1.51–1.41 (m, 1 H), 1.25 (s, 9 H), 1.01 (t, J = 7.48 Hz, 3 H), 0.51 (t, J = 7.6 Hz, 3 H); ^{13}CNMR (C_6D_6, 75.5 MHz) 169.20, 157.48, 149.69, 137.75, 135.01, 132.98, 129.54, 127.30, 81.53, 65.01, 28.06, 21.01, 19.74, 17.22, 13.56, 12.70.

[2-(Benzyloxy)-3,4-diethyl-5-(4-methylphenyl)-*N*-((2,2-dimethylethoxy)carbonyl)]pyrrole (29). A solution of **7j** (432 mg, 0.835 mmol) and 3-hexyne (0.115 mL, 1.00 mmol) in 15 mL of toluene was kept at 80 °C for 1 h. After oxidation (3 h, air) and filtration over SiO_2 the residue was chromatographed with petroleum ether/ether 9:1 to 1:1. The last band afforded **29** as viscous yellow oil (46 mg, 13%). MS (m/z) 419 (–%, M^+), 347 (90.67, $M^+ - H_2C{=}C(CH_3)_2$), 91 (100, $C_7H_7^+$), 57 (21.87, $H_2C{=}C(CH_3)_2$), 28 (44.06); ^{1}H NMR ($CDCl_3$, 300.1 MHz) 7.29–7.08 (m, 9 H), 5.38 (s, 2 H), 2.60 (q, J = 7.41 Hz, 2 H), 2.43 (q, J = 7.55 Hz, 3 H), 2.39 (s, 3 H), 1.13 (t, J = 7.43 Hz, 3 H), 0.97 (s, 9 H), 0.84 (t, J = 7.47 Hz, 3 H); ^{13}C NMR (C_6D_6, 75.5 MHz) 162.45, 151.45, 149.5, 137.55, 136.92, 134.01, 132.07, 128.81, 128.32, 127.54, 126.97, 126.85, 114.19, 86.29, 46.38, 28.82, 23.36, 21.22, 20.81, 14.25, 13.68.

Acknowledgment. Support for this work from the Deutsche Forschungsgemeinschaft, from the Graduiertenkolleg Metallorganische Chemie, and from the Fonds der Chemischen Industrie is gratefully acknowledged. D.B.G. thanks the National Science Foundation for a postdoctoral fellowship.

Registry No. **5**, 32370-47-1; **5b**, 35797-14-9; **5c**, 22852-50-2; **5d**, 137466-91-2; **5e**, 137466-92-3; **5f**, 137466-93-4; **5g**, 137466-94-5; **5h**, 122846-90-6; **5i**, 137467-02-8; **6a**, 122846-97-3; **6b**, 137466-95-6; **7a**, 122846-93-9; **7b**, 122846-92-8; **7c**, 122846-95-1; **7d**, 122846-94-0; **7e**, 122846-96-2; **7f**, 137466-96-7; **7g**, 137466-97-8; **7h**, 137466-98-9; **7i**, 137466-99-0; **7j**, 137467-00-6; **7k**, 137467-01-7; **7l**, 137494-43-0; **9**, 121809-50-5; **10a**, 29160-36-9; **10b**, 88426-08-8; **10c**, 20540-69-6; **10d**, 59335-55-6; **10e**, 122780-69-2; **10f**, 37823-96-4; **10g**, 38797-47-6; 11, 137467-04-0; **12**, 137467-05-1; **16a**, 122846-84-8; **16b**, 137466-83-2; **19a**, 137466-89-8; **19b**, 122846-86-0; **20**, 122846-89-3; **21a**, 137466-84-3; **21b**, 122846-88-2; **22**, 137466-85-4; **23a**, 137466-90-1; **23b**, 122846-87-1; **24**, 137466-87-6; **27b**, 137466-86-5; **28**, 137494-42-9; **29**, 137466-88-7; $(CH_3CO)_2O$, 108-24-7; $(BOC)_2O$, 24424-99-5; $PhNHCH_3$, 100-61-8; CH_3NH_2, 74-89-5; NH_3, 7664-41-7; $(CH_3)_2NCH_2CH_3$, 598-56-1; $PhCH_2NH_2$, 100-46-9; $CH_3CH_2C{\equiv}CCH_2CH_3$, 928-49-4; $CH{\equiv}C(CH_2)_4CH_3$, 628-71-7; 1,2-$(COCl)C_6H_4$, 88-95-9; $(CO)_5W{=}C(Ph)NH(CH_2Ph)$, 137467-06-2; pentacarbonyl[(*N*-phenylmethylamino)(4-methylphenyl)methylene]molybdenum, 137467-03-9; indole-3-ethanamine, 61-54-1; pentacarbonyl[((indole-3-ethyl)amino)(methyl)methylene]chromium, 40249-69-2.

Supplementary Material Available: Tables of atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles (3 pages). Ordering information is given on any current masthead page.

Photochemistry of Acyldisilanes

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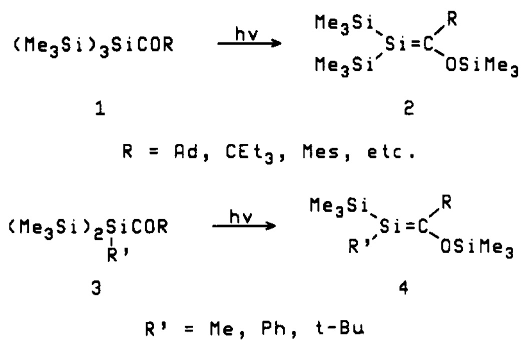
Received July 8, 1991

The new acyldisilanes $Me_3SiSiR'_2COAd$ (R′ = Ph, Mes) were prepared by coupling of the appropriate disilyl lithium or potassium reagent with adamantylcarbonyl chloride. Photolyses of the compounds in deuteriobenzene and in the presence of methanol were studied. In the presence of methanol the phenyl compound gave products from the trapping of the anticipated silene and disiloxycarbene, as well as products of radical recombination. Photolysis in C_6D_6 gave three dimers, two of which were a cis–trans pair of alkenes resulting from the initially formed silene undergoing cycloaddition with its parent unphotolyzed acyldisilane, followed by rearrangement. The third dimer was relatively unstable, being the head-to-head dimer of the silene. At room temperature, the dimesitylacyldisilane gave only a silaindane, even in the presence of methanol, while at –78 °C in addition to the silaindane, products of radical recombination and from trapping of a disiloxycarbene were obtained. Under no circumstances was the expected silene or its methanol-trapping product observed. These results are interpreted.

The photolysis of tris(trimethylsilyl)acylsilanes $(Me_3Si)_3SiCOR$ (**1**) gave rise to the first "stable" isolated silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$[1] (**2**) and to a family of related relatively stable silenes, which differed only in the R group attached to the sp^2-hybridized carbon atom, as shown in Scheme I. It is important to establish how the chemistry of the silicon–carbon double bond is influenced by the substituents on the ends of the double bond, i.e. by the Me_3Si and $OSiMe_3$ groups. Attempts were made to clarify this by replacing one of the Me_3Si groups on silicon by a hydrocarbon group, i.e. Me, Ph, or t-Bu.[2] The silenes $(Me_3Si)R'Si{=}C(OSiMe_3)Ad$ (**4**) prepared (Scheme 1) showed similar chemistry to **2** (e.g. addition of MeOH, [2 + 4] cycloadditions with dienes, etc.), but when R′ = Me or Ph, they tended to dimerize and/or rearrange. For R′ = t-Bu, the silene was relatively stable, surviving in solution for days like its Me_3Si analogue, although it rearranged on further photolysis.[2]

