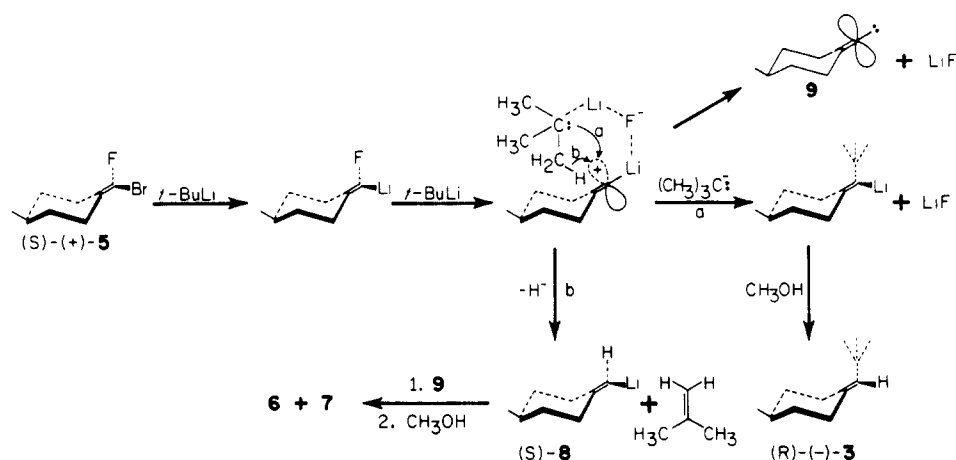
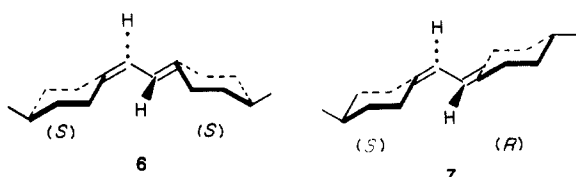


Scheme II



$\text{CHCl}_3$ ) and a 30% yield of  $(-)$ -1,2-bis(4-methylcyclohexylidene)ethane,  $[\alpha]_{\text{D}}^{22} -10.9^\circ$  ( $c$  1.0,  $\text{C}_2\text{H}_5\text{OH}$ ). The latter was shown by NMR to be a 1:1 mixture of chiral **6** and meso **7**.



There are surprising results. First is the observation that **3** was obtained with 100% optical purity and complete *retention* rather than *inversion* of configuration. Previously it was found that  $(S)-(+)-\mathbf{1}$  ( $\text{X} = \text{Cl}$ ), in ether at  $-75^\circ\text{C}$ , yielded  $(R)-(-)-\mathbf{3}$ , 31% optically pure<sup>8</sup> and of *inverted* configuration. Second is the formation of **6** and **7** which are products that were not observed in the reaction of  $(S)-(+)-\mathbf{1}$  ( $\text{X} = \text{Cl}$ ) with *tert*-butyllithium. However, both **6** and **7** (1:1) were obtained in the reaction of  $(S)-(+)-\mathbf{1}$  ( $\text{X} = \text{Br}$ ) because, besides metalation of the bromide to yield carbenoid, halogen metal exchange also occurred to produce the stable vinyl lithium **8**.<sup>9</sup> This latter reaction does not occur when  $\text{X} = \text{Cl}$ . The  $\alpha$ -addition of **8** to the carbenoid **9**, formed from carbenoid, gave a 1:1 mixture of adduct<sup>3</sup> which upon hydrolysis yielded **6** and **7**. Based on the previously established<sup>10</sup>



absolute configuration and optical purity, **6** was formed with 50% optical purity<sup>11</sup> and overall *retention* of configuration.

