β-Silylcarbenes from Isolable Diazosilanes

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Manganese dioxide oxidation of the hydrazone derivative of tert-butyldimethylsilyl acetophenone gave 2-tert-butyldimethylsilyl-1-phenyldiazoethane (17) an isolable diazocompound. Thermal and Rh(II)-catalyzed decomposition of diazosilane 17 in cyclohexane led to 1-tert-butyldimethylsilyl-1phenylethylene (19) as the major product. The formation of alkene 19 presumably involves (tertbutyldimethylsilyl)methylphenylcarbene (21), which undergoes preferential 1,2-silyl migration as opposed to 1,2-hydrogen migration. Thermal decomposition of **17** in cyclohexane under oxygen gave substantial amounts of tert-butyldimethylsilyl acetophenone, presumably by reaction of the intermediate carbene with oxygen. Thermal decomposition of 17 in methanol led to alkene 19 and 2-tert-butyldimethylsilyl-1-methoxy-1-phenylethane (22) as major products, along with a significant amount of trans-1-tert-butyldimethylsilyl-2-phenylethylene (20). Kinetic studies indicate that these products are not derived from acid-catalyzed decomposition of the diazocompound 17. Formation of the methyl ether product 22 suggests the involvement of a β -silyl carbocation intermediate, and solvent isotope effect studies indicate that this cation is at least partially derived from protonation of diazocompound 17 by neutral methanol. Photochemical decomposition of 17 in methanol produced the alkene 19 (97%) along with a small amount (2.4%) of the methyl ether 22. Capture of a photochemically generated carbene **21** by methanol is the proposed origin of this minor product. Geometry optimization of trimethylsilylmethylphenylcarbene (8) and carbene 21 at the HF/6-31G* computational level led to a conformation consistent with a hyperconjugative interaction between the vacant p-orbital of these carbones and the adjacent C-Si bond. Carbones 8 and 21 are not energy minima at the B3LYP/6-31G* level, where they rearrange to alkenes without barrier via silyl migration. These theoretical findings contrast with the proposed trapping of carbene 21 by methanol and oxygen.

The effect of silicon on reactive intermediates has received much attention. Stabilization of carbocations by adjacent silicon has been thoroughly investigated.¹ The effects of adjacent silicon on carbanions² and radicals³ have also been described. We⁴ and others⁵ have been interested in the chemistry of carbenes containing trimethylsilyl groups in the vicinity of the carbenic center. Toward this end, carbenes 1-8 gave been generated and the rearrangement processes that these carbenes undergo have been examined. Two general trends have developed from these studies. The trimethylsilyl group is quite prone to migrate to carbenic centers, as illustrated by the formation of **9** from **8**.^{4a} Additionally, the trimethyl-

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During the course of these studies the primary method that we have used to generate carbenes involved pyrolysis of tosylhydrazone salts **10**.⁶ This reaction generates diazosilanes **11** in situ, which lose molecular nitrogen under the pyrolysis conditions. In the case of carbenes **7**^{4e} and **8**,^{4a} tosylhydrazone derivatives of β -trimethylsilyl ketones were not readily synthesized. Therefore, an

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indirect method was used to generate the tosylhydrazone salt precursors to carbenes **7** and **8**. In the present study, we wanted to develop a synthetic route that would allow the isolation of β -diazosilanes **11** (Scheme 1). The preparation of β -diazosilanes has not been previously described in the literature. It was also of interest to see if carbenes **12** generated from the β -diazosilanes **11** could be trapped. This would allow us to determine if the carbene **12** was a discrete intermediate or whether loss of molecular nitrogen and silyl migration was a concerted process. Reported here are the results of these studies.

Results and Discussion

Synthesis. Our initial attempts to prepare an isolable β -diazosilane began with the readily available trimethylsilyl ketone **13**.⁷ However, all attempts to convert this ketone to the tosylhydrazone derivative led to desilylation and formation of acetophenone tosylhydrazone (Scheme 2). Reaction of **13** with hydrazine also led to desilylation and the formation of acetophenone hydrazone.