Scheme I



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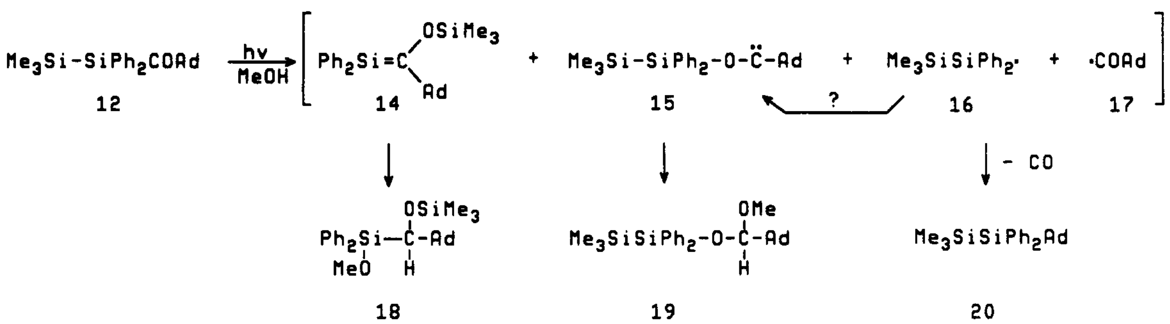
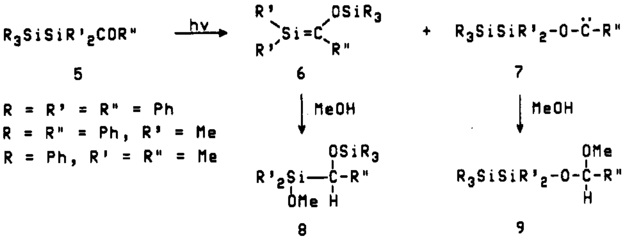
[1] Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

[2] Baines, K. M.; Brook, A. G.; Ford, R. R.; Lickiss, P. D.; Saxena, A. K.; Chatterton, W. J.; Sawyer, J. F.; Behnam, B. A. *Organometallics* **1989**, *6*, 693.

Scheme II



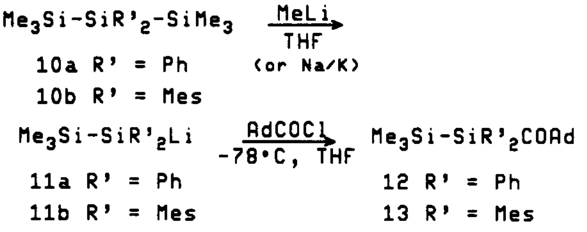
In our studies which led to the stable silenes derived from acylpolysilanes,[3] we had briefly examined the photochemistry in the presence of methanol of a few acyldisilanes, **5**. The structures of the isolated compounds **8** and **9** indicated that both silenes, **6**, and disiloxycarbenes, **7**, were formed competitively as intermediates in the course of the photolysis, as shown in eq 1.[3] Thus it appeared



(1)

possible that the synthesis of relatively stable (i.e. directly observable) silenes such as **6**, having two hydrocarbon groups attached to the sp^2-hybridized silicon atom, might be achieved from the photolysis of acyldisilanes which had moderately bulky groups attached to both the silicon and carbon atoms which were to form the double bond.

Thus the two acyldisilanes $Me_3SiSiPh_2COAd$ (**12**) and $Me_3SiSiMes_2COAd$ (**13**) were prepared and their photochemistry in various solvents was studied. The compounds were prepared, as shown in eq 2, in modest yields by



(2)

coupling of the appropriate disilylmetallic reagent **11**, formed by treatment of the trisilanes $(Me_3Si)_2SiR'_2$ (**10**) with MeLi solution or with sodium/potassium alloy, followed by coupling with AdCOCl. The yields of the coupling products from the use of the disilylpotassium reagents were substantially lower than those employing the lithium reagent.

Photolysis of **12** in deuteriobenzene containing 2 equiv of methanol at room temperature gave rise to three products, **18**–**20**, shown in Scheme II, in the ratio 3.5:1.5:1. These products clearly represent the trapping of an intermediary silene **14** as its methanol adduct **18** and of a disilyloxycarbene **15** as its methanol adduct **19** and the apparent recombination, following loss of carbon monoxide, of radicals **16** and **17** formed by Norrish type 1 cleavage of the acyl–silicon bond of **12**. The formation of both a silene and a disiloxycarbene is similar to the photochemical behavior of the acyldisilanes studied previously.[3] Also, simple acylsilanes are known to form siloxycarbenes when their photolysis is done in methanol,[4] but radicals were formed during photolyses in less polar inert solvents.[5] However, the reactions with **12** are the first occasion where products from a siloxycarbene and radical products have both been observed in the same reaction mixture. This allows the possibility that the intermediary disiloxycarbene may arise as a result of recombination of the radicals **16** and **17**, in which the disilyl radical attacks the oxygen of the acyl radical; hitherto, since radical products had not been observed, it had been presumed that formation of the siloxycarbenes was a concerted process. Both possible mechanisms have been proposed to explain the formation of oxycarbenes.[6]

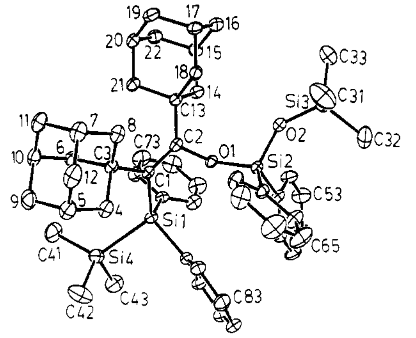


Figure 1. View of the alkene **21** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. Hydrogen atoms have been omitted for clarity. The molecule of C_6D_6 which is associated with each pair of molecules of **21** has also been omitted for clarity.

Photolyses of **12** in C_6D_6 gave a complex mixture of four major products, dimers **21**–**23** (Scheme III) derived from the anticipated silene **14**, and **20**, the product of radical recombination, as proposed above. The proportions of the products were sensitive to the concentration of the solution being photolyzed. There was no evidence for the presence of a stable silene in the crude reaction mixture, on the basis of ^{29}Si and ^{13}C NMR spectra. No products attributable to the disiloxycarbene **15**, observed from the photolysis in methanol, were found. This is as expected, since in the inert medium there is no trap for the carbene, which, from previous studies,[3] would be expected to revert to parent acyldisilane.

The identity of dimer **21** was shown by a crystal structure to be the *cis*-alkene whose ORTEP diagram is shown in Figure 1. On the basis of NMR and other data, dimer **22** is the related *trans* isomer.