To account for these observations we postulate that the highly electronegative fluorine is playing a role by coordinating with another molecule *tert*-butyllithium and thereby directing the *tert*-butyl group to enter by what could be considered an  $\text{S}_{\text{N}}\text{i}$  mechanism (Scheme II, path a) which leads to a stereospecific retention of configuration. As positive charge develops, the vinyl carbocation intermediate (carbenoid) becomes more of a loose ion pair and it can then become a good hydride abstractor and remove hydride from the *tert*-butyl group to produce  $(S)-\mathbf{8}$  and isobutylene<sup>12</sup> (Scheme II, path b). In this loose ion pair some

chirality can be lost and the partially racemized  $(S)-\mathbf{8}$  can then add to the carbenoid product **9** to yield **6** and **7** in an expected 1:1 ratio.<sup>11</sup>

If this postulate is correct then the use of perdeuterio-*tert*-butyllithium should give rise to  $(R)-(-)-\mathbf{3}$  possessing a perdeuterio-*tert*-butyl group and to  $(S)-\mathbf{8}$  containing a 1-deuterio atom which then condenses with carbenoid to yield **6** and **7** each possessing one vinyl deuterium atom. This is precisely what is observed.<sup>3,13</sup>

Fluorine not only participates in metal-assisted ionization by strong lithium coordination but also plays a unique role in directing the incoming nucleophile, *tert*-butyl or hydride.

**Supplementary Material Available:** Crystal data and tables of interatomic distances, selected bond angles, selected torsional angles, and positional and thermal parameters and their estimated standard deviations for  $\text{C}_{19}\text{H}_{26}\text{FNO}_2$  (6 pages); table of structure factors  $F_{\text{obsd}}$  and  $F_{\text{calcd}}$  for  $\text{C}_{19}\text{H}_{26}\text{FNO}_2$  (6 pages). Ordering information is given on any current masthead page.

(12) For other examples of hydride abstractions by carbenoid intermediates, see: Ritter, R. H.; Cohen, T. J. *Am. Chem. Soc.* **1986**, *108*, 3718. Harada, T.; Maeda, H.; Oku, A., *Tetrahedron Lett.* **1985**, *26*, 6489.

(13) All new compound gave satisfactory elemental analyses. Deuterium content was determined by NMR and mass spectral analyses.

## Reaction of Ethylene with a Coordinatively Unsaturated Iron Complex, $\text{Fe}(\text{DEPE})_2$ : $\text{sp}^2$ C-H Bond Activation without Prior Formation of a $\pi$ -Complex

Murray V. Baker and Leslie D. Field\*

Department of Organic Chemistry, University of Sydney  
Sydney, N.S.W. Australia 2006

Received July 17, 1986

In the reaction of coordinatively unsaturated transition metals with alkenes and arenes, the formation of a  $\pi$ -complex prior to  $\text{sp}^2$  C-H activation has frequently been invoked to account for the relative ease of C-H activation. In a study of the reaction of the iridium complex  $(\eta^5\text{-Me}_5\text{C}_5)\text{IrPMe}_3$ , however, it has been demonstrated that insertion of the iridium center into the  $\text{sp}^2$  C-H bonds of ethylene proceeds with concurrent and not prior formation of a  $\pi$ -complex.<sup>1</sup> We recently reported<sup>2</sup> that the coordinatively unsaturated iron complex  $\text{Fe}(\text{DMPE})_2$  (**1a**)<sup>3</sup> [DMPE = 1,2-bis-

(8) At this time it is not known whether the difference in optical purity is due to a difference in temperature,  $-100^\circ\text{C}$  vs.  $75^\circ\text{C}$ .

(9) Vinyl lithium (**7**) does not form  $(S)-\mathbf{1}$  ( $\text{X} = \text{Cl}$ ) since chlorides do not undergo halogen metal exchange at an appreciable rate.

(10) Walborsky, H. M.; Banks, R. B.; Banks, M. L. A.; Duraisamy, M. *Organometallics* **1982**, *1*, 667. (b) Banks, R. B.; Walborsky, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 3732.

