Formation and Detection of Neutral $FeCH_x$ (x = 0–3) Using Neutralization–Reionization Mass Spectrometry (NRMS)[†]

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Summary: Neutralization–reionization mass spectrometry (NRMS) has been used for the first time to generate and characterize in the gas phase neutral $FeCH_x$ (x = 0–3). Evidence is presented that neither ionic $FeCH_x^+$ (x = 0, 2, 3) nor its neutral analogue $FeCH_x$ (x = 0, 2, 3) rearranges to hydridometal complexes $HFeCH_x$ (x = 1, 2), in contrast to $FeCH^+$/FeCH which rearranges to $HFeC^+$ and HFeC, respectively.

Alkyl groups bonded to metals in varying states of saturation (MCH_x: M = transition-metal atom or complex: x = 0–3) are commonly proposed intermediates in many homogeneous[1] and heterogeneous[2] catalytic processes.

The cases where M corresponds to a single metal atom represent the simplest organometallic complexes possible. Analogous compounds have been the subject of considerable interest, particularly in the gas phase where the charged analogue can be readily detected.[3] However, the neutral, by virtue of being uncharged, represents a challenge to detect in the gas phase. On the other hand, in the condensed phase, such compounds are usually too reactive to study. Several theoretical studies have dealt with such neutrals; however, experimental studies are either limited or nonexistent.[4]

Recently, a method of producing neutrals in the gas phase from the cation by first neutralizing the monocation followed by reionization (NRMS)[5] has produced formerly unobtainable neutral compounds such as the long sought-after carbonic (HOCOOH)[6] and carbamic (H_2NCOOH)[7] acids, as well as unusual acetylenes of the type XC≡CY (X = H, Y = OH, NH_2; X, Y = OH, NH_2).[5b,8] We have applied the same technique to produce the title compounds from the corresponding cations in a multisector mass spectrometer. This process offers the possibility of eventually studying neutral organometallic reactions in the gas phase.

Experimental Section. The principal features, including a discussion of technical aspects, of NRMS have recently been reviewed in the literature.[5] Briefly, the process involves first generating cations in the ion source, followed by mass selection of the cation of interest with the sector B(1) of a triple sector mass spectrometer (in this case a Vacuum Generator ZAB-HF-3F mass spectrometer which is of BEB configuration; B stands for the magnetic and E for the electrostatic sector, respectively). The cation of 8 keV kinetic energy is then neutralized by collision with O_2 gas (although Xe as well as metal vapor can also be used). All surviving charged species are deflected by a positively charged electrode placed parallel to the path of the beam. The neutrals, however, proceed to a second collision chamber where they are reionized by collision with O_2. The resulting ionic fragments are recorded in a single focussing mode by scanning the electrostatic sector. The second magnet is not used in the present experiment in order to have higher sensitivity.

The $FeCH_x$ complexes were produced by ionizing, via electron impact (70 eV), a mixture containing $Fe(CO)_5$ and some appropriate organic precursors (in 1:5 respective proportion) in a chemical ionization source (pressure reacting in the pumping line ca. 10^{-5} mbar). Iron pentacarbonyl and all organic precursors are commercially available and were used without further purification.

Results and Discussion. Figure 1a shows the NR mass spectrum of $FeCH_3$ formed from the ionization of a $Fe(CO)_5$ and CH_3I mixture. The reionized neutral parent produces an abundant signal suggesting that $FeCH_3$ is quite stable both as a cation and as a neutral. It is seen that the parent $FeCH_3$ signals has a smaller width than the other signals in the spectrum. This observation provides a useful criterion for distinguishing between neutrals produced by direct ionization of neutralized species and fragment ions produced upon dissociation of the reionized neutrals. This is because ejection of an electron is not associated with a significant kinetic energy release whereas the dissociation of an ion generally is.[9] Prior to reionization a fraction of the neutralized species may dissociate into neutrals of smaller mass which are subsequently ionized. Depending on the kinetic energy release in the

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[†] Dedicated to Professor F. W. McLafferty on the occasion of his 65th birthday.