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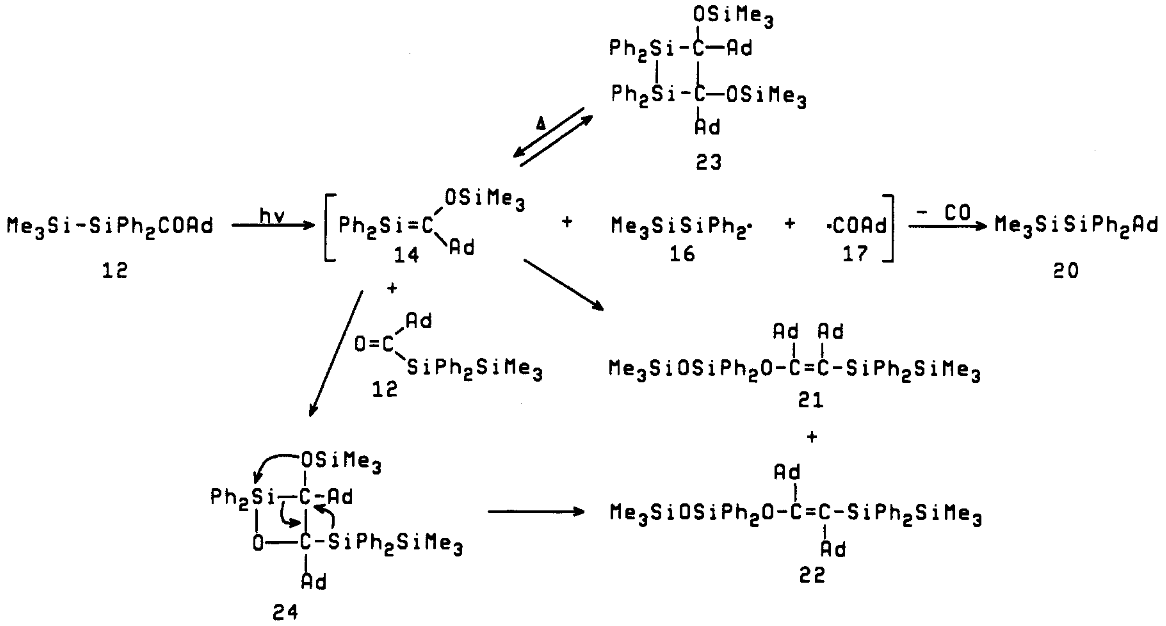
(3) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.

(4) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 454.

(5) Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 352.

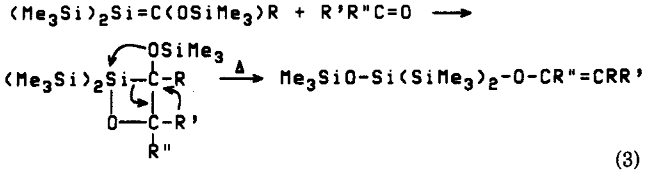
(6) Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *6*, 209.

Scheme III



Dimer **23**, which it has not yet been possible to isolate pure, appears to be the head-to-head dimer of silene **14**. Other silenes of this general family are known to form head-to-head dimers[3] of variable stability. In the present case, when the complex reaction mixture was warmed to 70 °C, the solution became red (due to silene **14**?). On cooling, the red color disappeared. This warming–cooling cycle could be repeated several times without affecting the concentrations of products, consistent with a temperature-sensitive decomposition–recombination process between the dimer **23** and its silene monomer **14**. Similar behavior was observed with the silene $(Me_3Si)_2Si{=}C(OSiMe_3)t\text{-}Bu$ and its dimer.[3,7] When the complex mixture of **21**–**23** and **20** was warmed and then methanol was added, the red color was immediately discharged and subsequent NMR spectra showed the absence of dimer **23** and the presence of the expected methanol adduct **18**, confirming that **23** was indeed the dimer of silene **14**.

The mechanism by which dimers **21** and **22** form is of considerable interest. Their structures are readily explained as the result of cycloaddition of the initially formed silene **14** with unchanged acyldisilane **12**, leading to the siloxetane **24**. Previous studies have shown that silenes readily undergo [2 + 2] cycloadditions with aldehydes and ketones,[8] including acylsilanes,[9] to form siloxetanes having structures analogous to **24**. However, this is the first time that a silene has been observed to react with its parent acylsilane precursor during the course of its photochemical generation. Some siloxetanes have been found to be relatively unstable, decomposing spontaneously even at room temperature, probably by the mechanism shown in eq 3.[8]



$$(Me_3Si)_2Si{=}C(OSiMe_3)R + R'R''C{=}O \longrightarrow (Me_3Si)_2\overset{}{Si}\!-\!C(OSiMe_3)R\!-\!O\!-\!CR'R'' \xrightarrow{\Delta} Me_3SiO\text{-}Si(SiMe_3)_2\text{-}O\text{-}CR''{=}CRR' \quad (3)$$

This involves migration of a trimethylsiloxy group from a ring carbon atom to the ring silicon atom, accompanied by ring opening, and the migration of a group (relative ease Ar ≈ Me_3Si ≫ H or alkyl) from one ring carbon atom to the ring carbon atom which originally bore the Me_3SiO group, to form a siloxyalkene.

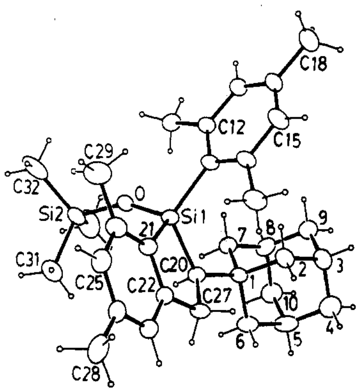


Figure 2. View of the silaindane **26** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. Hydrogen atoms have been assigned as spheres of arbitrary radii.

This same process would convert siloxetane **24** to the observed alkenes **21** and/or **22** (Scheme III), it being anticipated that the disilyl group would undergo 1,2-migration much more easily than an adamantyl group. Thus, formation of the dimeric alkenes **21** and **22** is readily explained as the result of a sequence of steps, each of which has been previously observed and studied with other silenes and carbonyl compounds.

Consistent with the above interpretation, when a more dilute solution of the acyldisilane **12** was photolyzed, NMR spectroscopy showed that very little of the dimers **21** and **22** were formed and that dimer **23** had become the major product. At higher dilution the probability of silene **14** encountering unchanged acylsilane **12** would be greatly reduced while the probability of **14** encountering a second molecule of silene leading to dimer **23** would be relatively enhanced, as observed. In very dilute solutions neither dimer **21** nor **22** were formed during photolysis.

Photolysis of the dimesitylacylsilane **13** was rather different. When photolysis took place at room temperature in C_6D_6, the silaindane **26** was formed in high yield. A crystal structure confirming the identity of this compound

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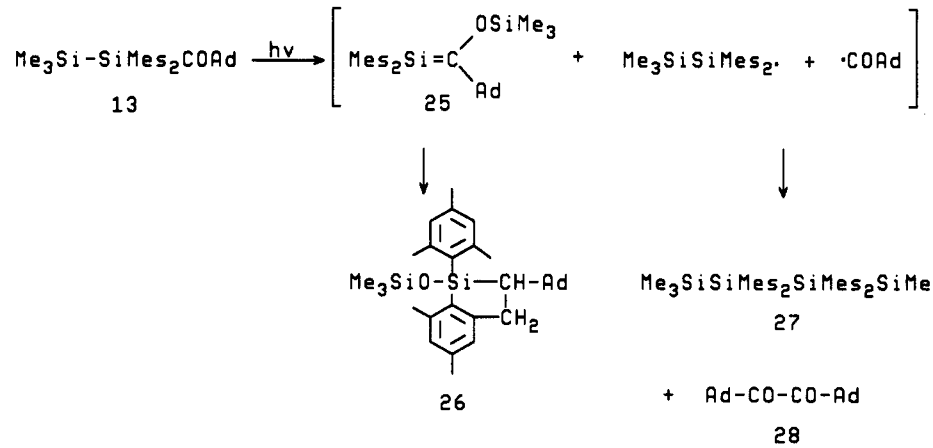
[7] Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S; Picard, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 6750.

[8] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

[9] Chatterton, W. J. Ph.D. Thesis, University of Toronto, 1990.

