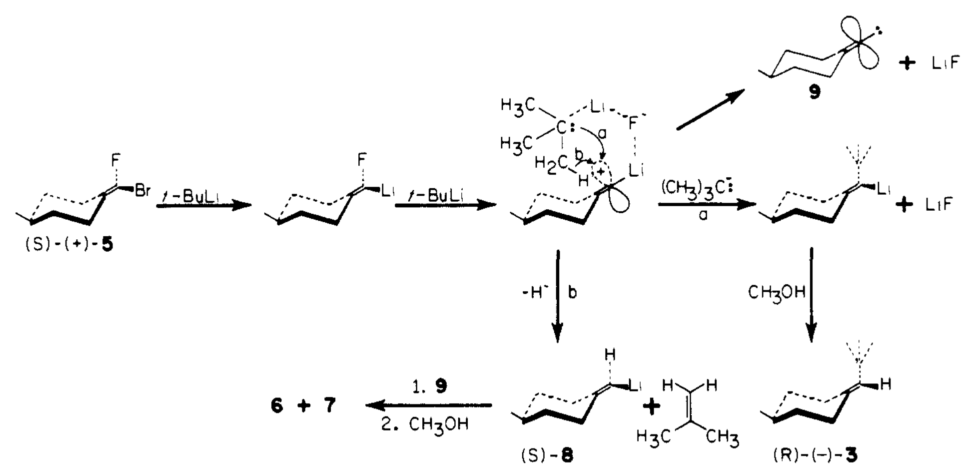
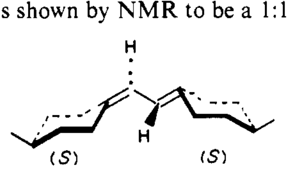
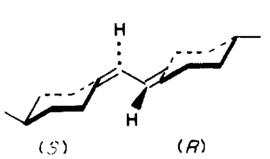
Scheme II



$CHCl_3$) and a 30% yield of (−)-1,2-bis(4-methylcyclohexylidene)ethane, $[\alpha]^{22}_{Hg}$ −10.9° (c 1.0, C_2H_5OH). The latter was shown by NMR to be a 1:1 mixture of chiral **6** and meso **7**.

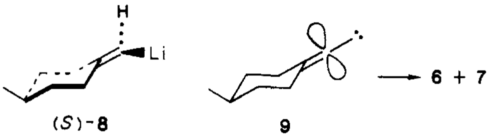


6



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-(+)-**1** (X = Cl), in ether at −75 °C, yielded (R-(−)-**3**, 31% optically pure[8] and of *inverted configuration*. Second is the formation of **6** and **7** which are products that were not observed in the reaction of (S)-(+)-**1** (X = Cl) with *tert*-butyllithium. However, both **6** and **7** (1:1) were obtained in the reaction of (S)-(+)-**1** (X = Br) because, besides metalation of the bromide to yield carbenoid, halogen metal exchange also occurred to produce the stable vinyllithium **8**.[7,9] This latter reaction does not occur when X = Cl. The α-addition of **8** to the carbene **9**, formed from carbenoid, gave a 1:1 mixture of adduct[3] which upon hydrolysis yielded **6** and **7**. Based on the previously established[10] absolute configuration and optical purity, **6** was formed with 50% optical purity[11] and overall *retention of configuration*.



(S)-**8** **9**

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 S_Ni 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)-**8** and isobutylene[12] (Scheme II, path b). In this loose ion pair some chirality can be lost and the partially racemized (S)-**8** can then add to the carbene product **9** to yield **6** and **7** in an expected 1:1 ratio.[11]

If this postulate is correct then the use of perdeuterio-*tert*-butyllithium should give rise to (R)-(−)-**3** possessing a perdeuterio-*tert*-butyl group and to (S)-**8** containing a 1-deuterio atom which then condenses with carbene to yield **6** and **7** each possessing one vinyl deuterium atom. This is precisely what is observed.[3,13]

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 $C_{19}H_{26}FNO_2$ (6 pages); table of structure factors F_{obsd} and F_{calcd} for $C_{19}H_{26}FNO_2$ (6 pages). Ordering information is given on any current masthead page.

---

(8) At this time it is not known whether the difference in optical purity is due to a difference in temperature, −100 °C vs. 75 °C.