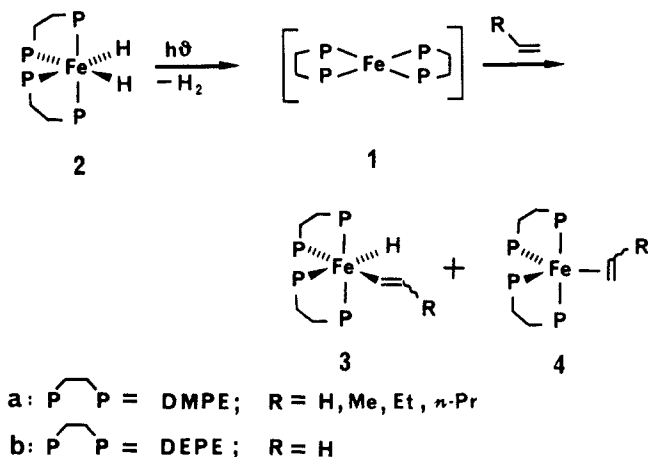
(11) This takes into account that the mixture contains 50% of inactive meso-**7**. Since **6** was found to be 50% optically pure it implies that **8** consisted of 75% *S* and 25% *R* configurations. Addition of this mixture of enantiomers to an achiral carbenoid **9** would lead to a 1:1 mixture of **6** and **7** being 50% optically pure.

(1) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581-4582.

(2) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.*, in press.

(3) For earlier studies on the chemistry of  $\text{Fe}(\text{DMPE})_2$ , see: (a) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080-4089. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577-7585. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742-1751. (d) Bergamini, P.; Sostero, S.; Traverso, O. *J. Organomet. Chem.* **1986**, *299*, C11-C14.

Scheme I



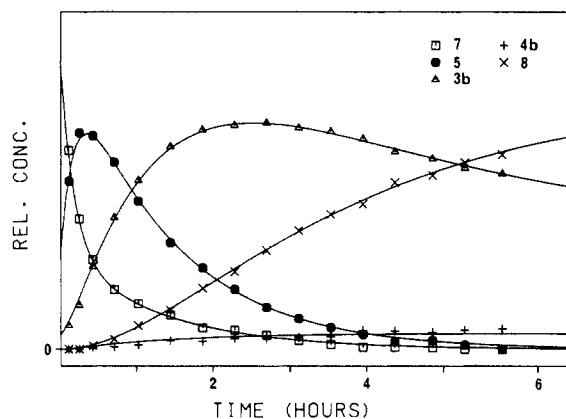
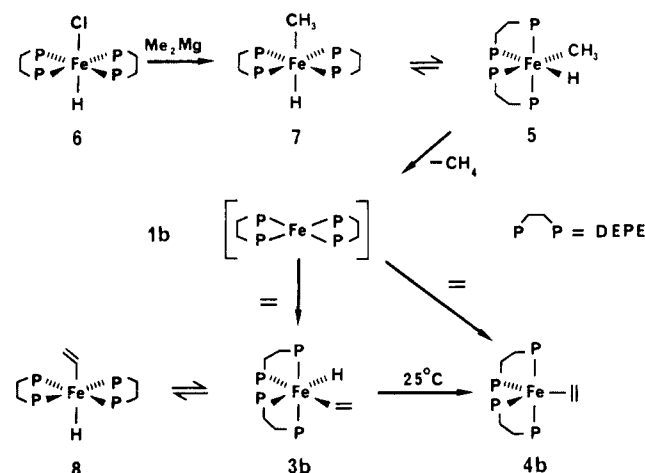
(dimethylphosphino)ethane], generated by photolysis of the dihydride  $\text{FeH}_2(\text{DMPE})_2$  (**2a**) at low temperature, reacts with alkenes to form a mixture of *cis*-alkenyl iron hydrides **3a** and the  $\pi$ -complexes **4a** (Scheme I). In that work, due to the photochemical lability of **3a** and **4a**, it was not apparent whether formation of the  $\pi$ -complex preceded that of the C-H insertion products.