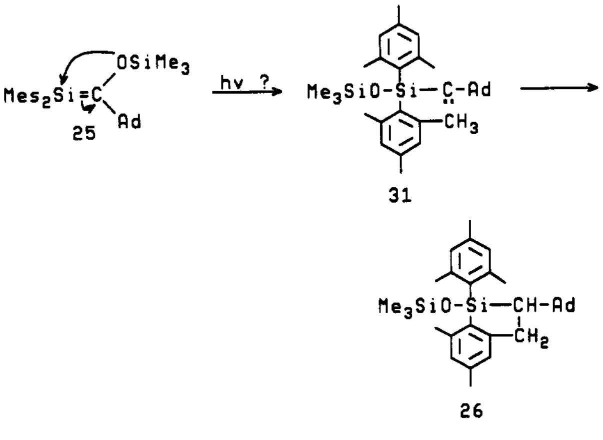
Scheme IV



was obtained: the ORTEP diagram is shown in Figure 2. This product, which was very rapidly formed, is believed to be derived from the silene **25**, as will be explained below. When the photolysis was carried out at −78 °C in C_6D_6, in addition to **26**, the tetrasilane **27** and diadamantoyl **28**, the self-dimerization products of the disilyl and adamantoyl radicals, were also formed, as shown in Scheme IV.

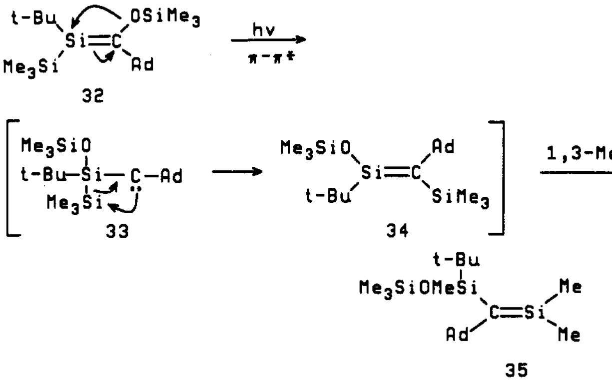
When the acyldisilane **13** was photolyzed at room temperature in the presence of methanol, only the silaindane **26** was isolated, while at −78 °C the silaindane **26**, the tetrasilane **27**, and diadamantoyl **28** were formed. In addition, compound **30** was isolated, which is obviously the methanol-trapped product of the disiloxycarbene intermediate **29**, as shown in Scheme V. Again, the disiloxycarbene could have arisen by recombination of the two radicals produced by Norrish type 1 cleavage of the acyldisilane or by a concerted process.

The formation of the silaindane **26** is believed to be derived from the anticipated silene **25**. It is obvious from the structure of **26** that a migration of a trimethylsiloxy group from carbon to silicon has occurred, probably by a photochemical process, and the existence of the CH–CH_2 proton pattern, derived from one of the *o*-methyl groups of the mesitylene nucleus, suggests that an insertion of a carbene into a C–H bond has occurred. Migration of trimethylsiloxy from sp^2-hybridized carbon to sp^2-hybridized silicon in **25** would yield an intermediary silylcarbene **31**, which after insertion into the benzylic C–H bond would form **26**, as shown in eq 4. Attempts to trap the proposed silylcarbene **31** have so far proven unsuccessful. This suggests, as did the failure of methanol to trap the silene **25**, that intermolecular processes cannot compete with the highly efficient and rapid intramolecular reactions leading to the silaindane **26**.



(4)

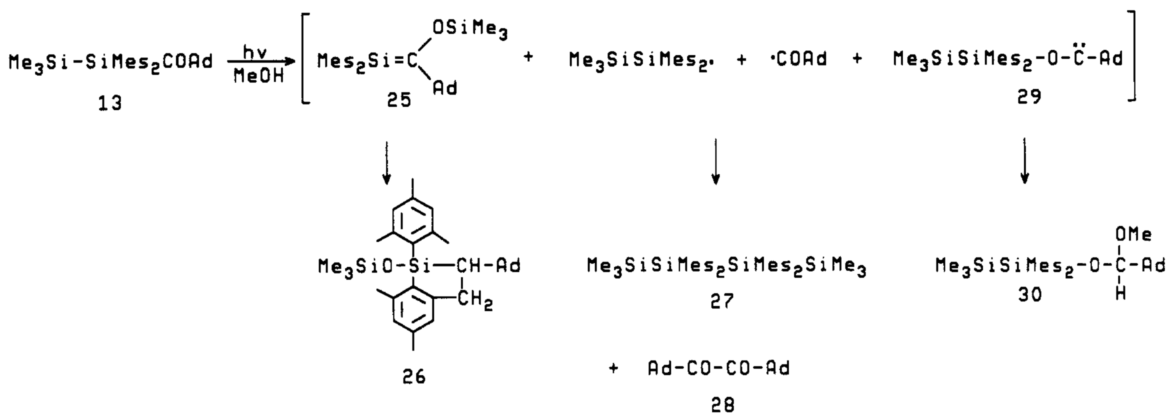
The mechanism proposed in eq 4 has implications for a previously described problem.[2] To explain the observed photochemical isomerization of the silene **32** to the silene **35**, eq 5, it was proposed that the Me_3Si group in **32** originally on the sp^2-hybridized silicon atom migrated to sp^2-hybridized carbon, and the $OSiMe_3$ group of **32** originally on sp^2-hybridized carbon migrated to sp^2-hybridized silicon,[2] forming the intermediate silene **34**. This process could involve simultaneous migrations (thus a dyotropic rearrangement) or result from successive migrations of the groups. For example, if the $OSiMe_3$ group migrated from carbon to silicon first, a silylcarbene intermediate **33** would be formed. Attempts to trap possible intermediates with silanes (Si–H) failed, consistent with, but not proving that the conversion of **32** and **34** was a dyotropic process. However, in light of the results described above for the photochemical rearrangement of the acyldisilane **13** leading to the silaindane **26**, which are consistent with the intermediacy of both silene **25** and the silylcarbene **31**, but where neither could be trapped, the results from the photochemical isomerization of silene **32** can now be recognized as probably proceeding via the silylcarbene **33**. Like **31**, this carbene is likely to be very reactive and shortlived, in this case inserting into the adjacent Me_3Si–Si bond to form silene **34** more rapidly than it can be trapped by an external reagent like a silane. While we have not yet been able to confirm these postulates, the fact that the rearrangements of two different but related systems can best be explained on the basis of $OSiMe_3$ group migrations from carbon to silicon in a silene to yield an intermediary silylcarbene provides some credibility for the proposal.



(5)

Based on the results reported above, together with previously reported data, it is possible to draw some conclusions about the relative stabilities of the $(Me_3Si)_nR_{2-n}Si{=}C(OSiMe_3)Ad$ family of silenes in relation to the number of Me_3Si groups attached to the sp^2-hy-

Scheme V



bridized silicon atom. When $n = 2$, the silene was formed cleanly, was isolable as a solid (a crystal structure was obtained), showed no tendency toward self-dimerization, reacted cleanly and readily with dienes, alkenes, carbonyl compounds etc., and was insensitive to further photolysis by the radiation ($\lambda \geq 360$ nm) employed to prepare it from its parent acylpolysilane.[1] When one of the Me_3Si groups was replaced by a hydrocarbon group, e.g. Me or Ph, the silenes produced formed head-to-head dimers, although these reverted readily to the silenes, which then reacted with added reagents. When R was *t*-Bu, the silene could be observed in solution as a single geometric isomer over a prolonged period of time (days), but unlike the bis(silyl) species, it was quite susceptible to further photochemical rearrangements to isomeric silenes.[2] It has now been shown above that when two aryl groups, Ph or Mes, are attached to the sp^2-hybridized silicon atom of the silenes, the expected silenes are not directly observable. In the case of the diphenyl species, dimerization appeared to be a major reaction pathway, but it was evident that the expected silene had been formed (amongst several other competing processes) since its methanol adduct and its dimer were formed. When R was Mes, no direct evidence at all was obtained for the formation of the expected silene, but the formation at room temperature of silaindane **26** as the only product from photolysis of the parent acylpolysilane (even in the presence of methanol) is best explained as the result of the expected, and evidently very reactive, silene **25** undergoing an intramolecular reaction. These observations indicate that the more Me_3Si groups that are attached to sp^2-hybridized silicon, the more stable is the resulting silene. These conclusions are in accord with calculations of Apeloig on model systems[10] which indicated that attaching a silyl group to the sp^2-hybridized silicon atom of a silene would lead to stabilization of the silene. We expect to prepare other acyldisilanes with bulkier R′ groups which should not allow C–H insertion or dimerization to occur, to see if stable silenes with two R′ groups on the sp^2-hybridized silicon atom can be isolated.