(9) Vinyllithium (7) does not form (S)-1 (X = 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 carbene 9 would lead to a 1:1 mixture of 6 and 7 with 6 being 50% optically pure.

(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, Fe(DEPE)$_2$: sp^2 C–H Bond Activation without Prior Formation of a π-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 π-complex prior to 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 (η^5-Me_5C_5)$IrPMe_3$, however, it has been demonstrated that insertion of the iridium center into the sp^2 C–H bonds of ethylene proceeds with concurrent and not prior formation of a π-complex.[1] We recently reported[2] that the coordinatively unsaturated iron complex $Fe(DMPE)_2$ (**1a**)[3] [DMPE = 1,2-bis-

---

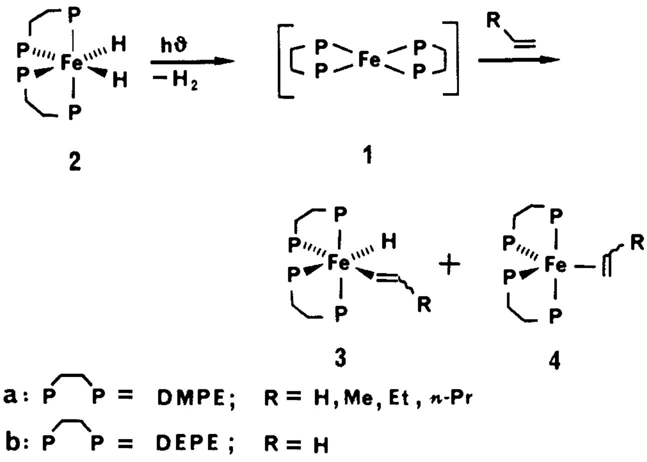
(1) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581–4582.

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

(3) For earlier studies on the chemistry of $Fe(DMPE)_2$, 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.

0002-7863/86/1508-7436$01.50/0

Scheme I



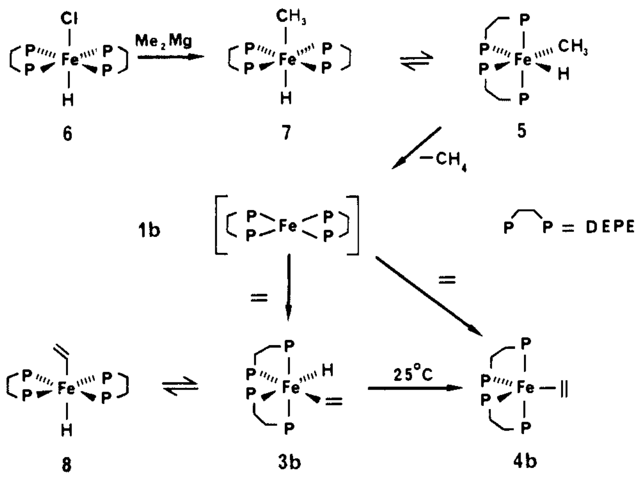
(dimethylphosphino)ethane], generated by photolysis of the dihydride FeH$_2$(DMPE)$_2$ (**2a**) at low temperature, reacts with alkenes to form a mixture of *cis*-alkenyl iron hydrides **3a** and the π-complexes **4a** (Scheme I). In that work, due to the photochemical lability of **3a** and **4a**,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

We have further examined the question of C–H vs. π addition of alkenes to zerovalent iron bis(diphosphine) complexes and report here reactions of Fe(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.[4]

Irradiation[5] of the dihydride FeH$_2$(DEPE)$_2$ (**2b**)[6,7] in pentane containing ethylene (ca. 5% mol/mol) at −80 °C for 2 h led to formation of the C–H insertion product *cis*-FeH(CH═CH$_2$)(DEPE)$_2$ (**3b**)[8] and the π-complex Fe(CH$_2$═CH$_2$)(DEPE)$_2$ (**4b**)[9] 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 °C regenerated the 90:10 mixture of **3b** and **4b**. This chemistry is exactly analogous to that previously reported for Fe(DMPE)$_2$.[2]

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**[10] (18 mM) and ethylene (280 mM) with dimethylmagnesium at −40 °C resulted in quantitative formation of the *trans*-methyl hydride **7**. On warming the solution to −28 °C, **7** isomerized slowly to the cis isomer **5** which rapidly eliminated methane.[4] 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 π-coordination product **4b**. At this temperature, the *cis*-vinyl hydride **3b** isomerized reversibly to the trans form **8**,[11] and after 5.8 h at −28 °C, the reaction mixture contained **3b**, **4b**, and **8** in the ratio 45:5:50. When the mixture was allowed to warm to 25 °C, both of the vinyl hydrides **3b** and **8** isomerized completely to the π-complex **4b** over a period of several hours (Scheme II).

