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# Flash Photolysis of ($\eta^3$-N-diene)W(CO)$_4$ (N-diene = *trans*-2-Methyl-2-aza-5,7-octadiene) in Triethylsilane: Regioselective 1,2-Hydrosilylation

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Flash photolysis of ($\eta^3$-N-diene)W(CO)$_4$ (N-diene = *trans*-2-methyl-2-aza-5,7-octadiene) in chlorobenzene (CB) solution gives rise to an intermediate in which the rapidly solvated, coordinatively unsaturated site is cis to the coordinated internal olefin. This intermediate reacts via CB displacement to form an ($\eta^4$-N-diene)W(CO)$_4$ complex in which both the $\pi$-bonds are coordinated to the metal. In triethylsilane solution *E*- and *Z*-hydrosilylation products arising from regiospecific 1,2-addition to the diene are isolated. An agostic interaction between the Si–H bond of the silane and the coordinatively unsaturated metal is shown to be consistent with the results.

Photolysis of solutions containing 1,3-dienes and hydrosilanes in the presence of Cr(CO)$_6$ as a precatalyst ("photocatalyst") affords 1,4-hydrosilylation products.[1] It has been noted that "The complexes Mo(CO)$_6$ and W(CO)$_6$ also function as photocatalysts for the hydrosilylation reaction, but their known[2] ability to serve as olefin isomerization photocatalysts makes Cr(CO)$_6$ the photocatalyst of choice. Bond migration in monoolefins with W(CO)$_6$ as the photocatalyst has also been observed.[4,5] For one of these studies[4] it was shown that this bond migration most probably involved an intermediate containing a vacant coordination site adjacent to a coordinated olefin.[6] In a photocatalytic reaction involving a diene and W(CO)$_6$, such a species would be expected to be produced after several reaction steps as a steady-state intermediate that could not be studied directly.

The creation of such an intermediate during a single flash, through the photolysis of a specifically designed precursor, could offer unprecedented insight into the mechanisms of these photocatalytic processes. The appropriate precursor should possess thermal stability and must undergo selective bond breaking upon flash photolysis to afford a cis coordinatively unsaturated [($\eta^2$-1,3-diene)M(CO)$_4$] transient. These qualities should be exhibited by *cis*-($\eta^3$-N-diene)W(CO)$_4$ complexes, where N-diene is a 1,3-diene that can form a chelate ring via coordination through a nitrogen and one of the olefinic $\pi$ bonds. Complexes similar to this type that contain one olefinic functionality, such as *cis*-($\eta^3$-N-ene)W(CO)$_4$, have been reported.[7] In these complexes thermal stability arises from both chelate ring formation and the use of W as the metal.[8] Additionally, upon photolysis at 365 nm, it has been found that M–N bonds are broken preferentially to those which involve ligand to metal $\pi$-bonding[9] because the excitation populates a $\sigma^*$ level in the metal carbonyl complex.[10] Herein is reported the synthesis of such a photocatalytic precursor, *cis*-($\eta^3$-N-diene)W(CO)$_4$ (1; N-diene = *trans*-2-methyl-2-aza-5,7-octadiene (2)), and a study of its reactions after flash photolysis in chlorobenzene or triethylsilane solutions.

**Scheme I. Synthesis of *cis*-($\eta^3$-N-diene)W(CO)$_4$ (1)**

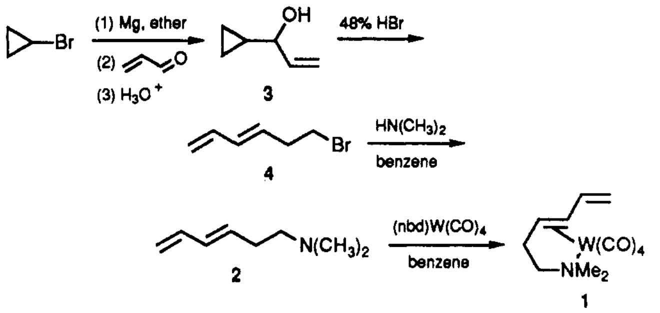
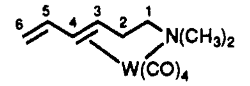