Crystal Structures

The alkene **21** has a highly hindered structure, undoubtedly due largely to the "cis" oriented adamantyl groups on the ends of the carbon–carbon double bond. Neither the length of the C(1)–C(2) double bond (found 1.349 (8) Å) nor the lengths of other bonds are significantly stretched. However, there is significant distortion of the bond angles of the nominally sp^2-hybridized C(1) and C(2) atoms and of the torsion angles involving them. Thus two of the C(1) angles (C(2)–C(1)–C(3) = 126.7 (5)°, C(3)–C(1)–Si(1) = 119.8 (4)°, and C(2)–C(1)–Si(1) = 113.0 (4)°) deviate markedly from the expected 120°, and all of the C(2) angles (C(1)–C(2)–C(13) = 134.5 (5)°, C(13)–C(2)–O(1) = 109.6 (4)°, and C(1)–C(2)–O(1) = 114.4 (4)°) deviated strongly from 120°. Neither C(1) nor C(2) is planar. There is considerable twisting of the C═C bond as would be expected in a highly hindered alkene. Thus the torsion angles C(3)–C(1)–C(2)–C(13) = −38.8 (3)° (0° in an unhindered *cis*-alkene) and C(3)–C(1)–C(2)–O(1) = 157.1 (6)° (normally 180° for a "trans" relationship) reflect significant twisting in relief of steric strain. The structure also contains C_6D_6 solvent molecules which lie on crystallographic 2-fold axes, and hence there is half a solvent molecule per asymmetric unit.

The crystal structure of the silaindane **26** showed that in the five-membered ring containing silicon, the angle at silicon was 92.6 (2)°, much less than the angles at the ring carbon atoms which for sp^3-hybridized carbon atoms were 105.6 (2) and 110.6 (3)° and for sp^2-hybridized carbon atoms were 110.6 (3) and 116.8 (3)°. The sum of the ring angles, 536.1°, suggests that the ring is nearly planar, and indeed atoms C(20), Si(1), C(21), and C(20) lie within 0.04 Å of the best plane, with atom C(27) lying only 0.293 (4) Å above the plane. In cyclopentane in the half-chair conformation, the out-of-plane atom is in excess of 0.5 Å above the plane. The atoms C(21)–C(26) comprising the attached six-membered aromatic ring all lie within 0.02 Å of the best plane, and the angle between the five- and six-membered rings is 6.7°. It appears that steric congestion has caused some widening of the angles C(20)–Si(1)–C(11) (119.49 (15)°), C(21)–Si(1)–C(11) (116.87 (16)°), and especially Si(1)–O–Si(2) (150.34 (17)°).

Experimental Section

Experiments were performed with oven-dried glassware under argon using standard inert-atmosphere and vacuum line techniques. Reaction solvents were dried and distilled before use: diethyl ether and tetrahydrofuran were dried over sodium and benzophenone; pentanes and toluene were dried over lithium aluminum hydride. Photolysis experiments were carried out using two or three 100-W PAR 38 mercury spot lamps irradiating at 360 nm and longer.

All NMR spectra were obtained on either a Varian XL400 spectrometer or a Gemini 200 spectrometer and were run in C_6D_6 unless otherwise specified. Where necessary, APT[11] and DEPT[12] pulse sequences were used in obtaining ^{13}C NMR spectra, and most ^{29}Si NMR spectra were obtained using the DEPT sequence.

IR spectra were obtained using KBr pellets on a Nicolet 5DX FT-IR instrument.

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Low-resolution and high-resolution mass spectra were obtained on a VG70-250S mass spectrometer. The peaks were reported in mass-to-charge units (*m/e*), followed by their intensities, relative to the base peak in parentheses.

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

(Trimethylsilyl)(1-adamantylcarbonyl)diphenylsilane (12). To a solution of 3.80 g (11.6 mmol) 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane [$(Me_3Si)_2SiPh_2$][13] in 40 mL of THF was added 11 mL (13.2 mmol) of MeLi solution in ether. After stirring for 5 h, the golden yellow silyllithium solution was added dropwise to a solution of 2.3 g (11.6 mmol) of AdCOCl in 40 mL of THF at −78 °C. After stirring for 1 h at −78 °C, the mixture was allowed to warm up with stirring continued over another 15 h. The THF was evaporated off and replaced with hexanes. The hexane solution was decanted from the insoluble salts and filtered through silica gel to remove unreacted AdCOCl. The yellow oil obtained from removal of the hexanes gave 2.18 g (45%) of white crystals of **12** after crystallization from methanol, mp 90–91 °C. Anal. Calcd for $C_{26}H_{34}OSi_2$: C, 74.60; H, 8.19. Found: C, 74.46; H, 8.20. ^{1}H NMR: δ 0.27 (9 H, s, Me_3Si), 1.35–1.80 (15 H, m, Ad), 7.1–7.2 (6 H, m, Ph), 7.6–7.7 (4 H, m, Ph). ^{13}C NMR: δ −1.33 (Me_3Si), 27.88 (Ad CH), 36.54, 36.65 (Ad CH_2), 53.22 (Ad quat C), 128.40, 129.59, 136.54 (Ph CH), 134.92 (Ph ipso C), 245.46 (C═O). ^{29}Si NMR: δ −15.80 (Me_3Si), −30.45 ($SiPh_2$). IR: 1614 cm^{-1} (C═O). MS [calcd for M^+ 418.21482, found 418.21413]: *m/e* 418 (7, M^+), 403 (4, $M^+ - Me$), 345 (9, $M^+ - Me_3Si$), 283 (29, $M^+ - Ad$), 255 (100, $M^+ - COAd$), 197 (55, $SiPh_2Me^+$), 181 (22, $SiPh_2^+$), 135 (65, Ad^+), 105 (30, $PhSi^+$), 73 (37, Me_3Si^+).