(1) For a recent review see: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(2) See for example: (a) Lebrilla, C. B.; Maier, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 1606. (b) Cogen, J. M.; Maier, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 7752. (c) Koel, B. E.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1984**, *146*, 211. (d) Frennet, A. *Catal. Rev.—Sci. Eng.* **1974**, *10*, 37. (e) Kemball, C. *Trans. Faraday Soc.* **1954**, *50*, 1344.

(3) See for example: (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501. (b) Georgiadis, R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 2119. (c) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (d) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (e) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316. (f) Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 2180. (g) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1829. (h) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (i) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962. (j) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403. (k) Kang, H.; Jacobson, D. B.; Shin, S. K.; Beauchamp, J. L.; Bowers, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 5668. (l) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891. (m) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67, 5876. (n) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537. (o) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (p) Allison, J.; Ridge, D. P.; *J. Organomet. Chem.* **1975**, *99*, C11. (q) Allison, J.; Ridge, D. P.; *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(4) (a) Ziegler, T.; Tschinke, V.; Becker, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351. (b) Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1983**, *105*, 5557. (c) Bäckvall, J. E.; Björkman, E. E.; Petterson, L.; Siegbahn, P.; Strich, A. *J. Am. Chem. Soc.* **1985**, *107*, 7408. (d) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057. (e) Ozin, G. A.; McCaffrey, J. G.; Parnis, J. M. *Angew. Chem.* **1986**, *98*, 1076 and references cited therein. (f) Barrett, P. H.; Pasternak, M.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 222. (g) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574. (h) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; Vol. 193, p 97. Chang, S.-C.; Kafafi, Z. H.; Hange, R. M.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *707*, 1447.

(5) (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Burgers, P. C.; van Baer, B. L. M.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 357. (c) Terlouw, J. K.; Schwarz, H. *Angew Chem.* **1987**, *99*, 829. (d) Holmes, J. L. *Acc. Chem. Res.*, submitted for publication.

(6) Terlouw, J. K.; Lebrilla, C. B.; Schwarz, H. *Angew, Chem., Int. Ed. Engl.* **1987**, *26*, 354.

(7) Van den Berg, K. J.; Lebrilla, C. B.; Terlouw, J. K.; Schwarz, H. *Chimia* **1987**, *41*, 122.

(8) (a) Van Baar, B. L. M.; Weiske, T.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 282. (b) Van Baar, B. L. M.; Koch, W.; Lebrilla, C. B.; Terlouw, J. K.; Weiske, T.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 827.

(9) (a) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973. (b) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

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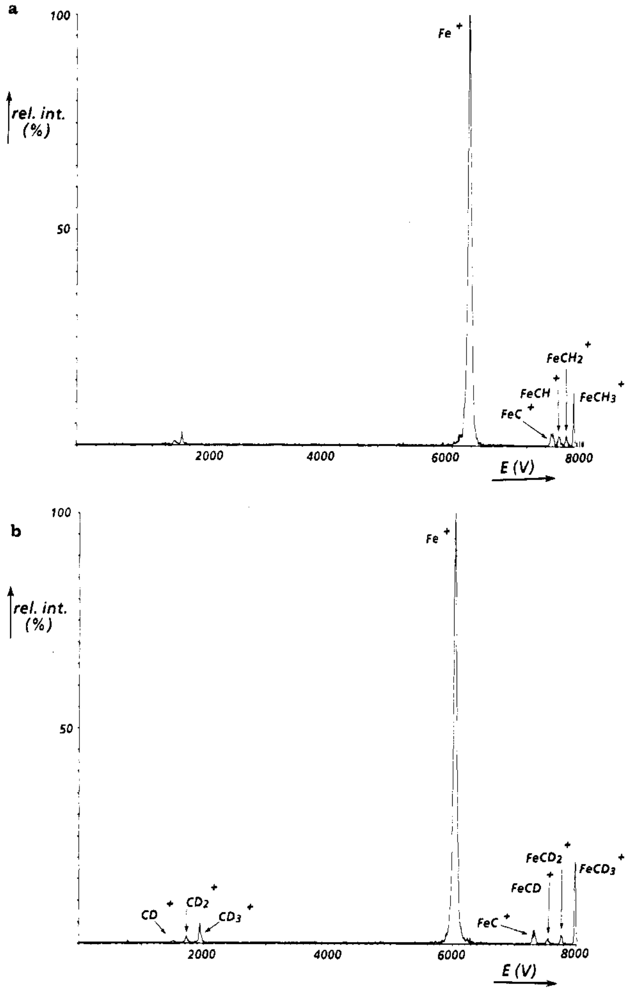
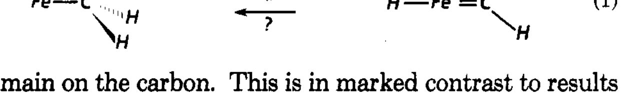