**Table I. NMR Data for *cis*-($\eta^3$-N-diene)W(CO)$_4$[a]**



| atom | $^{13}$C (APT mult) | $^1$H (mult; *J*, Hz) |
|---|---|---|
| 1 | 60.43 (t) | 2.43 (m) |
| 2 | 29.35 (t) | 2.49 (m) |
| 3 | 84.31 (d) | 4.90 (m) |
| 4 | 84.57 (d) | 5.21 (m) |
| 5 | 138.55 (d) | 5.70 (dt; 16.8, 9.9) |
| 6 | 112.53 (t) | 4.83 (d; 9.9) |
| CH$_3$ | 59.09 (q) | 2.77 (s) |
| | 57.30 (q) | 2.69 (s) |
| CO | 213.95 (s) | |
| | 208.09 (s) | |
| | 205.46 (s) | |
| | 205.00 (s) | |

[a] Chemical shifts in ppm downfield from tetramethylsilane referenced to CDCl$_3$ (solvent) for $^1$H NMR spectra at 300 MHz and $^{13}$C NMR spectra at 75 MHz. Assignments are based on a $^1$H–$^{13}$C COSY (HETCOR, *J* = 140 Hz) spectrum.

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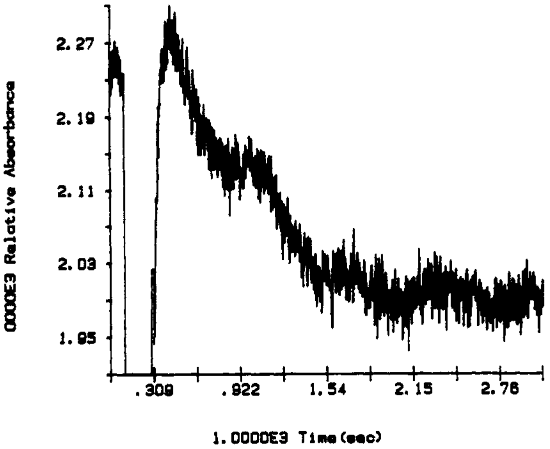


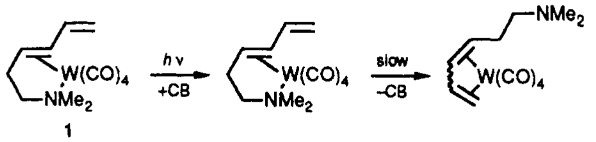
**Figure 1.** Transient absorption spectrum for the flash photolysis of *cis*-($\eta^3$-N-diene)W(CO)$_4$ (1) in chlorobenzene. The observation wavelength is 400 nm.

## Results and Discussion

**Synthesis and Characterization of *cis*-($\eta^3$-N-diene)W(CO)$_4$ (1).** The preparation of the ligand 2 was accomplished by the method outlined in Scheme I. Following the procedure of Julia, cyclopropylvinylcarbinol (3) was prepared by the reaction of cyclopropylmagnesium bromide with acrolein.[11,12] Subsequent hydrobromic acid cleavage of 3 gave the conjugated *trans*-1-bromo-3,5-hexadiene (4).[13] The bromide 4 was then converted to the tertiary amine 2[14] by ammonolysis with dimethylamine with use of Cope's method.[15] To prepare the N-diene complex 1, ($\eta^4$-nbd)W(CO)$_4$ (nbd = norbordiene) was synthesized with use of the procedure of King and Fronzaglia.[16] Treatment of ($\eta^4$-nbd)W(CO)$_4$ with 2 in refluxing benzene solution afforded a high yield (>70%) of the N-diene complex 1 as yellow needles after recrystallization from *n*-heptane. The IR spectrum of the N-diene complex in the $\nu$(CO) stretching region shows four absorption bands (2025 (s), 1925 (s), 1913 (vs), 1882 (s) cm$^{-1}$), which indicates a cis coordination of the N-diene ligand in the complex. The UV–vis absorption spectrum shows a maximum at 320 nm ($\epsilon$ = 4.23 × 10$^3$ cm$^{-1}$ M$^{-1}$). The structural characterization of 1 as the $\eta^3$ complex was made possible by NMR spectroscopy (Table I).