The synthesis of an isolable β -diazosilane was finally achieved starting with the known silyl ketone **15**.⁸ Conversion to the hydrazone **16** was achieved without desilylation (Scheme 3). Manganese dioxide⁹ oxidation of this hydrazone gave the diazosilane **17** in reasonable yield along with variable amounts of an overoxidized product **18**. The alkyne **18** is derived from further reaction of the diazosilane **17** with excess MnO₂, and the yield of **18** therefore depends on the amount of MnO_2 used in the oxidation. The mechanistic origin of this alkyne is uncertain. Although relatively unstable, the purple diazosilane **17** could be isolated and most of the impurities could be removed by rapidly filtering a dilute hexane solution through basic alumina containing added Na_2CO_3 . Diazosilane **17** showed a characteristic strong absorption at 2030 cm⁻¹ in the infrared.

Thermal and Rh(II)-Catalyzed Reactions in Cyclohexane. Thermal decomposition of diazosilane 17 in cyclohexane at 78 °C in the absence of oxygen gave the alkene **19** as the major product, along with a trace (1%) of the alkene 20 (Scheme 4). Rhodium(II) acetate catalyzed decomposition in cyclohexane at room temperature led to the same product mixture. These products are suggested to be derived from the carbene 21 (or the rhodium-complexed carbenoid analogue **21-Rh**), which preferentially migrates the silvl group to the carbene center. This preferential migration of the silyl group, as opposed to the typically facile migration of an adjacent hydrogen, is suggested to be a result of a favorable interaction of the carbene vacant orbital with the adjacent Si-C bond. This interaction is analogous to that seen in β -silyl carbocations.¹

Thermal Reaction in Methanol. It has been suggested¹⁰ that certain diazocompounds give reactions that appear to be carbene processes. However, they actually involve concerted loss of nitrogen and simultaneous rearrangement, i.e., carbenes are not discrete intermediates in these processes. The thermal decomposition of diazosilane 17 in methanol was therefore examined in an attempt to trap a thermally generated free carbene 21 since methanol is a very efficient trap for both electrophilic and nucleophilic carbenes.¹¹ Heating a solution of 17 in methanol at 60 °C led to the alkenes 19 and 20 along with the methyl ether 22 (Scheme 5). To rule out a trace acid-catalyzed decomposition of 17 via a diazonium ion, 2,6-lutidine or triethylamine was added to the methanol solution. First-order rate constants for the thermal decomposition of 17 in methanol are given in Table 1, and they are independent of the amount and nature of the base added to the methanol, even though these solutions differ in acidity by many orders of magnitude. The decomposition of 17 in methanol is therefore *not* catalyzed by protic acid (CH₃OH₂⁺). Table 1 also gives products under various conditions, and they are also independent of added base.

Diazosilane **17** was also thermally decomposed in CH₃OD. Figure 1 shows the olefinic region of the ¹H NMR spectrum of **20** formed by reaction of **17** in methanol as well as the product formed in CH₃OD. Only **20**-*d* is formed in CH₃OD (as well as **22**-*d*). This verifies that **20** is *not* a product of hydrogen migration in carbene **21** but arises from a reaction with CH₃OD. It is also interesting to note the decreased amounts of **20**-*d* and **22**-*d* formed in CH₃OD (42% total yield) relative to CH₃OH (57% total yield).