Photolysis of the Diphenylacyldisilane 12 with Methanol. Photolysis of 0.30 g (0.72 mmol) of **12** in 0.8 mL of C_6D_6 and 58 μL (1.43 mmol) of methanol for 15 h using three 100-W Par 38 mercury lamps gave a mixture of compounds **18–20** in the ratio 3.5:1.5:1 which were separated by radial chromatography and crystallization. 18: mp 96–97 °C from acetone. Anal. Calcd for $C_{27}H_{38}O_2Si_2$: C, 71.99; H, 8.51. Found: C, 71.75; H, 8.36. ^{1}H NMR: δ −0.01 (9 H, s, Me_3Si), 1.6–1.9 (15 H, m, Ad), 3.37 (3 H, s, MeO), 3.79 (1 H, s, CH), 7.1–7.4 (6 H, m Ph), 7.7–7.8 (2 H, m, Ph), 7.95–8.05 (2 H, m, Ph). ^{13}C NMR: δ 0.44 (Me_3Si), 28.76 (Ad CH), 37.18, 40.44 (Ad CH_2), 38.07 (Ad quat C), 51.55 (MeO), 77.32 (CH), 128.00, 129.94, 130.04, 135.92, 136.12 (Ph CH), 135.15, 135.44 (Ph ipso C) (Ph groups are diastereotopic?). ^{29}Si NMR: δ −14.35 (Ph_2Si), 16.78 ($OSiMe_3$). MS [calcd for M^+ 450.24104, found 450.23778] *m/e* 450 (4, M^+), 449 (5, $M^+ - H$), 435 (15, $M^+ - Me$), 377 (30, $M^+ - Me_3Si$), 237 (91), 183 (59), 149 (85), 73 (100, Me_3Si). **19**: viscous oil. ^{1}H NMR: δ 0.27 (9 H, s, Me_3Si), 1.6–1.9 (15 H, m, Ad), 2.96 (3 H, s, MeO), 4.08 (1 H, s, CH), 7.1–7.3 (6 H, m, Ph), 7.7–7.9 (4 H, m, Ph). ^{13}C NMR: δ −1.45 (Me_3Si), 28.39 (Ad CH), 37.34, 37.43 (Ad CH_2), 39.42 (Ad quat C), 57.71 (MeO), 107.74 (CH), 128.81, 129.76, 129.83, 135.37, 135.52 (Ph CH), 137.28, 137.46 (Ph quat C) (Ph's are nonequivalent). ^{29}Si NMR: δ −20.80 (Me_3Si), −4.31 ($SiPh_2$). IR: 2847 cm^{-1} (MeO). MS [calcd for $C_{27}H_{37}O_2Si_2 = M^+ - H$ 449.23321, found 449.22958 (by CI)]: *m/e* 450 (8, M^+), 449 (14, $M^+ - H$), 435 (16, $M^+ - Me$), 419 (100, $M^+ - MeO$), 377 (62, $M^+ - Me_3Si$), 255 (22, $Me_3SiSiPh_2^+$). **20**: mp 97–99 °C from methanol. Anal. Calcd for $C_{25}H_{34}Si_2$: C, 76.92; H, 8.79. Found: C, 76.45; H, 8.79. ^{1}H NMR: δ 0.23 (9 H, s, Me_3Si), 1.6–2.1 (15 H, m, Ad), 7.17–7.24 (6 H, m, Ph), 7.64–7.70 (4 H, m, Ph). ^{13}C NMR: δ −0.26 (Me_3Si), 25.10 (Ad quat C), 28.10 (Ad CH), 37.39, 39.61 (Ad CH_2), 128.01, 128.95, 136.95 (Ph CH), 135.93 (Ph ipso C). ^{29}Si NMR: δ −13.87 −19.15 ($SiPh_2$, Me_3Si). MS [calcd for M^+ 390.21991, found 390.21841]: *m/e* 390 (59, M^+), 375 (19, $M^+ - Me$), 317 (100, $M^+ - Me_3Si$), 255 (90, $M^+ - Ad$), 183 (87, Ph_2SiH^+), 135 (44, Ad^+).

When **12** was photolyzed in the presence of a 16-fold excess of methanol, the proportions of **18–20** were 2.9:2.8:1.

Photolysis of Acyldisilane 12 in Inert Solvent. Photolysis of 0.20 g (0.48 mmol) of **12** in 0.8 mL of C_6D_6 in a sealed NMR tube for 15 h using three Par 38 100-W lamps gave rise to a pale orange solution containing a complex mixture of four compounds, **21–23** and **20**, in the approximate ratio **21**:**22**:**23**:**20** of 2.2:1:0.9:1.8. When warmed to 70 °C, the solution became red but, on cooling, returned to pale orange. This heating–cooling cycle was done several times without affecting the proportions of compounds. From this mixture small amounts of **21**, **22**, and **20** were obtained pure as solids. **21**: mp 229–230 °C from C_6D_6 (colorless transparent crystals lost the C_6D_6 of crystallization at about 120 °C without melting to become an opaque solid which melted sharply). Anal. Calcd for $C_{52}H_{68}O_2Si_4$: C, 74.58; H, 8.19. Found: C, 73.99; H, 8.20. ^{1}H NMR: δ −0.10, 0.10 (each 9 H, s, Me_3Si), 1.6–2.45 (15 H, m, Ad), 6.95–7.45 (Ph). ^{13}C NMR (400 MHz): δ 1.58, 1.88 (Me_3Si), 29.53, 29.93 (Ad CH, two nonequivalent Ad groups), 37.04, 37.15, 39.91, 44.22 (Ad CH_2), 40.08, 45.04 (Ad quat C), 127.21, 127.57, 128.53, 129.98, 135.88, 136.42 (Ph CH), 133.95, 135.01, 139.25 (Ar ipso and C═), 169.85 (–O—C═). ^{29}Si NMR (non-DEPT mode at 60 °C due to low solubility): δ 9.77 ($OSiMe_3$), −13.45 (Me_3Si), −23.44 ($OSiPh_2$), −45.44 ($Si\mathit{Si}Ph_2$). MS (CI, methane) 836 (9, M^+), 835 (11, $M^+ - H$), 821 (4, $M^+ - Me$), 764 (22, $M^+ - Me_3Si + H$), 763 (28, $M^+ - Me_3Si$), 581 (5, $M^+ - Me_3SiSiPh_2^+$), 527 (26), 469 (43), 419 ($M^+/2 + H$), 345 (49), 293 (75), 255 (43, $Me_3SiSiPh_2^+$), 197 (31), 135 (100, Ad and/or $PhMe_2Si^+$). The ORTEP diagram for **21** is given in Figure 1. **22**: mp 261–263 °C, recrystallized from hexanes. Anal. Calcd for $C_{52}H_{68}O_2Si_4$: C, 74.58; H, 8.19. Found: C, 73.42; H, 8.09. ^{1}H NMR: δ 0.05, 0.10 (each 9 H, s, Me_3Si), 1.5–2.4 (15 H, m, Ad), 6.9–8.2 (Ph). ^{13}C NMR (400 MHz): δ 1.48, 1.91 (Me_3Si), 29.07, 29.98 (Ad CH), 36.63, 36.83, 39.42, 42.03 (Ad CH_2), 41.06, 44.66 (Ad quat C), 127.88, 130.47, 135.72, 136.30 (Ph CH), 124.13, 135.14, 140.79 (Ph ipso and C═), 172.90 (–O—C═). ^{29}Si NMR (non-DEPT mode at 60 °C): δ 10.52 ($OSiMe_3$), −10.07 (Me_3Si), −24.63 ($OSiPh_2$), −48.26 ($Si\text{–}\mathit{Si}Ph_2$). MS [calcd for $C_{49}H_{59}O_2Si_3$ ($M^+ - Me_3Si$) 763.3823, found 763.3827]: *m/e* 836 (3, M^+), 764 (28, $M^+ - Me_3Si + H$), 551 (17), 469 (42), 255 (55, $Me_3SiSiPh_2^+$), 193 (86), 135 (100, Ad and $PhMe_2Si^+$). **23**: the assignment of signals for this unstable compound was very difficult because of the presence of **20–22**. ^{1}H NMR: δ −0.13 (9 H, s, Me_3Si), 1.4–2.6 (Ad), 6.95–8.27 (Ph). ^{13}C NMR: 6.42 (Me_3Si), 29.53 (Ad CH), 42.76, 44.08 (Ad CH_2), 44.91 (Ad quat C), 112.23, 127.10, 127.69, 128.62, 128.78, 137.97, 139.50 (Ph CH, nonequivalent Ph groups), 140.15 (Ph ipso). ^{29}Si NMR δ 5.05 ($OSiMe_3$), 0.65 (ring $SiPh_2$). **20**: the material isolated had NMR spectra identical to the compound characterized above.

When 96 mg of **12** in 1 mL of C_6D_6 was photolyzed for 17 h, a pale orange solution was obtained which contained **21–23** and **20** in the ratio 1:1:5.3:3.8. When warmed, the solution turned red and on addition of 10 μL of methanol (1.1 equiv) the red color disappeared immediately. The NMR spectra showed signals for **21**, **22**, **20**, and **18**, the methanol adduct of silene **14**.