In both the $^{13}$C and $^1$H NMR spectra of 1 two separate resonances are observed for the two *N*-methyl carbons and their protons. These are nonequivalent due to the lack of free rotation, indicating that the dimethylamino group is coordinated to W. The APT spectrum clearly indicates the presence of an uncoordinated terminal alkene. The olefin region shows one positive signal at 112.56 ppm and three negative signals at 138.55, 84.57, and 84.31 ppm. The resonances at 112.56 and 138.55 ppm are assigned to the terminal olefin carbons, bearing two and one hydrogens, respectively. The resonances at 84.57 and 84.31 ppm are assigned to the coordinated internal olefin carbons, each bearing one hydrogen.[17] The assignments of $^1$H NMR chemical shifts were based on coupling patterns. The lowest field resonance at 5.70 ppm was assigned to H-5 due to the olefinic proton coupling with H-4 ($J$ = 16.8 Hz) and two H-6 atoms ($J$ = 9.9 Hz). Two-dimensional $^1$H–$^{13}$C heteronuclear chemical shift correlation (HETCOR) spectra afforded the complete carbon and proton assignments compiled in Table I.[18]

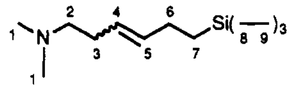
**Scheme II. Photolysis of 1 in Chlorobenzene**



CB = chlorobenzene

**Flash Photolysis Studies.** Absorbance changes taking place after flash photolysis of 1 in chlorobenzene (CB) solution monitored at 400 nm indicate that the W–N bond is broken on photolysis. The solvated "ring-opened" intermediate closes to give an ($\eta^4$-N-diene)W(CO)$_4$ complex formed by coordination of the second olefin of the ligand. It can be seen in Figure 1 that decay of the solvated species generated after flash photolysis leads to a stable product which has an absorbance less than that of 1. In the flash photolysis of *cis*-(pip)(P-ene)W(CO)$_4$ (pip = piperidine; P-ene = $Ph_2P(CH_2)_nCH{=}CH_2$, $n$ = 1–4) complexes, an analogous decrease in absorbance accompanies the conversion of the photolysis precursor to isolable ($\eta^3$-P-ene)W(CO)$_4$ complexes.[19] This behavior has unequivocally been shown to be diagnostic of replacement of the amine (pip) by chelated olefin in the metal's coordination sphere.[20] Thus, the species formed upon flash photolysis of 1 is one in which the internal $\pi$-bond of the N-diene ligand is coordinated cis to a vacant coordination site (Scheme II).

In contrast, flash photolysis of *cis*-($\eta^3$-N-diene)W(CO)$_4$ in triethylsilane solution shows that products are produced at a rate faster than the time resolution of the instrument (>100 $\mu$s). If an ($\eta^4$-diene)W(CO)$_4$ complex were being formed, behavior similar to that observed in chlorobenzene would have been observed. In order to identify the products without introducing complications due to the formation of additional photoproducts, the solutions resulting from 15 separate single-flash experiments were combined. NMR spectra of this mixture indicated the presence of hydrosilylation products.[21] Fractional distillation afforded a mixture of two hydrosilylation products:



Proton nuclear Overhauser effect (NOE) difference experiments on olefinic protons revealed the presence of *E* and *Z* isomers. Irradiation of the downfield olefinic proton at $\delta$ 5.48 resulted in an enhancement at $\delta$ 5.34 and no enhancement at $\delta$ 5.28. The assignment of the proton chemical shifts is possible from the 2D $^1$H,$^1$H-COSY spectrum, where the resonances at H-6 and H-7, and H-2 and H-3 show a pronounced cross correlation. There is also a cross correlation due to the allylic couplings between H-3 and H-5, and H-6 and H-4. The assignment of the

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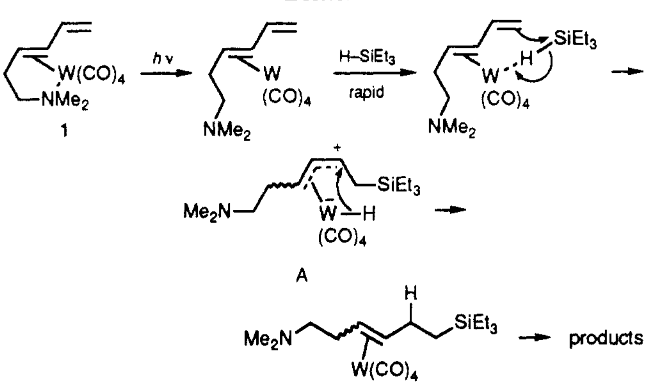
[21] This observation demonstrates that hydrosilylation occurred in the course of the photolysis experiment and not during the distillation of the combined reaction mixtures, as had been suggested by a reviewer.