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Table 1. Rate Constants and Product Ratios for
Reaction of 17 in Methanol at 60.0 °C under Various
Conditions

conditions	<i>k</i> (s ⁻¹)	19	22	20
CH ₃ OH/no base	$(2.5\pm0.1) imes10^{-4}{}^a$	42.9	49.5	7.6
$CH_3OH/2, 6$ -lutidine ^b	$(2.6\pm0.1) imes10^{-4}$ c	42.8	49.6	7.6
CH ₃ OH/Et ₃ N ^b	$(2.6 \pm 0.1) imes 10^{-4}$ d	42.6	49.9	7.5
$CH_3OD/2, 6$ -lutidine ^b	$(2.2\pm0.1) imes10^{-4}$ e	57.6	36.0 ^f	6.4 ^g
CH ₃ OH/ <i>hv</i> at 23 °C		96.9	2.4	0.7

^{*a*} $k = 2.7 \times 10^{-5} \text{ s}^{-1}$ at 40.0 °C. ^{*b*} 0.015 M. ^{*c*} $k = 2.8 \times 10^{-5} \text{ s}^{-1}$ at 40.0 °C. ^{*d*} $k = 2.8 \times 10^{-5} \text{ s}^{-1}$ at 40.0 °C. ^{*e*} $k = 2.0 \times 10^{-5} \text{ s}^{-1}$ at 40.0 °C. ^{*f*} Product is **22**-*d*. ^{*g*} Product is **20**-*d*.

As before, the alkene 19 is proposed to be derived from silyl migration in the thermally generated carbene 21 (Scheme 6). Significantly more of the alkene 20 (7%) is formed in methanol than in the thermal reaction of 17 in cyclohexane (1%). There are a number of reasonable mechanisms for the formation of the alkene 20 and the methyl ether **22**. It is suggested that the β -silyl carbocation 24 is the immediate precursor of the methyl ether 22 as well as the alkene 20. While catalysis by protic acid has been ruled out as a mechanism for formation of 24, proton transfer from *neutral* methanol $(k_{\text{MeOH}})^{11-13}$ acting as a general acid could generate the cation 24 via the diazonium ion 23. According to this scheme, the observed rate constants in Table 1 for disappearance of 17 $(k_{obs(MeOH)})$ would be the sum of $k_{carbene}$ and k_{MeOH} . There is also another interesting mechanistic possibility. If the thermally generated carbene 21 has nucleophilic properties, then protonation of **21** by methanol (in competition with silvl migration) would generate the same ion pair **24**. Ion pair collapse would generate the methyl ether **22**, whereas β -proton elimination would give the alkene 20 (or 20-d). In this case the observed rate constants represent k_{carbene} since methanol is not involved in the rate-determining step.



In an attempt to distinguish between these two mechanisms for formation of 20 and 22, solvent isotope effects were measured. The first-order rate constant (Table 1) for decomposition of 17 in CH₃OD ($k_{obs(MeOD)}$) is smaller than in CH_3OH ($k_{obs(MeOH)}$). However, our NMR method for determination of rate constants has an error of approximately $\pm 3.5\%$. Therefore the ratio of our observed rate constant in CH₃OH to that in CH₃OD (1.3 \pm 0.2) has a significant error. From this value and the ratio of the products given in Table 1, it is possible to extract values of $k_{\text{MeOH}}/k_{\text{MeOD}}$, but this value will also have a large error. Regardless of the error, the solvent isotope effect is greater than 1.0. Complete decomposition of 17 in methanol via the k_{carbene} process should give no solvent isotope effect. This indicates that at least some of products 20 and 22 arise from protonation of diazosilane 17 by methanol.

There is an alternative method, based on products formed, for determining $k_{\text{MeOH}}/k_{\text{MeOD}}$ if the products are derived from competing k_{carbene} and k_{MeoH} processes. If one assumes that alkene **19** is derived from the k_{carbene} process and **20** and **22** are derived from the k_{MeOH} process, then the ratio of the products formed in CH₃OD to the products

⁽¹²⁾ k_{MeOH} is equivalent to k_0 in a general acid-catalyzed scheme. $k_{\text{H}^-}[\text{H}^+] = 0$ under the neutral or basic conditions in Table 1.

⁽¹³⁾ Such a protonation has been proposed for reaction of $RCHN_2$ in methanol; see: Kirmse, W.; Rinkler, H. A. *Ann. Chem.* **1967**, *707*, 57.