Figure 1. NR mass spectra of (a) $FeCH_3$ (generated from Fe$(CO)_5/CH_3I$) and (b) $FeCD_3$ (generated from $Fe(CO)_5/CD_3I$).

above reionization the width of the resulting signals in the NR spectra may vary from narrow to very broad;[9] moreover, the presence of a "composite" peak may indicate the simultaneous operation of both reactions, i.e., formation of an ion by direct electron ejection from a stable neutral ("narrow" peak) and via dissociation of ions (neutrals) ("broad" component). In the present case, we cannot detect a composite signal.

The spectrum is further dominated by a large *m/z* 56, presumably Fe^+. Signals corresponding to FeH, FeH_2, etc. are *not* observed. Hence, hydrogen migration such as in reaction 1 probably does not occur and the hydrogen atoms remain on the carbon. This is in marked contrast to results based on low-temperature matrix[4f] and chemisorption studies of methane on iron films.[10] From these studies it was concluded that an irreversible rearrangement, $FeCH_3 \rightarrow HFeCH_2$, occurs. However, a series of peaks near the parent peak suggest consecutive losses of hydrogen atoms. These losses are confirmed by the spectrum of $FeCD_3$ (Figure 1b) produced under similar conditions. Interestingly, signals corresponding to CH_3^+, CH_2^+, and CH^+, albeit weak, are also observed. This result clearly demonstrates that not only $FeCH_3^+$[11] but also the neutral analogue exist largely if not exclusively as metal–methyl $FeCH_3$ and *not* as hydrido–methylidene structure HFe=CH_2. When the NR mass spectra of $FeCH_3$ and $FeCD_3$ are compared, note the increased abundancy of the parent peak in the latter, indicating that the propensities of $FeCD_3$ and $FeCD_3^+$ to fragment are significantly reduced in comparison with the hydrogen analogues. This may be well (i) due to a kinetic isotope effect retarding the breaking of a CD versus a CH bond and (ii) as suggested by a reviewer due to a simple mass effect in the collision processes. Our experiments do not permit a distinction.



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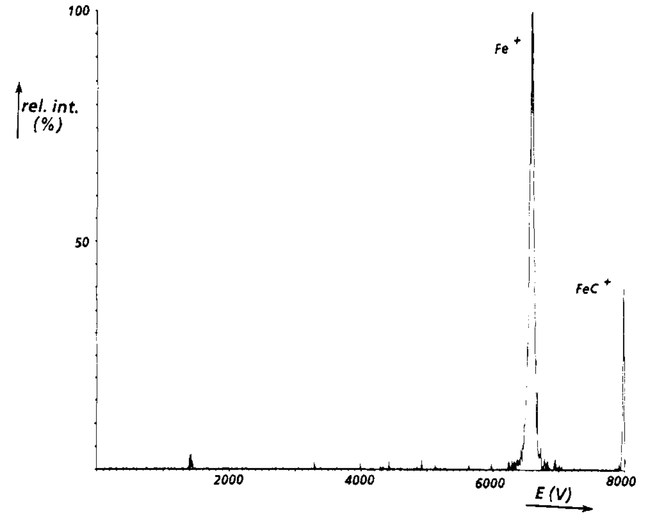
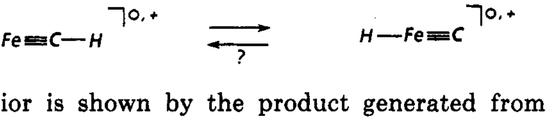


Figure 2. NR mass spectrum of FeC generated from Fe$(CO)_5/CH_3I$.

