The structure of 17 is the first to be determined in which a [1]ferrocenophane acts as a ligand although a number of derivatives of 1a are known, e.g. Fe(CO)$_4$L,[2] Cr(CO)$_5$L,[2] and L$_2$PdCl$_2$.[38]

(38) Butler, I. R.; Cullen, W. R., unpublished results.

Communications

Relative Rate Constants for the Reactions of Methylphenylsilylene[1]

J. A. Hawari, M. Lesage, and D. Griller*

Division of Chemistry, National Research Council of Canada Ottawa, Ontario, Canada K1A 0R6

W. P. Weber

Department of Chemistry, University of Southern California Los Angeles, California 90007

Received August 12, 1986

Summary: Photolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7-methyl-7-phenyl-7-silanorbornadiene (I) in benzene-cyclohexane solutions gave methylphenylsilylene (II) that was efficiently scavenged by ethanol, triethylsilane, and 2,3-dimethyl-1,3-butadiene (III) with the following relative rate constants $k_{\text{EtOH}}/k_{\text{Et}_3\text{SiH}} = 4.8$ and $k_{\text{III}}/k_{\text{Et}_3\text{SiH}} = 3.0$ at 298 K. Methylphenylsilylene did not appear to react rapidly with oxygen. The results conflict with those of a recent flash photolysis study.

The chemistry of silylenes has been the subject of considerable interest in recent years.[2–11] These transient species have normally been generated from cyclic[2–9,11] and open-chain[9,10] polysilane precursors. However, it is known that polysilanes are not clean sources of silylenes, since radical formation and rearrangement often occur together with silylene extrusion.[5,9] These underlying difficulties have prompted us to search out clean photochemical precursors of silylenes[11] and to use them in the measurement of the relative rate constants for silylene reactions. In this work, we have focused attention upon methylphenylsilylene, which has been the subject of a recent flash photolysis investigation.[12]

Photolysis of the silanorbornadiene, I, at 254 and 350 nm in solution proved to be an excellent source of methylphenylsilylene, II (vide infra, eq 1). The fact that I
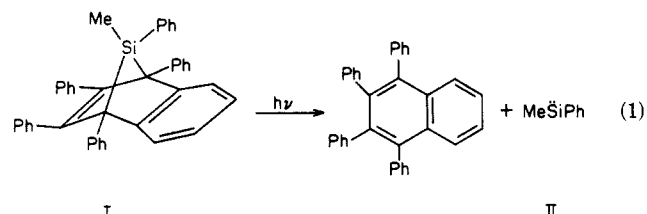
can be photolyzed over a wide range of wavelengths, in order to generate methylphenylsilylene, gives it a unique advantage as a precursor, since wavelengths can be chosen to avoid the photolysis of coreagents.

Photolysis of I in benzene-cyclohexane mixtures containing ethanol, triethylsilane, or 2,3-dimethyl-1,3-butadiene, III, gave the products shown in Scheme I. These were identified by their GC/mass spectra and were quantified by GC using authentic samples as calibrants wherever possible. The overall yields of products con-

(1) Issued as NRCC Publication No. 27348.

(2) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972,** *42,* 325.

(3) Sakurai, H.; Murakami, M. *J. Am. Chem. Soc.* **1972,** *94,* 5080. Ando, W.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1979,** 655. Tzeng, D.; Weber, W. *J. Am. Chem. Soc.* **1980,** *102,* 1451. Gu, T.-Y.Y.; Weber, W. P. *Ibid* **1980,** *102,* 1641. Tortorelli, V. J.; Jones, M., Jr. *J. Chem. Soc., Chem. Commun.* **1980,** 785; *J. Am. Chem. Soc.* **1980,** *102,* 1425. Chichi, A.; Weber, W. P. *J. Organomet. Chem.* **1981,** *210,* 163; *Inorg. Chem.* **1981,** *20,* 2822.

(4) Gu, T.-Y.Y.; Weber, W. P. *J. Organomet. Chem.* **1980,** *184,* 7. Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980,** *102,* 6095. Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981,** *20,* 1302. Steele, K. P.; Tzeng, D.; Weber, W. P. *J. Organomet. Chem.* **1982,** *231,* 291.

(5) Nazran, A. S.; Hawari, J. A.; Griller, D.; Alnaimi, I. S.; Weber, W. P. *J. Am. Chem. Soc.* **1984,** *106,* 7267. The assignment of the transient absorption spectrum due to dimethylsilylene that was described in this work may be in error and is currently being reinvestigated.

(6) Vančik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985,** *107,* 4097.

(7) Carlson, C. W.; West, R. *Organometallics* **1983,** *2,* 1792.

(8) Arrington, C. A.; Klingensmith, K. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984,** *106,* 525. Maier, G.; Mihm, G.; Reisenauer, H. P.; Littmann, D. *Chem. Ber.* **1984,** *117,* 2369.

(9) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981,** *19,* 51.

(10) Trefona III, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985,** *107,* 2737.

(11) Hawari, J. A.; Griller, D. *Organometallics* **1984,** *3,* 1123.

(12) Gaspar, P. P.; Boo, B. H.; Chari, S.; Ghosh, A. K.; Holten, D.; Kirmaier, C.; Konieczny, S. *Chem. Phys. Lett.* **1984,** *105,* 153.

