68. Found: C, 63.73; H, 7.44; P, 17.42; Fe, 11.27. Mass spectrum, *m/e* 524.162 (calcd for (M)<sup>+</sup> 524.161), 386 [(M - PMe<sub>2</sub>Ph)<sup>+</sup>], 248 [(M - 2PMe<sub>2</sub>Ph)<sup>+</sup>], 332 [(M - C<sub>4</sub>H<sub>6</sub>)<sup>+</sup>].

(10) Complex **3**. Anal. Calcd for C<sub>13</sub>H<sub>13</sub>P<sub>3</sub>Fe: C, 46.15; H, 9.76. Found: C, 46.87; H, 9.74. Mass spectrum, *m/e* 338.113 (calcd for M<sup>+</sup> (C<sub>13</sub>H<sub>13</sub>P<sub>3</sub>Fe) 338.114), 262 [(M - PMe<sub>3</sub>)<sup>+</sup>], 208 [(M - PMe<sub>2</sub> - C<sub>4</sub>H<sub>6</sub>)<sup>+</sup>], 186 [(M - 2PMe<sub>3</sub>)<sup>+</sup>], 132 [(M - 2PMe<sub>3</sub> - C<sub>4</sub>H<sub>6</sub>)<sup>+</sup>].