We have further examined the question of C-H vs.  $\pi$  addition of alkenes to zerovalent iron bis(diphosphine) complexes and report here reactions of  $\text{Fe}(\text{DEPE})_2$  (**1b**) [DEPE = 1,2-bis(diethylphosphino)ethane], an analogue of **1a**, which can be generated at low temperature either photochemically or by nonphotochemical methods.<sup>4</sup>

Irradiation<sup>5</sup> of the dihydride  $\text{FeH}_2(\text{DEPE})_2$  (**2b**)<sup>6,7</sup> in pentane containing ethylene (ca. 5% mol/mol) at  $-80^\circ\text{C}$  for 2 h led to formation of the C-H insertion product *cis*- $\text{FeH}(\text{CH}=\text{CH}_2)(\text{DEPE})_2$  (**3b**)<sup>8</sup> and the  $\pi$ -complex  $\text{Fe}(\text{CH}_2=\text{CH}_2)(\text{DEPE})_2$  (**4b**)<sup>9</sup> in a ratio of 90:10. When the reaction mixture was warmed to room temperature, **3b** isomerized completely to **4b**, but further irradiation at  $-80^\circ\text{C}$  regenerated the 90:10 mixture of **3b** and **4b**. This chemistry is exactly analogous to that previously reported for  $\text{Fe}(\text{DMPE})_2$ .<sup>2</sup>

The coordinatively unsaturated complex **1b** was also generated by the reductive elimination of methane from the *cis*-hydrido methyl complex **5**. Treatment of a mesitylene solution containing the hydrochloride **6**<sup>10</sup> (18 mM) and ethylene (280 mM) with dimethylmagnesium at  $-40^\circ\text{C}$  resulted in quantitative formation of the *trans*-methyl hydride **7**. On warming the solution to  $-28^\circ\text{C}$ , **7** isomerized slowly to the *cis* isomer **5** which rapidly eliminated methane.<sup>4</sup> The coordinatively unsaturated species **1b** formed in this way reacted quantitatively with ethylene in solution to form a C-H insertion product **3b** and the  $\pi$ -coordination product **4b**.

Scheme II



**Figure 1.** Composition of the reaction mixture on thermal decomposition of *trans*- $\text{FeH}(\text{DEPE})_2\text{Me}$  (**7**) (18 mM) in mesitylene solution in the presence of ethylene (280 mM) at  $-28^\circ\text{C}$ . Experimental points were obtained by integration of  $^{31}\text{P}$  NMR spectra; curves are the result of a least-squares fit of the experimental data to kinetic equations on the basis of Scheme II.

**4b.** At this temperature, the *cis*-vinyl hydride **3b** isomerized reversibly to the *trans* form **8**,<sup>11</sup> and after 5.8 h at  $-28^\circ\text{C}$ , the reaction mixture contained **3b**, **4b**, and **8** in the ratio 45:5:50. When the mixture was allowed to warm to  $25^\circ\text{C}$ , both of the vinyl hydrides **3b** and **8** isomerized completely to the  $\pi$ -complex **4b** over a period of several hours (Scheme II).

The  $\pi$ -complex **4b** remained as the sole product even after the reaction mixture was returned to  $-28^\circ\text{C}$ . This established conclusively that there was no reaction pathway from the  $\pi$ -complex to the vinyl hydrides under the reaction conditions. In the reaction of  $\text{Fe}(\text{DEPE})_2$  with ethylene, the formation of the C-H insertion product is kinetically favored although the  $\pi$ -coordinated isomer is thermodynamically more stable.

The entire reaction sequence outlined in Scheme II could be monitored conveniently by  $^{31}\text{P}$  NMR spectroscopy and the transformation of **7** into a mixture of **3b**, **8**, and **4b** (and on warming, to **4b** alone) was followed quantitatively (Figure 1). A kinetic analysis in terms of Scheme II showed that under the reaction conditions, **1b** reacts with ethylene to form the C-H insertion product **3b** 23 times faster than to form the  $\pi$ -product **4b**.

This chemistry is not peculiar to ethylene, and indeed generation of **1b** at low temperature in the presence of 1-pentene affords a mixture of C-H insertion and  $\pi$ -coordinated products. We reported previously<sup>2</sup> that  $\text{Fe}(\text{DMPE})_2$  (generated photochemically

(4) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821-823.