(Trimethylsilyl)(1-adamantylcarbonyl)dimesitylsilane (13). To a solution of 3.16 g (7.6 mmol) of 2,2-dimesitylhexamethyltrisilane **10b**[14] in 40 mL of THF was added 7 mL of 1.4 M (9.8 mmol) of methyllithium in diethyl ether, together with 1.5 g of HMPA. Stirring for 16 h gave a reddish brown solution which was added dropwise to a solution of 1.52 g (7.6 mmol) of AdCOCl in 40 mL of THF at − 78 °C. After stirring for 1 h at −78 °C and 5 h at room temperature, workup and recrystallization from acetone gave 1.65 g (44%) of **13** as colorless crystals, mp 182–184 °C. Anal. Calcd for $C_{32}H_{46}OSi_2$: C, 76.44; H, 9.23. Found: C, 76.32; H, 9.21. ^{1}H NMR: δ 0.31 (9 H, s, Me_3Si), 1.4–2.0 (15 H, m, Ad), 2.08 (6 H s, *p*-Me), 2.29 (12 H, s, *o*-Me), 6.72 (4 H, s, Ar CH). ^{13}C NMR: δ 1.51 (Me_3Si), 20.67 (*p*-Me), 26.02 (*o*-Me), 28.20 (Ad CH), 36.63, 37.22 (Ad CH_2), 54.05 (Ad quat C), 129.73, 133.55, 138.62, 143.85 (Ar C), 250.79 (C═O). ^{29}Si NMR: δ −7.89 (Me_3Si), −36.19 ($SiMes_2$). Calcd for M^+: 502.3087. Found: 502.3070.

The potassium analogue of the disilyllithium compound was prepared by treatment of a mixture of 3.25 g (7.89 mmol) of the trisilane **13** in 100 mL of THF with 0.82 g of 3:1 Na/K alloy (stoichiometric amount of K). The mixture was placed in an ultrasonic bath for 3 days at which time only traces of alloy remained in the brown suspension. Mercury was added to amalgamate the residual alloy. The mixture was cooled to −78 °C, and 3.12 g (15.7 mmol) of AdCOCl in 40 mL of THF was added slowly. After stirring for 1 h at −78 °C and overnight at room temperature, workup and recrystallization from hexanes gave 0.51 g (13%) of **13**.

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Photolysis of Acyldisilane 13 in Inert Solvent. A sample of the dimesitylacyldisilane **13** in C_6D_6 was photolyzed for 90 min using three Par 38 100-W mercury lamps. NMR spectroscopy indicated that all the starting material had been converted into a single product, shown to be the silaindane **26**, purified by recrystallization from acetone, mp 164–166 °C. Anal. Calcd for $C_{32}H_{46}OSi_2$: C, 76.44; H, 9.22. Found: C, 75.80; H, 9.15. ^1H NMR: δ 0.08 (9 H, s, Me_3Si), 1.49 (1 H, d × d, H_A of ABC system, J_{AB} = 10.6, J_{AC} = 9.2 Hz), 1.56–1.87 (15 H, m, Ad), 1.93, 2.05, 2.20, 2.24, 2.88 (each 3 H, s, Me), 3.06 (1 H, d × d, H_B, J_{BC} = 16.5 Hz), 3.22 (1 H, d × d, H_C), 6.63, 6.76, 6.88, 6.95 (each 1 H, s, Ar CH). ^{13}C NMR: δ 2.15 (Me_3Si), 21.03, 21.64 (*p*-Me), 21.98, 24.48, 25.72, (*o*-Me), 29.25 (Ad CH), 32.27 (CH_BH_C), 34.36 (Ad quat C), 37.39, 42.83 (Ad CH_2), 46.62 (CH_A), 125.16, 128.12, 129.70, 130.63 (Ar CH), 130.81, 137.42 (Ar ipso), 139.32, 140.08, 141.77, 144.59, 145.68, 151.12 (Ar quat C). ^{29}Si NMR: δ 8.27 ($OSiMe_3$), 1.05 (ring Si). MS [calcd for M^+ 502.30872, found 502.30630]: *m/e* 502 (2, M^+), 487 (12, $M^+ - Me$), 415 (2, $M^+ - Me_3Si - CH_2$), 383 (63, $M^+ - Mes$), 382 (100, $M^+ - Mes - H$), 339 (21, $Me_3SiSiMes_2^+$), 248 (75, 383 – Ad), 247 (82, 382 – Ad), 135 (52, Ad). Photolysis of **13** at −78 °C gave the silaindane **26** and in addition the tetramesityltetrasilane **27** and diadamantoyl **28** in the ratio 1.7:1:1. **27**: mp 193–195 °C. Anal. Calcd for $C_{42}H_{62}Si_4$: C, 74.25; H, 9.21. Found: 73.89; H, 8.91. ^1H NMR: δ 0.25 (18 H, br, Me_3Si), 1.77, 2.03, 2.06, 2.12, 2.23, 2.83 (each 6 H, s, Me), 6.47, 6.60, 6.69, 6.85 (8 H, m Ar CH). ^{13}C NMR: δ 4.08 (w), 5.12 (s) Me_3Si, collapses to singlet at 55 °C and higher), 20.84, 20.90, 26.03, 26.18, 28.00, 30.71 (Me), 128.28, 128.91, 129.36, 129.67, 129.82, 135.48, 137.04, 137.12, 137.65, 142.31, 144.41, 145.62 (Ar C). ^{29}Si NMR: δ −6.19 (Me_3Si), −33.41 ($SiMes_2$). MS [calcd for $C_{39}H_{53}Si_3$ ($M^+ - Me_3Si$) 605.34551, found 605.34123]: *m/e* 679 ($M^+ + 1$), 605 ($M^+ - Me_3Si$), 339 (100, $M^+/2$). **28** was isolated by precipitation from methanol, followed by sublimation at 130 −150 °C to give a semicrystalline oil. The following spectroscopic properties of the material isolated are identical with literature data where available.[15] ^1H NMR: δ 1.51–1.95 (Ad), 28.10 (Ad CH), 36.55, 38.21 (Ad CH_2), 44.57 (Ad quat C), 210.21 (C=O). IR: 1689.9 cm^{-1} (C=O). MS [calcd for $C_{22}H_{31}O_2$ (MH^+) 327.23240, found 327.22937]: *m/e* 327 (20, MH^+), 299 (16, $MH^+ - CO$), 163 (15, $AdCO^+$), 135 (100, Ad^+).

Photolysis of Dimesitylacyldisilane 13 in Methanol. Photolysis of **13** at room temperature in methanol containing a trace of pyridine (to inhibit subsequent reaction) gave rise only to the silaindane **26**, as described above. When the photolysis was carried out at −78 °C in methanol, in addition to **26–28**, the methanol adduct **30** of the siloxycarbene was also isolated, the products being obtained in the approximate ratio 1.2:1.16:1.16:1. **30**: mp 181–182 °C. Anal. Calcd for $C_{33}H_{50}O_2Si_4$: C, 74.09; H, 9.43. Found: C, 73.90; H, 9.22. ^1H NMR: δ 0.36 (9 H, s, Me_3Si), 1.68, 1.73, 1.97 (15 H, s, Ad), 2.10, 2.12 (6 H, 2s, *p*-Me, nonequivalent), 2.46, 2.49 (12 H, 2s, *o*-Me, nonequivalent), 2.77 (3 H, s, MeO), 3.74 (1 H, s, CH), 6.75 (4 H, s, Ar CH). ^{13}C NMR: δ −0.73 (Me_3Si), 20.70, 20.77, 23.54, 24.50 (Me), 28.36 (Ad CH), 37.41 (Ad CH_2, 2 unresolved peaks), 40.18 (Ad quat C), 57.68 (MeO), 108.83 (CH–OMe), 129.24, 129.77 (Ar CH), 138.20, 138.98, 143.46, 144.11 (Ar C), 133.60, 134.03 (Ar ipso). ^{29}Si NMR: δ −15.41 (Me_3Si), −1.69 ($SiMes_2$). MS [calcd for $C_{33}H_{49}O_2Si_2$ ($M^+ - H$) 533.32711, found 533.32802]: *m/e* 533 (7, $M^+ - H$), 503 (41, $M^+ - MeO$), 461 (45, $M^+ - Me_3Si$), 339 (52, $Me_3Si{-}SiMes_2^+$), 297 (100, $M - Mes_2 + H$), 179 (23, $AdCHOMe^+$), 135 (46, Ad^+), 73 (45, Me_3Si). IR: 2848 (OMe), 1069 cm^{-1} (Si–O–C).