Figure 1. Partial ¹H NMR spectra for reaction of 17 with CH₃OD and CH₃OH.

formed in CH₃OH gives the solvent isotope effect.¹⁴ From the data in Table 1, the value of $k_{\rm MeOH}/k_{\rm MeOD}$ is 1.8 ± 0.2 by this method. Previous studies¹⁵ have shown solvent isotope effects in the range of $k_{\rm EtOH}/k_{\rm EtOD} = 3.5$ for rate-limiting protonation of diazocompounds, and the value of 1.8 is therefore somewhat smaller than expected.

This method for calculating the solvent isotope effect from product ratios is not based on absolute rate measurements, and the calculated value of 1.8 could also be the solvent isotope effect for protonation of carbene **21** with methanol. We therefore cannot completely exclude protonation of carbene **21** as a source of some of the products **20** and **22**. Neither can we rule out nucleophilic reaction of methanol with an electrophilic carbene **21** to give the ylid **25**, which could also serve as a source of the methyl ether **22**.

Photochemical Reaction in Methanol. The photochemical reaction of diazosilane **17** in methanol at 23 °C follows a somewhat different course. The silyl migration product **19** dominates (97%), and only a small amount (2.4%) of the methanol-trapped product **22** is observed. This result suggests that the free ground state of carbene **21** may be largely bypassed in the photochemical decomposition of **17**. Photochemical decomposition of certain carbene precursors has been proposed to involve excited precursor states that bypass carbenes as discrete intermediates.^{10c,d} As such, the photochemical decomposition of **17** in methanol may largely involve an excited state of **17**, which loses nitrogen in a concerted process along with silyl migration. Nonetheless one sees 2.4% of the methyl ether **22**. This small amount of **22** cannot arise from a thermal reaction of **17** in methanol. Our rate data on the thermal reaction ($k = 3.4 \times 10^{-6} \text{ s}^{-1}$ at 23 °C)¹⁶ indicate that a maximum of 0.12% of **17** could have reacted thermally at 23 °C during the 6 min required for mixing of **17** with methanol and completion of the photochemical reaction. Hence the 2.4% of product **22** represents a photogenerated intermediate that is trapped by methanol. This intermediate (presumably a carbene) must have a finite lifetime long enough to permit trapping by methanol.

Thermal Reaction in Cyclohexane under O₂. When the thermal decomposition of diazosilane **17** in cyclohexane is carried out under an oxygen atmosphere (Scheme 7), large amounts of the ketone **15** (63%) are formed, along with alkenes **19** (31%) and **20** (6%). There are two reasonable mechanisms for the formation of **15**. The first involves trapping of the carbene **21** with molecular oxygen to give the triplet biradical **26**. Intersystem crossing would generate a carbonyl oxide **27**, and ring closure would give the dioxirane **28**. Subsequent oxygen atom transfer from **27** or **28** to the diazosilane **17** would produce a second equivalent of ketone **15** via **29**. This mechanism requires that carbene **21** live long enough to undergo bimolecular trapping with oxygen.

⁽¹⁴⁾ The solvent isotope effect is $k_{\text{MeOH}}/k_{\text{MeOD}} = [19/(20 + 22)]_{\text{MeOH}} = [.95. (20 + 22)/19]_{\text{MeOH}} = 1.95. (4.15)$

⁽¹⁵⁾ Roberts, J. D.; Regan, C. M. J. Am. Chem. Soc. 1952, 74, 3695.

⁽¹⁶⁾ This extrapolated rate constant at 23 $^\circ C$ is determined from data in Table 1.







However, an alternative mechanism for formation of **15** involves the direct reaction of dioxygen with the diazosilane **17** to give the triplet biradical **29**. Loss of nitrogen from **29** provides an alternative entry to the biradical **26**. This latter mechanism would require that diazosilane **17** decompose to the carbene **21** and react with dioxygen at comparable rates. It would be quite fortuitous if this were

the case in reactions with both methanol and with oxygen.