**Scheme III. Mechanism for the 1,2-Hydrosilylation of Dienes**



product was also confirmed by $^{13}C$ NMR and APT experiments. The APT spectrum shows four negative signals (one or three attached protons) for olefinic carbons at 134.64, 128.06, 126.49, and 125.93 ppm. These results indicate that 1,2-hydrosilylation of **2** leading to a mixture of both the *E* and *Z* isomers had occurred.

No hydrosilylation products were produced under thermal conditions. When the *cis*-($\eta^3$-N-diene)$W(CO)_4$ complex and an equal molar ratio of triphenylphosphine were refluxed in *n*-heptane solvent and monitored by FT-IR spectroscopy, the $A_1$ carbonyl stretching band (2025 $cm^{-1}$) of complex **1** shifted to lower frequency (2016 $cm^{-1}$). This indicates that $Ph_3P$ replaced the olefin ligand.[22] If $Ph_3P$ had replaced the nitrogen ligand, $\nu$(CO) would have shifted to higher frequency.[23] These results indicate that the olefin–tungsten rather than the nitrogen–tungsten bond breaks under thermal conditions. Thus, hydrosilylation does not occur under thermal conditions because a vacant coordination site cis to a coordinated olefin is not generated. A related study has demonstrated that, under similar conditions, olefin bond migration does not occur unless a vacant coordination site is generated cis to the coordinated olefin.[6]

In contrast to Wrighton's observations of 1,4-hydrosilylation of 1,3-dienes photocatalyzed by $Cr(CO)_6$,[1,3] the hydrosilylation products obtained in this noncatalytic study result from the 1,2-addition of triethylsilane. The generally accepted mechanism for catalyzed hydrosilylation involves oxidative addition of the Si–H bond to a coordinatively unsaturated metal–olefin complex, insertion of the olefin into the M–H bond, and reductive elimination of the product.[1] If this were occurring in our system, a cis-1,4-adduct would be expected rather than the *E*- and *Z*-1,2-adducts that we observe. However, our results are consistent with hydrosilylation occurring with a silane activated by an agostic Si–H or an $\eta^2$ Si–H interaction involving two-electron-three-center bonds between the silane solvent and the coordinatively unsaturated species generated by photolysis (Scheme III). Recently, chemical and spectroscopic evidence for similar interactions has been reported which indicated that an agostic M–H–Si bonding occurs early along the potential energy surface, leading to oxidative addition of the silane to the metal.[24] It has been concluded that the degree to which the Si–H bond is bound to the metal center depends both on the electronic and steric properties of the metal center and on the $SiR_3$ group.[25] Agostic Si–H intermediates have been observed to undergo nucleophilic attack by alcohols to produce silyl ethers.[26] Because triethylsilane is the solvent in our experiments, such an agostic interaction with the coordinatively unsaturated species generated by photolysis is probable.[27] Binding to the vacant coordination site activates the silane toward nucleophilic attack.[28] The two nucleophiles in the immediate vicinity of the activated silicon are the nitrogen of the dimethylamino group and the uncoordinated terminal olefin. While reversible coordination of the nitrogen with silicon would be nonproductive, attack by the terminal olefin would give rise to the metal–hydride intermediate A. This process amounts to electrophilic attack of the triethylsilyl group on the terminal carbon of the diene system, which would be favored by both the known ability of silicon to stabilize electron-deficient centers at the $\beta$-positon[29] and the partial $\eta^3$ coordination of the allyl "cation" with the metal. The stereochemical integrity of the alkene is lost in this intermediate, accounting for the formation of both the *E* and *Z* isomers of the product. If the 1,2-product were due to a shift of the metal from the internal to the terminal double bond of the diene, the stereochemistry would be retained to give only *E* product. Subsequent hydride transfer to the position $\beta$ to silicon leads to the regiospecific 1,2-hydrosilylation, giving the *E* and *Z* products that were isolated.