(5) Samples were irradiated in Pyrex NMR tubes, positioned ca. 10 cm from a 125-W mercury vapor lamp. The tubes were supported within a quartz cylinder and cooled by a stream of nitrogen gas.

(6)  $^{31}\text{P}$  NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite, taken as 140.85 ppm, at the temperature quoted.  $^1\text{H}$  NMR spectra (400.1 MHz) were referenced to solvent resonances.

(7) Prepared by reduction of  $\text{FeHCl}(\text{DEPE})_2$  with KH in DMF/THF solution. In toluene solution the compound exists as a mixture of *cis* and *trans* isomers.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (toluene- $d_8$ , 220 K): *trans*  $\delta$  111.66; *cis*  $\delta$  102.35, 89.11 (apparent t, spacing 20.5 Hz).  $^1\text{H}$  NMR spectra (toluene- $d_8$ , 220 K): *trans*  $\delta$  -14.02 (quintet,  $J_{\text{PH}} = 39.9$  Hz, Fe-H); *cis*  $\delta$  -14.66 (m, Fe-H).

(8)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (pentane, 220 K):  $\delta$  92.91 ( $P_A$ ); 89.29 ( $P_B$ ); 83.51 ( $P_C$ ); 69.60 ( $P_D$ ,  $J_{AB} = 96.0$ ,  $J_{AC} = 22.6$ ,  $J_{AD} = 21.5$ ,  $J_{BC} = 25.3$ ,  $J_{BD} = 19.9$ ,  $J_{CD} = 9.3$  Hz).  $^1\text{H}$  NMR spectrum (pentane, 220 K):  $\delta$  -13.46 (Fe-H, dddd,  $J = 34.1$ , 53.9, 53.9, 59.5 Hz); 5.84 ( $J_{AB} = 11.4$ ,  $J_{BC} = 5.3$ , Fe- $\text{CH}_A=\text{CH}_B\text{H}_C$ ); 6.99 ( $J_{AB} = 11.4$ ,  $J_{AC} = 18.5$  Hz, Fe- $\text{CH}_A=\text{CH}_B\text{H}_C$ );  $H_C$  obscured by resonance of ethylene at ca. 5.3 ppm.

(9)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (THF- $d_8$ , 220 K):  $\delta$  84.58, 73.03 (apparent triplets, spacing 41.3 Hz).  $^1\text{H}$  NMR spectrum (THF- $d_8$ , 220 K):  $\delta$  0.029 and 0.644 ( $\text{CH}_2=\text{CH}_2$ ).

(10) Mays, M. J.; Prayter, B. E. *Inorg. Synth.* **1974**, *15*, 21-25.

(11)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (pentane, 220 K):  $\delta$  97.34.  $^1\text{H}$  NMR spectrum (pentane, 220 K):  $\delta$  -17.41 ( $J_{\text{PH}} = 43.0$  Hz, Fe-H); 4.71 ( $J_{AC} = 19.7$ ,  $J_{BC} = 5.2$  Hz, Fe- $\text{CH}_A=\text{CH}_B\text{H}_C$ ); 5.92 ( $J_{AB} = 13.0$ ,  $J_{BC} = 5.2$  Hz, Fe- $\text{CH}_A=\text{CH}_B\text{H}_C$ ); 7.26 ( $J_{AB} = 13.0$ ,  $J_{AC} = 19.7$  Hz, Fe- $\text{CH}_A=\text{CH}_B\text{H}_C$ ).

at  $-80^{\circ}\text{C}$ ) reacted with 1-alkenes (propylene, 1-butene, 1-pentene) to form mixtures of C-H insertion and  $\pi$ -coordination compounds. In all cases examined, the C-H insertion products<sup>12</sup> predominated ( $>90\%$ ) at low temperature, and on warming, the thermodynamically more stable  $\pi$ -complexes were formed.