Computational Studies. Computational studies on carbene intermediates have been numerous in the recent literature, and density functional methods have become the way of choice for calculating carbene structures and energies.^{4d,e,17-22} Molecular orbital calculations have now been carried out to provide additional insights into the structures of carbenes 8 and 21. Calculations were carried out at both the HF/6-31G* level and the B3LYP/ 6-31G* level. The geometry optimized HF/6-31G* structure of carbenes 8 and 21 both show conformations consistent with an interaction of the carbene center with the adjacent C-Si bond (Figure 2). Frequency calculations showed no imaginary frequencies, indicating that these structures are indeed energy minima at the HF/ 6-31G* level. The transition states, 8-TS and 21-TS, for trimethylsilyl and tert-butyldimethylsilyl migrations to the carbene centers have also been located at the HF/ 6-31G* level, and these transition states lie 5.4 and 6.1 kcal/mol above the respective carbenes. These calculated barriers for silyl migration are quite small for HF/6-31G* calculated barriers, which usually overestimates the actual barrier for migrations to carbenic centers.²³

Inspection of bond lengths in **8** and **21** shows an increase in the Si-CH₂ bond lengths (1.939 and 1.944 Å) relative to the average length of the Si-CH₃ bonds (1.890 Å). This is understood in terms of hyperconjugative electron donation from the C-Si bonds into the vacant p-orbitals of the carbenic centers. Further evidence for

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this hyperconjugative interaction comes from a comparison of the $C-CH_2$ bond lengths in **8** and **21** (1.455 and 1.456 Å) with that of the β -H analogue Ph–C–CH₃ (1.492 Å). The decreased $C-CH_2$ lengths in **8** and **21** argue in favor of this hyperconjugative interaction. The optimized structures of 8 and 21 also have Si-CH₂-C-C dihedral angles of 106° and 107°, respectively. A dihedral angle of 90° would provide for the optimal hyperconjugative interaction in these carbenes.

We have not been able to locate energy minima corresponding to carbenes 8 and 21 at the B3LYP/6-31G* computational level. Beginning with the HF/6-31G* geometry, attempted B3LYP/6-31G* geometry optimizations led to the rearranged olefins 9 and 19. B3LYP/ 6-31G* single point calculations (using HF/6-31G* optimized geometries) actually place the transition states 8-TS and 21-TS lower in energy than the corresponding carbenes 8 and 21. Hence density functional theory suggests that there is no barrier to rearrangement of carbenes 8 and 21, i.e., these carbenes may not be energy minima at the B3LYP/6-31G* level. These computational results contrast with the HF/6-31G* calculations. The mechanistic possibilities involving trapping of carbene **21** with methanol and dioxygen need to be further examined in view of these computational results. However, the trapping of carbene **21** under photochemical conditions suggests that a further evaluation of the B3LYP/6-31G* computational results is necessary. There is a conflict between theory and interpretation of experimental results.

A final point to be considered is the ease of silvl migration to carbenic centers. A reviewer has suggested that, as a result of the ability of silicon to become hypervalent, the filled orbital of the singlet carbene may be involved in the migration process. Stated another way, the transition state for migration of the silicon is potentially stabilized by the ability of silicon to interact with the nonbonding orbital of the carbene as well as the vacant carbene orbital. The Si-CH₂-C-C dihedral angles in carbenes 8 and 21 (106° and 107°) suggests a tilt of the silicon atom toward the filled carbene orbital and away from the ideal hyperconjugative angle of 90°.