## Experimental Section

**General Information.** All air- and moisture-sensitive reactions were carried out under a nitrogen atmosphere. Solvents were dried immediately prior to use.[30] Ether was distilled from benzophenone and sodium, benzene was distilled from sodium and stored over dried 4-A molecular sieves, and *n*-heptane was distilled from sodium. Dimethylamine was obtained from the Aldrich Chemical Co. and was used without further purification. Norbornadiene and triethylsilane were purchased from the Aldrich Chemical Co. and were distilled before use. Cyclopropyl bromide and 4-bromobutene were obtained from Lancaster Synthesis, Inc., and were used without further purification. Acrolein was obtained from Aldrich Chemical Co. and dried with $MgSO_4$ before use. $W(CO)_6$ was obtained from Pressure Chemical Co. and used without further purification. All proton and carbon NMR spectra were obtained with use of a Varian VXR-300 spectrometer with $CDCl_3$ as the solvent, which was used as an internal standard for the carbon spectra. For proton spectra, residual $CHCl_3$ was used as the internal standard. Chemical shifts are reported in ppm downfield from tetramethylsilane. The interpretation of some $^1H$ and $^{13}C$ NMR spectra was facilitated by 2D-COSY and 2D-HETCOR experiments. The multiplicities of $^{13}C$ spectra were determined by the attached proton test (APT), which produces positive (+) quaternary C and $CH_2$ signals and negative (–) CH and $CH_3$ signals. Infrared spectra were determined on a Nicolet 20 SXB Fourier transform spectrometer. Mass spectra were obtained with a Hewlett-Packard Model 5970A GC/MS spectrometer. The flash photolysis apparatus, which utilized a Xenon Corp. Model 720 photolysis system, has been described elsewhere.[31] Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

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**Preparation of Ligands and Complexes. Cyclopropylvinylcarbinol (5).** Magnesium (0.99 g, 0.041 mol), a crystal of iodine, and 40 mL of dry diethyl ether were placed under a nitrogen atmosphere in a flame-dried 100-mL round-bottom flask provided with a condenser, addition funnel, and stirring bar. A solution of cyclopropyl bromide (4.2 g, 35 mmol) in dry ether (15 mL) was added at such a rate as to maintain gentle reflux. The mixture was stirred at room temperature for 1 h, and then a solution of acrolein (2.0 g, 35 mmol) in dry ether (10 mL) was added slowly at -5 °C. The resulting solution was warmed to room temperature. After being stirred for 1 h, the mixture was poured onto ice (50 g) and decanted from excess magnesium. The precipitate was dissolved in saturated aqueous ammonium chloride, and the organic layer was separated. The aqueous layer was extracted with ether (2 × 50 mL), and the combined organic extracts were washed with saturated NaCl, dried ($MgSO_4$), and concentrated. The residue was distilled to give 2.2 g (64%) of cyclopropylvinylcarbinol (5) as a colorless oil: bp 70 °C (0.1 Torr); IR ($CCl_4$) 3300 (br), 3049, 1650 $cm^{-1}$.

***trans*-6-Bromo-1,3-hexadiene (6).**[13] By the method of Julia et al.,[11,12] 20 mL of hydrobromic acid (48% aqueous solution) was added dropwise to cyclopropylvinylcarbinol (2.0 g, 0.020 mol) while it was stirred at 0 °C. After it was stirred for an additional 30 min at 0 °C, the cooled mixture was extracted with petroleum ether (3 × 50 mL). The combined organic extracts were washed with 10% aqueous sodium bicarbonate solution (35 mL) and saturated NaCl (30 mL), dried ($MgSO_4$), and evaporated to leave a light brown oil. The residue was purified by vacuum distillation at 50 °C (0.1 Torr) to give 2.0 g (62%) of 6 as a colorless oil: MS (relative intensity) $m/z$ 162 (14, $(P + 2)^+$), 160 (15, $(P)^+$), 81 (100, $(P - Br)^+$), 67 (37, $(P - CH_2Br)^+$), 53 (25), 39 (74).