The C-H vs.  $\pi$  reactivity described here is similar to that which has been reported in reactions of carbenes with alkenes<sup>13</sup> and lends support to the analogy which has been drawn between carbenes and coordinatively unsaturated transition-metal complexes.<sup>14</sup> The iron bis(diphosphine) systems differ significantly from the  $(\eta^5\text{-Me}_5\text{C}_5)\text{IrPMe}_3$  system previously reported and would suggest that the type of reactivity exhibited by the coordinatively unsaturated complexes of iron and iridium toward alkenes is probably widespread among the other transition-metal complexes.

**Acknowledgment.** We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M.V.B.).

(12) For propylene, 1-butene, and 1-pentene only metalation at the terminal C-H bonds was observed.

(13) See, for example: Kirmse, W. In *Carbene Chemistry*, 2nd ed.; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1971, Chapters 7, 8 and references cited therein.

(14) (a) Hoffmann, R. *Prix Nobel* 1981, pp 173-205. (b) Giannotti, C.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* 1972, 1114-1115. (c) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* 1985, 57, 1897-1910 and references cited therein.

## Electronic Excitation in Poly(di-*n*-hexylsilane)

Kenneth A. Klingensmith,<sup>1a</sup> John W. Downing,<sup>1a</sup>  
Robert D. Miller,\*<sup>1b</sup> and Josef Michl\*<sup>1a</sup>

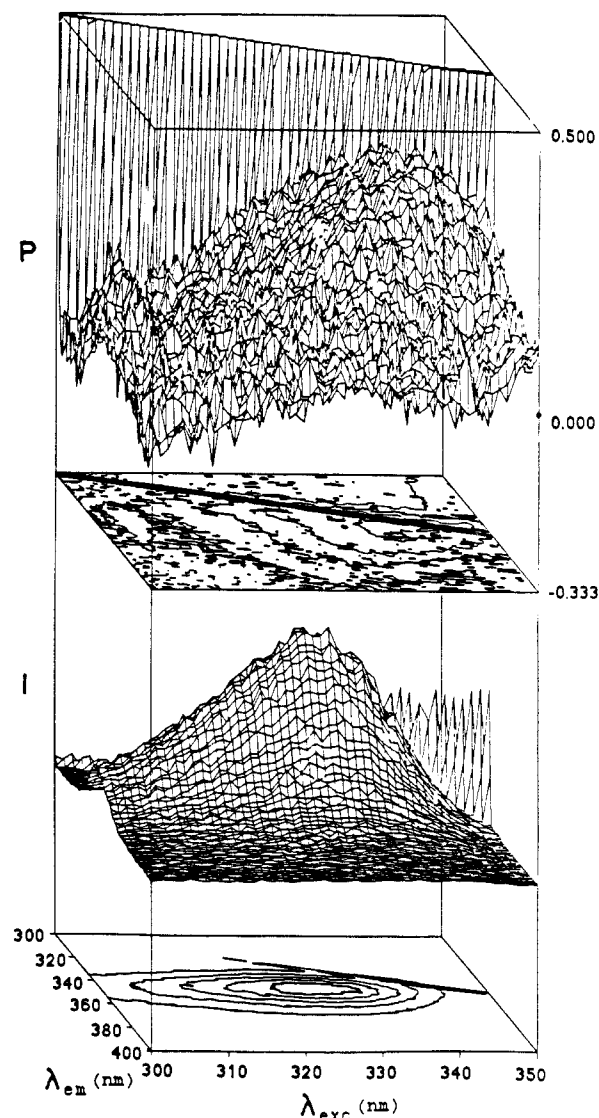
Department of Chemistry, University of Utah  
Salt Lake City, Utah 84112  
IBM Research Laboratories, Almaden Research Center  
San Jose, California 95120-6099

Received June 23, 1986

The saturated chain of silicon atoms in the potential photore-sists,<sup>2</sup> polysilanes, acts as a near-UV chromophore ( $\lambda_{\text{max}} = 300\text{--}400$  nm). The nature of the excited states is important for their photochemistry. Herein we report experimental and theoretical results for a model peralkylpolysilane.