Scheme II



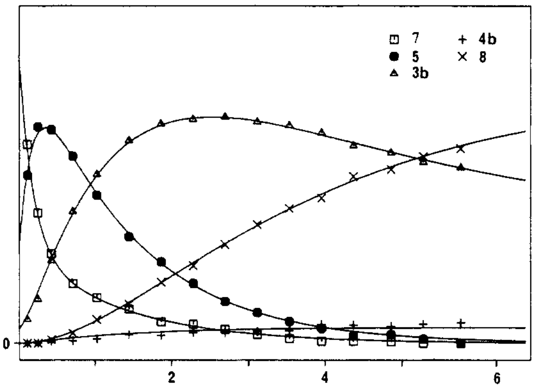


Figure 1. Composition of the reaction mixture on thermal decomposition of *trans*-FeH(DEPE)$_2$Me (**7**) (18 mM) in mesitylene solution in the presence of ethylene (280 mM) at −28 °C. Experimental points were obtained by integration of ^{31}P NMR spectra; curves are the result of a least-squares fit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

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

The entire reaction sequence outlined in Scheme II could be monitored conveniently by ^{31}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 π-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 π-coordinated products. We reported previously[2] that Fe(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}P NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite, taken as 140.85 ppm, at the temperature quoted. ^{1}H NMR spectra (400.1 MHz) were referenced to solvent resonances.

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

(8) ^{31}P{^{1}H} NMR spectrum (pentane, 220 K): δ 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}H NMR spectrum (pentane, 220 K): δ −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, $\mathrm{Fe{-}CH_A{=}C}H_\mathrm{B}\mathrm{H_C}$); 6.99 ($J_{AB}$ = 11.4, J_{AC} = 18.5 Hz, $\mathrm{Fe{-}C}H_\mathrm{A}\mathrm{{=}CH_BH_C}$); H$_C$ obscured by resonance of ethylene at ca. 5.3 ppm.

(9) ^{31}P{^{1}H} NMR spectrum (THF-d_8, 220 K): δ 84.58, 73.03 (apparent triplets, spacing 41.3 Hz). ^{1}H NMR spectrum (THF-d_8, 220 K): δ 0.029 and 0.644 ($\mathrm{C}H_2\mathrm{{=}C}H_2$).

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

(11) ^{31}P{^{1}H} NMR spectrum (pentane, 220 K): δ 97.34. ^{1}H NMR spectrum (pentane, 220 K): δ −17.41 (J_{PH} = 43.0 Hz, Fe—H); 4.71 (J_{AC} = 19.7, J_{BC} = 5.2 Hz, $\mathrm{Fe{-}CH_A{=}CH_B}H_\mathrm{C}$); 5.92 ($J_{AB}$ = 13.0, J_{BC} = 5.2 Hz, $\mathrm{Fe{-}CH_A{=}C}H_\mathrm{B}\mathrm{CH_C}$); 7.26 ($J_{AB}$ = 13.0, J_{AC} = 19.7 Hz, $\mathrm{FeC}H_\mathrm{A}\mathrm{{=}CH_BH_C}$).

at −80 °C) reacted with 1-alkenes (propylene, 1-butene, 1-pentene) to form mixtures of C–H insertion and π-coordination compounds. In all cases examined, the C–H insertion products[12] predominated (>90%) at low temperature, and on warming, the thermodynamically more stable π-complexes were formed.