The only other complex to come out cleanly from the $Fe(CO)_5/CH_3I$ mixture is FeC (Figure 2) which also exhibits a strong parent peak in the NRMS experiment. Not surprisingly, the only fragment observed is Fe^+ resulting from the loss of a neutral carbon atom.

NRMS spectra of $FeCH_2$ and FeCH could conversely be produced by ionizing mixtures of $Fe(CO)_5$ and CH_2Br_2 and $CHBr_3$, respectively. In the spectra of $FeCH_2$ and FeCH the relative abundance of the parent peak is 28% ($FeCH_2$) and 42% (FeCH) enhanced in comparison to that of the $FeCH_3$ species (12%); this may indicate that the stability of the $FeCH_x$ species increases with decreasing hydrogenation. The base peak in both spectra, again, corresponds to Fe^+, and from the absence of FeH^+ signals in the specra of $FeCH_2$ and $FeCH_2^+$ we conclude that no hydridometal species are present (eq 2). A distinct behavior is shown by the product generated from Fe$(CO)_5/CHBr_3$. The collisional activation spectrum of [Fe, C, H]$^+$ contains signals for both Fe^+ and FeH^+ in the approximate ratio 1:2, which are also present in NR spectrum. Thus, part of the $FeCH^+$ species must be present as H—Fe≡C$^+$.



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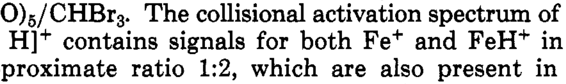

(3)

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[10] Andersen, J. R., Ed. *Chemisorption and Reaction on Metallic Films*; Academic: New York, 1971; Chapter VIII.

[11] For studies on MCH_3^+ (M = Fe, Co) see (a) ref 31,o. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

In conclusion, neutralization of $FeCH_x^+$ (x = 0–3) species generates neutral analogues $FeCH_x$ (x = 0–3), having lifetimes $t \geq 10^{-5}$ s. No evidence is available for the involvement of hydridometal species, for x = 2 or 3.

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Silacarbonyl and Silathiocarbonyl Ylides

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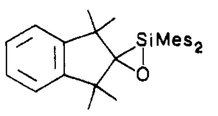
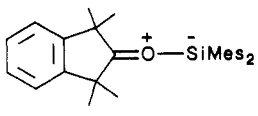
Summary: The silacarbonyl ylide **4a** has been observed by the photolysis of oxasilirane **5a** in an isopentane/3-methylpentane matrix at 77 K. The ylide was also generated independently by the direct reaction of dimesitylsilylene with tetramethyl-2-indanone. The silacarbonyl ylide is intensely blue in color with a maximum at 610 nm. Excitation of this band with visible light resulted in the formation of oxasilirane **5a**. A silathiocarbonyl ylide has also been generated by either photolysis of a thiasilirane or the direct reaction of silylenes with indanethione.

The formation and characterization of carbonyl ylides in the photochemical ring opening of aryloxiranes[1] or in the reaction of carbenes with ketones[2] have been well-established by low-temperature photolysis or flash laser photolysis. However, the chemistry of silacarbonyl ylides, the silicon analogues of carbonyl ylides, is completely unknown. Recently we reported synthesis of oxasilirane **5a**[3] and thiasilirane **5b**[4] and the photochemical fragmentation of **5a** to a silylene and a ketone in solution, probably via a silacarbonyl ylide intermediate.[5] We report here the first spectroscopic evidence for the intermediacy of the hitherto unknown silacarbonyl and silathiocarbonyl ylides in a low temperature matrix.