Figure 1 shows the solution excitation-emission spectrum of  $[(n\text{-C}_6\text{H}_{13})_2\text{Si}]_n$  ( $M_w = 1.1 \times 10^6$ ,  $M_w/M_n = 2.4$ ) (**1**), with a fluorescence band independent of  $\lambda_{\text{exc}}$  and narrower than the excitation band, which is similar to the absorption band. At  $\lambda_{\text{exc}} = 335$  nm, the decay is exponential,  $\tau_F = 130 \pm 10$  ps. The polarization degree  $P$  ranges from values near the theoretical limit 0.5 at long  $\lambda_{\text{exc}}$  (absorbing and emitting transition moments parallel) to about zero at short  $\lambda_{\text{exc}}$  (the moments uncorrelated). The ridge of highest  $P$  runs near  $\lambda_{\text{exc}} = \lambda_{\text{em}}$  and peaks at long wavelengths.

These results fit expectations for the random-coil geometry<sup>3</sup> of **1**: electronic excitation localizes in chain segments of various



**Figure 1.** Fluorescence emission-excitation spectrum (bottom) and the polarization degree  $P$  (top) for **1** (3-methylpentane, flow cell,  $25^{\circ}\text{C}$ ).

lengths, leading to a distribution of excited states of differing energies, although the  $\sigma$ -conjugated nature of the backbone precludes full interruption of conjugation, possible in the analogous  $\pi$ -conjugated polyacetylene.<sup>4</sup> Energy transfer from short to long segments must be fast on the  $10^{-10}$  s time scale, since emission occurs primarily from the longest segments, regardless of  $\lambda_{\text{exc}}$ . An increase in the average transfer distance ( $\lambda_{\text{exc}} < \lambda_{\text{em}}$ ) reduces the correlation between the directions of absorbing and emitting moments, presumably parallel to chain segments.

The nature of the chain segments that support localized singlet excitation was explored by INDO/S<sup>5a</sup> calculations for  $[(\text{CH}_3)_2\text{Si}]_n$  and  $(\text{H}_2\text{Si})_m$  ( $n \leq 20$ ,  $m \leq 40$ ), using molecular mechanics<sup>5b</sup> geometries. For interpretation, the results were transformed from the original AO basis to a basis of maximally orthogonal  $\text{sp}^k$  hybrids oriented along bond directions ( $k \approx 3$ ).

As in prior work by simpler methods,<sup>6</sup> the first transition at any conformation corresponds predominantly to  $\sigma(\text{HOMO}) \rightarrow$

(1) (a) University of Utah. Present address: Department of Chemistry, University of Texas, Austin, TX 78712-1167. (b) IBM Almaden Research Center.

(2) Hofer, D. C.; Miller, R. D.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* 1984, 469, 16. Hofer, D. C.; Miller, R. D.; Willson, C. G.; Neureuther, A. R. *Proc. SPIE-Int. Soc. Opt. Eng.* 1984, 469, 108. Miller, R. D.; Hofer, D.; Willson, C. G.; Trefonas, P.; West, R. In *Materials for Microlithography: Radiation-Sensitive Polymers*; Thompson, L.; Willson, C. G., Fréchet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984. Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Proc. SPIE-Int. Soc. Opt. Eng.* 1985, 539, 166. West, R. J. *Organomet. Chem.* 1986, 300, 327.

(3) Cotts, P. M. *Proc. Polym. Mat. Sci. Eng.* 1985, 53, 336.

(4) Kuzmany, H.; Mehring, M.; Roth, S. *Electronic Properties of Polymers and Related Compounds*; Springer Series in Solid State Sciences Vol. 63; Springer Verlag: New York, 1985. Kuzmany, H. *Phys. Stat. Sol.* (b) 1980, 97, 521. Brédas, J. L. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. II.

(5) (a) Zerner, M.; Ridley, J. *Theor. Chim. Acta* 1973, 32, 111. (b) Hummel, J. P.; Stackhouse, J.; Mislow, K. *Tetrahedron* 1977, 33, 1925.

(6) Pitt, C. G. In *Homoatomic Rings, Chains and Macromolecules of the Main Group Elements*; Rheingold, A. L., Ed.; Elsevier: New York, 1977; and references cited therein.