Conclusion

Diazosilane 17, prepared by MnO₂ oxidation of hydrazone 16, undergoes thermal and rhodium-catalyzed decomposition in cyclohexane to give alkene **19**, a product of silyl migration to the carbene center. Thermal reaction in methanol led to products derived from silvl migration in the carbene intermediate as well as capture of a β -silyl carbocation. This β -silvl carbocation is potentially derived from protonation of a nucleophilic carbene intermediate by methanol. An alternative mechanism for formation of the β -silvl carbocation involves protonation of diazosilane 17 by neutral methanol followed by loss of molecular nitrogen from the diazonium ion. Under photochemical conditions, a methanol-trapped product is formed in small amounts under conditions where protonation of diazosilane 17 by neutral methanol is too slow to give this product. Computational studies on carbenes 8 and 21 at the HF/6-31G* level show a substantial interaction of the vacant carbene orbital with the adjacent C-Si bond and a barrier to silvl migration. At the B3LYP/6-31G* level, carbenes 8 and 21 are not energy minima but rearrange without barrier via a silyl migration process.

A conflict therefore exists between B3LYP/6-31G* theory and our suggestion that carbene 21 must live long enough to permit bimolecular reaction.

Experimental Section

Preparation of Hydrazone 16. A solution of 283 mg of hydrazine monohydrate (5.66 mmol) and 444 mg of α -silyl ketone 15⁸ (1.88 mmol) in 12 mL of absolute ethanol was heated at reflux for 56 h. The mixture was then taken up into ether, and the ether was washed with water and saturated NaCl solution and then dried over a mixture of Na₂SO₄ and MgSO₄. After filtration, the ether solvent was removed using a rotary evaporator to give 462 mg of crude hydrazone 16 (99% yield). Data for 16: ¹H NMR (CDCl₃) δ 7.60 (d, J = 8.1 Hz, 2 H), 7.38-7.28 (m, 3 H), 5.15 (bs, 2 H), 2.21 (s, 2 H), 0.94 (s, 9 H), -0.085 (s, 6 H); ¹³C NMR (CDCl₃) δ 150.93 (s), 139.86 (s), 128.22 (d, J = 156 Hz), 128.10 (d, J = 154 Hz), 126.06 (d, J =154 Hz), 26.30 (q, J = 125 Hz), 17.09 (s), 13.51 (t, J = 121 Hz), -4.95 (q, J = 120 Hz); HRMS (EI) calcd for $C_{14}H_{24}N_2Si$ 248.1709, found 248.1705.

Oxidation of Hydrazone 16 to Diazosilane 17. A mixture of 394 mg of hydrazone 16 and 1.0 g of anhydrous MgSO4 in 25 mL of ether at room temperature was stirred as 1.026 g of activated MnO₂⁹ was added in portions. The mixture was stirred at room temperature for 80 min and then filtered through a small amount of MgSO₄. The ether solvent was removed using a rotary evaporator to give 342 mg of a purple oil that contained diazosilane 17, ketone 15, and alkyne 18 in a 4.2:1.1:1.0 molar ratio as determined by NMR.²⁴ A sample of diazosilane 17 was purified by dissolving a small amount of the crude product obtained above in 1 mL of hexane and rapidly filtering through a short column of basic alumina/ sodium carbonate (2:1 mixture). The hexane were removed using a rotary evaporator to give the unstable diazosilane 17, which was stored in the dark at -20 °C and used as soon as possible after preparation. Data for 17: ¹H NMR (CDCl₃) δ 7.32 (t, J = 7.5 Hz, 2 H), 7.01 (t, J = 7.5 Hz, 1 H), 6.93 (d, J= 8.4 Hz, 2 H), 1.66 (s, 2 H), 0.95 (s, 9 H), 0.029 (s, 6 H); ^{13}C NMR (CDCl₃) δ 132.9 (s), 128.8 (d, J = 158 Hz), 123.2 (d, J =161 Hz), 121.7 (d, J = 156 Hz), 26.4 (q, J = 125 Hz), 16.7 (s), 6.1 (t, J = 121 Hz), -5.4 (q, J = 119 Hz). Data for **18**: ¹H NMR (CDCl₃) δ 7.47 (d, J = 7.5 Hz, 2 H), 7.32–7.28 (m, 3 H), 1.00, (s, 9 H), 0.19 (s, 6 H); ¹³C NMR (CDCl₃) δ 132.0 (d, J =161 Hz), 128.5 (d, J = 161 Hz), 128.2 (d, J = 159 Hz), 123.3 (s), 105.8 (s), 92.5 (s), 26.2 (q, J = 125 Hz), 16.8 (s), -4.5 (q, J= 121 Hz).