X-ray Structure Determinations. Both compounds **21** and **26** were stable to air exposure. Intensity data for both compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The $\omega - 2\theta$ scan technique was applied with variable scan speeds. The intensities of three standard reflections measured every 2 h showed no decay. Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods. C, O, and Si atoms were refined anisotropically by full-matrix least squares. All calculations were performed using NRCVAX,[17] SHELX76,[18] and SHELXS86[19] on a Microvax II and an Apollo computer.

Table I. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for Alkene 21

empirical formula	$C_{52}H_{68}O_2Si_4{\cdot}{}^1/{}_2C_6D_6$
M_r	879.5
cryst size, mm	0.40 × 0.30 × 0.35
cryst class	monoclinic
space group	*C*2/*c*
a, Å	35.169 (12)
b, Å	10.505 (2)
c, Å	27.316 (6)
β, deg	97.74 (2)
V, $Å^3$	10 000 (4)
Z	8
D_{calc}, g cm^{-3}	1.17
μ(Mo Kα), cm^{-1}	1.5
F(000)	3784
ω scan width, deg	0.7 + 0.35 tan θ
range θ collctd, deg	1–22.5 ($\pm h,k,l$)
total no. of rflns	6674
no. of unique rflns	6519
no. of obsd data [$I > 3\sigma(I)$]	4016
R	0.061
R_w	0.069
goodness of fit	1.79
largest Δ/σ	0.003
no. of params refined	552
max density of ΔF map, e/$Å^3$	0.54

Table II. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for Silaindane 26

empirical formula	$C_{32}H_{46}OSi_2$
M_r	502.9
cryst size, mm	0.40 × 0.35 × 0.50
cryst class	triclinic
space group	*P*1
a, Å	9.706 (7)
b, Å	11.491 (5)
c, Å	13.523 (6)
α, deg	88.34 (4)
β, deg	86.18 (5)
γ, deg	81.92 (5)
V, $Å^3$	1489.7 (14)
Z	2
D_{calc}, g cm^{-3}	1.12
μ(Mo Kα), cm^{-1}	1.4
F(000)	548
ω scan width, deg	0.8 + 0.35 tan θ
range θ collctd, deg	1–23 ($\pm h,\pm k,l$)
total no. of rflns	4315
no. of obsd data [$I > 3\sigma(I)$]	2992
weighting *g*	0.001 04
R	0.058
R_w	0.064
goodness of fit	2.02
largest Δ/σ	0.002
no. of params refined	317
max density in ΔF map, e/$Å^3$	0.40

For compound **21** hydrogen atoms were positioned on geometric grounds (C–H 0.95 Å, $U_{iso}(H) = U_{iso}(C) + 0.01$). Crystal data, data collection, and least-squares parameters are listed in Table I. An ORTEP diagram of the structure is given in Figure 1.

For compound **26** an empirical absorption correction was applied using the program DIFFABS;[16] minimum and maximum absorption corrections were 0.653 and 1.444. Hydrogen atoms were

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positioned on geometric grounds (C–H 0.95 Å) and an overall hydrogen atom thermal parameter refined to a value of 0.0687 (3) Å^2. Crystal data, data collection, and least-squares parameters are listed in Table II. An ORTEP[20] diagram of the structure is given in Figure 2.

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Registry No. **10a**, 18549-83-2; **10b**, 79184-72-8; **12**, 136804-43-8; **13**, 136804-44-9; **18**, 136804-45-0; **19**, 136804-46-1; **20**, 136804-47-2; **21**, 136804-48-3; **21**·$^1/_2C_6D_6$, 136804-49-4; **22**, 136804-50-7; **23**, 136804-51-8; **26**, 136804-52-9; **27**, 136804-53-0; **28**, 84966-07-4; **30**, 136804-54-1; AdCOCl, 2094-72-6; MeOH, 67-56-1.

Supplementary Material Available: For **21** and **26**, tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, torsion angles, and least-squares planes (20 pages); listings of observed and calculated structure factors for compounds **21** and **26** (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Fluxional Behavior of [Bis(trialkylphosphine)nickelio]anthracene (Alkyl = Et, Bu)[1]

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The title compounds were prepared from the respective $(R_3P)_2NiCl_2$ complexes and magnesium–anthracene–$(THF)_3$ (or anthracene in the presence of Mg or C_8K). The assignment of the anthracene proton NMR signals using NOE in conjunction with magnetization-transfer techniques is described. The complexes undergo haptotropic rearrangements in which the $(R_3P)_2Ni$ moiety migrates between the two terminal rings of the coordinated anthracene. The rates of these processes are concentration independent and unaffected by the presence of free anthracene and tris(trialkylphosphine)nickel. Kinetic studies in the temperature range −60 to +70 °C using line shape analysis and spin saturation transfer techniques were carried out. It was found that $\Delta H^{\ddagger} = 13.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.3$ eu for the haptotropic rearrangement in **2**, and similar values were found for **1**. Possible mechanisms are discussed. According to ^{1}H, ^{13}C, and ^{31}P NMR data, the coordination number between the anthracene and the $(R_3P)_2Ni$ moiety is 4. However, an equilibrium between two η^2 structures with $\Delta G^{\ddagger} \leq 4$ kcal mol^{-1} cannot be ruled out.

Introduction

The fluxional behavior of numerous transition-metal arene complexes has been investigated.[3] However, not many such species containing anthracene are known, and very few have been studied with respect to their dynamic properties.[4] It is of general interest to investigate the dynamic, structural, and chemical behavior of these complexes because of the haptotropic rearrangements they may undergo, processes that are isolobal to some sigmatropic rearrangements in organic chemistry. The haptotropic rearrangement of a metal fragment on polyaromatic systems could also be viewed as a soluble model for a metallic moiety migrating on a surface. Thus, these studies have potential interest for the understanding of surface chemistry.

Ni(0)–anthracene complexes exhibit in addition two main unique features. The first arises from the possibility of nickel to form stable 16e and 18e complexes. The stable electronic configuration of such a complex is probably ligand dependent. For example, $(R_3P)_2Ni(olefin)$ is more stable than $(R_3P)_2Ni(olefin)_2$ [although η^4-butadiene–Ni$(PR_3)_2$ has been prepared[5]] but $Ni(CO)_3$ is far less stable than $Ni(CO)_4$. [Bis(trialkylphosphine)nickelio]anthracene can probably adopt both coordination numbers, depending

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(4) To the best of our knowledge, the only transition-metal anthracene complex studied for its fluxional behavior is $(dmpe)_2(Cl)Ta$–anthracene, revealing rotations around the metal arene bond. Bianconi, P. A.; Williams, I. D.; Lippard, S. J. Submitted for publication. We are grateful to professor Lippard for sending us the data prior to publication.

(5) Albright, T. A.; Krüger, C. Personal communication.

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