The C–H vs. π reactivity described here is similar to that which has been reported in reactions of carbenes with alkenes[13] and lends support to the analogy which has been drawn between carbenes and coordinatively unsaturated transition-metal complexes.[14] The iron bis(diphosphine) systems differ significantly from the (η^5-Me_5C_5)$IrPMe_3$ 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,[1a] John W. Downing,[1a]
Robert D. Miller,*[1b] and Josef Michl*[1a]

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 photoresists,[2] polysilanes, acts as a near-UV chromophore (λ_{max} = 300–400 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 $[(n\text{-}C_6H_{13})_2Si]_n$ ($M_w = 1.1 \times 10^6$, $M_w/M_n = 2.4$) (**1**), with a fluorescence band independent of λ_{exc} and narrower than the excitation band, which is similar to the absorption band. At λ_{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 λ_{exc} (absorbing and emitting transition moments parallel) to about zero at short λ_{exc} (the moments uncorrelated). The ridge of highest P runs near $\lambda_{exc} = \lambda_{em}$ and peaks at long wavelengths.

These results fit expectations for the random-coil geometry[3] of **1**: electronic excitation localizes in chain segments of various lengths, leading to a distribution of excited states of differing energies, although the σ-conjugated nature of the backbone precludes full interruption of conjugation, possible in the analogous π-conjugated polyacetylene.[4] 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 λ_{exc}. An increase in the average transfer distance ($\lambda_{exc} < \lambda_{em}$) reduces the correlation between the directions of absorbing and emitting moments, presumably parallel to chain segments.

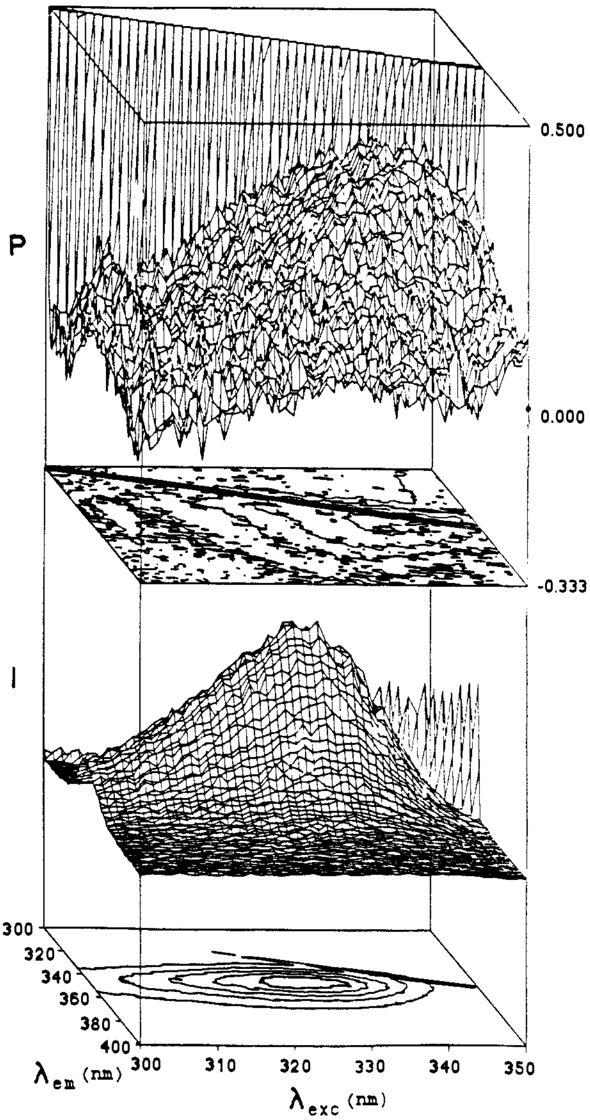


Figure 1. Fluorescence emission–excitation spectrum (bottom) and the polarization degree P (top) for **1** (3-methylpentane, flow cell, 25 °C).

The nature of the chain segments that support localized singlet excitation was explored by INDO/S[5a] calculations for $[(CH_3)_2Si]_n$ and $(H_2Si)_m$ ($n \leq 20$, $m \leq 40$), using molecular mechanics[5b] geometries. For interpretation, the results were transformed from the original AO basis to a basis of maximally orthogonal sp^k hybrids oriented along bond directions ($k \simeq 3$).

As in prior work by simpler methods,[6] the first transition at any conformation corresponds predominantly to σ(HOMO) →

---

[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., Frêchet, 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.

0002-7863/86/1508-7438$01.50/0