Thermal Decomposition of Diazosilane 17 in Cyclohexane. A solution containing 341 mg of the diazosilane 17 in 30 mL of cyclohexane under nitrogen was heated at reflux for 17 h during which time the purple color of **17** disappeared. The cyclohexane was then removed by distillation (with the last traces of solvent being removed at 15 mm pressure) to give 299 mg of crude alkene 19.25 A pure sample of 19 was isolated by preparative gas chromatography. Data for 19: ¹H NMR (CDCl₃) δ 7.28 (t, J = 7.5 Hz, 2 H), 7.21 (t, J = 7.2 Hz, 1 H), 7.15 (d, J = 8.1 Hz, 2 H), 5.83 (d, J = 3.1 Hz, 1 H), 5.63 (d, J = 3.1 Hz, 1 H), 0.80 (s, 9 H), 0.18 (s, 6 H); ¹³C NMR $(CDCl_3) \delta 151.9 \text{ (s)}, 146.3 \text{ (s)}, 129.8 \text{ (d of d, } J = 154, 158 \text{ Hz}),$ 128.0 (d, J = 160 Hz), 127.2 (d, J = 160 Hz), 126.0 (d, J = 161Hz), 26.9 (q, J = 125 Hz), 17.3 (s), -4.9 (q, J = 120 Hz).

In a separate run, a 7 mg sample of diazosilane 17 was dissolved in 0.6 mL of cyclohexane. The solution was placed in a tube under nitrogen and cooled to -78 °C, and the tube was then sealed under vacuum (0.1 mm). The tube was heated at 78 °C for 15 h. Analysis of the contents of the tube by gas chromatography and 600 MHz ¹H NMR showed alkenes 19 and 20²⁶ in a 99:1 molar ratio.

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Rhodium Acetate Catalyzed Decomposition of Diazosilane 17 in Cyclohexane. A solution of 130 mg of diazosilane **17** in 15 mL of cyclohexane under nitrogen was stirred as 3 mg of $Rh_2(OAc)_4$ was added. The mixture was stirred for 5 h at room temperature, and the purple color of **17** was no longer present. The cyclohexane was removed using a rotary evaporator to give 119 mg of crude **19**. A pure sample of **19** was isolated by preparative gas chromatography. In a separate run, gas chromatographic and ¹H NMR analysis of a $Rh_2(OAc)_4$ -catalyzed reaction showed alkenes **19** and **20** in a 99:1 molar ratio.

Thermal Reaction of Diazosilane 17 in Cyclohexane under O₂. A solution of 6 mg of diazosilane 17 in 0.8 mL of cyclohexane was sealed in a 5 mL glass ampule containing a stir bar under an oxygen atmosphere. The ampule was placed in a refluxing ethanol bath (78 °C) and stirred vigorously for 75 min. During this time the color of the diazosilane disappeared. The cyclohexane was carefully removed using a rotary evaporator, and the residue was analyzed by 600 MHz NMR, which showed **15**, **19**, and **20** in a 63:31:6 molar ratio.