***trans*-2-Methyl-2-aza-5,7-octadiene (N-diene, 2).**[14] To 20 mL of anhydrous dimethylamine stirred at -10 °C under a nitrogen atmosphere was added a solution of 6 (1.3 g, 8.1 mmol) in 5 mL of dry benzene. The mixture was set aside at room temperature for 4 h. Ten milliliters of concentrated hydrochloric acid and 30 mL of water were added. The aqueous layer was separated, and the benzene layer was extracted twice with 5-mL portions of 10% hydrochloric acid. The combined aqueous solutions were cooled and made alkaline by the slow addition of 30 mL of a 40% sodium hydroxide solution. The aqueous phase was extracted two times with 50-mL portions of ether. After the ether extract was dried with solid potassium hydroxide, the organic mixture was concentrated and distilled under vacuum at 45 °C (0.1 Torr) to yield 0.56 g (55%) of 2 as a colorless oil: MS (relative intensity) $m/z$ 125 (2, $(P)^+$), 58 (100, $((CH_3)_2NCH_2)^+$), 42 (69); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.32 (m, 1 H), 5.11 (m, 1 H), 4.71 (m, 1 H), 4.04 (m, 2 H), 1.32 (m, 4 H), 1.25 (s, 6 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 136.94, 132.40, 131.84, 114.89, 59.07, 45.18, 30.78.

***cis*-($\eta^3$-N-diene)W(CO)$_4$ (1).** A solution of 2 (0.5 g, 4 mmol) and (nbd)W(CO)$_4$ (0.3 g, 0.7 mmol)[16] in degassed dry benzene was refluxed for 4 h under a nitrogen atmosphere. The reaction mixture was filtered with the aid of Celite and then concentrated. The brown residue was recrystallized three times from *n*-heptane, giving 0.30 g (85%) of 1 as yellow needles: mp 143–148 °C dec; IR (*n*-heptane) $\nu$(CO) 2025 (s), 1925 (s), 1913 (vs), 1882 (s) $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.7 (m, 1 H), 5.2 (m, 2 H), 4.85 (m, 2 H), 2.75 (s, 3 H), 2.68 (s, 3 H), 2.45 (m, 4 H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 213.95, 208.09, 205.46, 205.00, 138.55, 112.53, 84.57, 84.31, 60.43, 59.09, 57.30, 29.35. Anal. Calcd for $C_{12}H_{15}O_4NW$: C, 34.22; H, 3.59. Found: C, 34.06; H, 3.33.

**Flash Photolysis of *cis*-($\eta^3$-N-diene)W(CO)$_4$ in Et$_3$SiH Solution and Identification of the Photolyzed Products.** The *cis*-($\eta^3$-N-diene)W(CO)$_4$ complex (2 mg) was flashed one time in triethylsilane solutin (10 mL) at 25.1 °C and monitored at 500 nm. This procedure was performed on 15 separate samples. The resulting photolysis solutions were combined. The $^1H$ NMR spectrum of the mixture indicated the presence of hydrosilylation products. Microdistillation of the mixture at 78–80 °C (0.1 Torr) gave a colorless oil, which was rinsed from the receiver with $CDCl_3$.[32] Evaporation of the solvent gave the hydrosilylated product 1-(triethylsilyl)-6-(dimethylamino)-hex-3-ene (ca. 10 mg, 59% yield), which NMR spectra showed to be a mixture of the *E* and *Z* isomers: MS (relative intensity) $m/z$ 243 (0.4, $(P + 2)^+$), 242 (1.5, $(P + 1)^+$), 241 (6.2, $(P)^+$), 126 (23, $(M - SiEt_3)^+$), 59 (75, $((CH_3)_2NCH_3)^+$), 58 (100, $(CH_3)_2NCH_2)^+$); $^1H$ NMR ($CDCl_3$, for a mixture of isomers) $\delta$ 5.15–5.52 (olefinic protons, 2 H), 2.22 ($-NCH_2-$, m, 2 H), 2.15 ($(CH_3)_2N-$, m, 6 H), 1.94 ($=CH_2C$, m, 2 H), 1.42 ($-CH_2CH_2CH_2-$, m, 6 H), 0.88 ($-SiCH_2CH_3$, m, 9 H), 0.52 ($-CH_2SiEt_3$, m, 2 H), 0.45 ($-SiCH_2-$, m, 6 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 134.64, 128.06, 126.49, 125.93, 59.79, 59.56, 45.42, 45.33, 30.89, 30.60, 27.93, 26.75, 7.32, 7.25, 3.25, 3.19, 2.07.

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(32) This procedure cannot be carried out on a preparative scale because of the limited solubility of 1 in triethylsilane and the danger of introducing additional complexity to the mixture by prolonged photolysis.