5a



4a (λ_{max} = 610 nm)

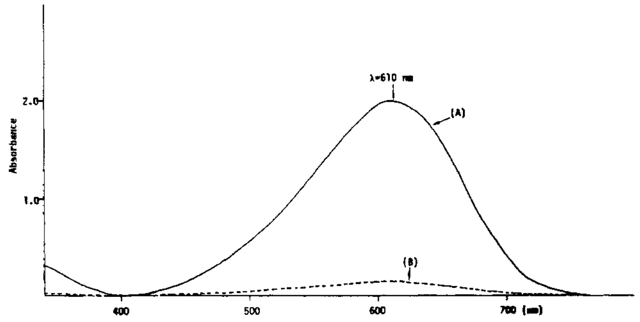


Figure 1. (A) After photolysis of **5a** with a low-pressure mercury lamp (254 nm) for 10 min in IP/3-MP (6:4) at 77 K (—). (B) After the additional irradiation of the above sample for 5 s with a xenon lamp (λ > 460 nm) (- - -). The band completely disappeared by 60-s irradiation with λ > 460 nm.

Irradiation of oxasilirane **5a** (0.02 mmol) in an isopentane (IP)/3-methylpentane (3-MP) matrix[6] at 77 K with a low-pressure mercury lamp led to the appearance of a new band at 610 nm in the UV–vis spectrum, and the matrix became intensely blue in color (Figure 1). This absorption band was stable at 77 K on prolonged standing. However, it immediately disappeared on brief irradiation with a xenon lamp (λ > 460nm) or when the matrix was allowed to melt. These results appear to be related to the photochemistry of aryloxiranes in rigid organic glasses to give colored intermediates that can be eradicated either by irradiation into the visible absorption band or by warming the matrix.[1] The colored species was also observable at 610 nm in the photolysis of **5a** in 3-MP glass at 77 K.[7]

This colored species was independently generated by the reaction of dimesitylsilylene (**2**) with 1,1,3,3-tetramethyl-2-indanone (**3a**). Thus, irradiation of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**1**) in the presence of **3a** in IP/3MP at 77 K with a low-pressure mercury lamp produced a colored species with λ_{max} at 573 nm due to dimesitylsilylene (**2**).[8] The absorption bands at 610 and 420 nm increased in intensity in the dark at the almost same rate as the decrease of the band at 573 nm, showing that **2** reacts with **3a** or dimerizes to tetramesityldisilene (420 nm) in the matrix at 77 K (Figure 2).[9] Irradiation of the red solution of the 610-nm species, with a wavelength of light greater than 460 nm, or melting the matrix resulted in production of the oxasilirane **5a**.[10]

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[1] (a) Trozzolo, A. M.; Leslide, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261. (b) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 5639. (c) Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2818. (d) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (e) McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547. (f) Franco, P. G. *Rev. Chem. Intermed.* **1986**, *7*, 155. (g) Ibata, T.; Liu, M. T. H.; Toyoda, J. *Tetrahedron Lett.* **1986**, *27*, 4383.

[2] (a) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106. (b) Bekhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289. (c) Prakash, G. K. S.; Ellis, R. W.; Felberg, J. D.; Olah, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1341.

[3] Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5323.

[4] Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033.

[5] Ando, W.; Hamada, Y.; Sekiguchi, A. *J. Chem. Soc., Chem. Commun.* **1983**, 952.

[6] The IP/3-MP matrix is a relatively soft matrix compared to the 3-MP matrix. The viscosities of the matrices at 77 K are as follows: IP/3-MP (6:4), 1.8×10^8 P; 3-MP, 9.4×10^{11} P. Lambardi, J. R.; Raymonda, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964**, *40*, 1148.

[7] The band at 564 nm gradually shifted to 610 nm without annealing when the matrix was allowed to stand at 77 K in the dark (ca. 5 h). The change of the conformation of **4a** will result in a bathochromic shift due to electronic reasons. In a soft matrix, the most stable conformation will be readily achieved.

[8] The bands at 573 and 420 nm are due to dimesitylsilylene (**2**) and tetramesityldisilene, respectively. In 3-MP matrix, the bands of **2** appeared at 577 nm. West, R.; Fink, M. J.; Michel, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R. *Silicon, Germanium, Tin Lead Compds.* **1986**, *1*, 75–80. The small hypsochromic shift to **2** from the 3-MP matrix to the IP/3-MP matrix is probably due to solvent effects.

[9] Dimesitylsilylene can dimerize to tetramesityldisilene at 77 K in a soft matrix without annealing the matrix. Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, 209.

[10] The products **5a** and **5b** were identified by comparison of their spectra with those of authentic samples.