Thermal Decomposition of Diazosilane 17 in Methanol. A solution containing 54 mg of diazosilane 17 in 4 mL of methanol was heated to reflux for 6.5 h during which time the purple color of the diazosilane disappeared. The methanol was then removed using a rotary evaporator to give 35 mg of a crude residue containing 19,²⁵ 20,²⁶ and 22.²⁷ Samples of each product were isolated by preparative gas chromatography. Data for **20**: ¹H NMR (CDCl₃) δ 7.45 (d, J = 7.2 Hz, 2 H), 7.33 (t, J = 7.2 Hz, 2 H), 7.26–7.24 (m, 1 H), 6.89 (d, J = 19.3Hz, 1 H), 6.48 (d, J = 19.3 Hz, 1 H), 0.92 (s, 9 H), 0.12 (s, 6 H). Data for 22: ¹H NMR (CDCl₃) δ 7.34 (t, J = 7.2 Hz, 2 H), 7.31– 7.25 (m, 3 H), 4.19 (d of d, J = 7.0, 8.1 Hz, 1 H), 3.13 (s, 3 H), 1.26 (d of d, J = 8.1, 14.4 Hz, 1 H), 1.05 (d of d, J = 7.0, 14.4 Hz, 1 H), 0.84 (s, 9H), -0.009 (s, 3 H), -0.31 (s, 3 H); ¹³C NMR $(CDCl_3) \delta 144.2$ (s), 128.4 (d, J = 159 Hz), 127.5 (d, J = 160Hz), 126.7 (d, J = 157 Hz), 82.1 (d, J = 149 Hz), 56.1 (q, J =140 Hz), 26.5 (q, J = 125 Hz), 23.2 (t, J = 119 Hz), 16.6 (s), -5.5 (q, J = 119 Hz), -6.3 (q, J = 120 Hz).

The molar ratios of products given in Table 1 were determined by 600 MHz ¹H NMR analysis of separate reactions. In a typical product analysis study, 6 mg of diazosilane **17** was dissolved in 0.8 mL of methanol and the sample was sealed in a tube under nitrogen. The tube was heated at 60.0 °C for 10 h, and the solvent was carefully removed using a rotary evaporator. The residue was dissolved in CDCl₃ and analyzed by ¹H NMR. Product molar ratios were determined by integration of signals for **19**, **20**, and **22** at δ 5.83, 6.48, and 4.19, respectively. Estimated error is ±0.5%.

Photochemical Decomposition of Diazosilane 17 in Methanol. Methanol (0.8 mL) was added to 6 mg of diazosilane **17**, and the solution was rapidly placed in a NMR tube under nitrogen. The tube was maintained at room temperature (23 °C) by air cooling and then immediately irradiated with a Hanovia 450 W lamp for 4 min. The purple color of the diazosilane **17** had completely disappeared after the irradiation. The total time required for mixing of **17** with methanol and completion of the photolysis was 6 min. The methanol was then carefully removed using a rotary evaporator, and the residue was dissolved in CDCl₃ and analyzed by 600 MHz NMR. Product ratios are given in Table 1.

Thermal Decomposition of Diazosilane 17 in Methanol. Kinetic Studies. A solution containing approximately 5 mg of diazosilane 17 in 0.8 mL of the appropriate solvent (methanol, 0.015 M 2,6-lutidine in methanol, 0.015 M 2,6lutidine in CH₃OD, or 0.015M Et₃N in methanol) was sealed in a NMR tube under nitrogen and the tube was placed in a constant-temperature bath at 40.0 or 60.0 °C. The amount of 17 in the tube was periodically determined by quenching the tube in a 15 °C bath and then analyzing by 600 MHz NMR spectroscopy (unlocked mode). The disappearance of the signal at δ -0.04 was monitored as a function of time and the small amount of alkyne **18** present (δ 0.12) in the sample served as an internal standard. Rate constants were calculated using standard least squares procedures and are given in Table 1. Correlation coefficients were all greater than 0.999. Rate constants in Table 1 represent an average of multiple runs.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 98 series of programs.²⁸ Carbene **8** showed no imaginary frequencies, while **8-TS** showed one imaginary frequency.

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Supporting Information Available: Structures, energies, and Cartesian coordinates of carbenes **8**, **21**, and transition states **8-TS** and **21-TS**. This material is available free of charge via the Internet at http://pubs.acs.org.

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