Table I. Relative Rate Constants for the Reactions of Methylphenylsilylene with a Variety of Substrates[a]

substrates [A]:[B], M	[I], M	photolysis wavelength, nm	conversn,[b] %	yield, %	k_A/k_B (this work)	k_A/k_B[c] (ref 12)
EtOH (0.427):Et₃SiH (0.314)	1×10^{-4}	254	48[d]	96	4.8	1.9×10^3
III (0.10):Et₃SiH (0.10)	1×10^{-2}	350	65[d]	100	3.0	4.4
O₂ (1.2 × 10⁻³)[e]:EtOH (5 × 10⁻³)	5×10^{-3}	254	6 (32)[f]	33 (50)[f]	<2.2[g]	2.7×10^3
			35 (59)	36 (50)		
			59 (59)	38 (53)		
O₂ (1.2 × 10⁻³)[e]:EtOH (0.2)	1×10^{-3}	350	12 (26)[f]	60 (57)[f]	0[h]	2.7×10^3
			36 (32)	65 (60)		
			37 (37)	64 (59)		
O₂ (1.2 × 10⁻³)[e]:Et₃SiH (0.2)	5×10^{-3}	350	14 (15)[f]	62 (80)[f]	<59[h]	1.2×10^4
			23 (25)	62 (84)		
			36 (44)	62 (88)		

[a] In benzene–cyclohexane (1:1 v/v) as solvent; 298 K. [b] Based on the yield of 1,2,3,4-tetraphenylnapthalene. [c] Including some revisions to the data originally published.[12] (Gaspar, P. ., private communication). [d] Maximum values; ratios of rate constants independent of conversion. [e] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. [f] Results for matched samples purged with argon rather than oxygen reported in parentheses. [g] At 6% conversion. [h] Average value.

Scheme I
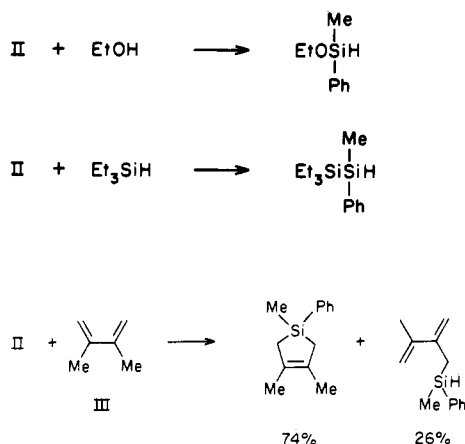
taining the methylphenylsilylene moiety depended on the concentrations of the substrates but were essentially quantitative at ca. 0.5 M substrate concentration (Table I). In those cases where the yields were less than 100%, high molecular weight products were detected but could not be identified because they were present in small amounts. However, no products were detected in any experiment that could have been associated with multiple insertion reactions of II nor was any evidence found for chemistry involving its dimer, 1,2-dimethyl-1,2-diphenyldisilene.[13]

Competition experiments were carried out by taking pairs of the above substrates and by analyzing for the respective products by GC. Details of the reaction conditions are given in Table I. Ratios of product yields were independent of the conversion of I up to the maximum values reported in Table I and led to relative rate constants for the various reactions. However, error limits on both the yields and rate constant ratios are probably ca. 10–20%. These rather high values reflect the difficulty in carrying out accurate GC analysis on materials that, because of large differences in their molecular weights, have widely differing retention times.

The possibility that oxygen could act as a scavenger of the methylphenylsilylene was investigated by carrying out photolyses using matched pairs of sample tubes containing benzene–cyclohexane solutions of I and triethylsilane or ethanol and by continuously purging one tube with argon and the other with oxygen. No products due to the re-

action between methylphenylsilylene and oxygen were detected. However, small effects due to oxygen were discovered. It was found that oxygen slowed the rate of photolysis of I presumably by acting as a quencher of its triplet state. This effect disappeared at ca. 50% conversion (Table I) at which point the overall rate of photolysis had slowed considerably presumably because the 1,2,3,4-tetraphenylnaphthalene formed in the reaction was absorbing most of the photolyzing light.

Product yields in the samples that had been purged with oxygen tended to be slightly lower than those obtained in the argon-purged solutions. There are two possible reasons for this effect. First, oxygen could have acted as a genuine scavenger of the silylene to give products that were not readily detected by GC/mass spectrometry. Second, the reaction products could have been partially destroyed by free radical oxidation initiated by the UV irradiation. To allow for the first possibility, we have assumed that the differences in yields between the oxygenated and oxygen-free samples reflected a silylene–oxygen reaction, even though products for such a reaction were not detected. In each case we have calculated an upper limit for the relative rate constants (Table I).

The relative rate constants obtained in these product studies are at variance with data obtained by using a laser flash photolysis technique[12] (Table I). In the flash photolysis study, a transient absorption spectrum at 440 nm was obtained by photolysis of 2-phenylheptamethyltrisilane and was assigned to methylphenylsilylene (eq 2). Both ethanol and oxygen proved to be very efficient scavengers of the transient while triethylsilane and 2,3-dimethylbuta-1,3-diene were orders of magnitude less effective.

$$Me_3SiSiMe(Ph)SiMe_3 \rightarrow Me_6Si_2 + Me\ddot{S}iPh \quad (2)$$
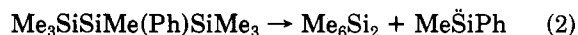
In sharp contrast to the laser flash photolysis results, the product studies described in this work show that ethanol is only ca. 5 times more reactive toward methylphenylsilylene than is triethylsilane, a result which has been confirmed independently by Gaspar and his colleagues.[14] Moreover, there was no evidence in the product studies which suggested that oxygen was a more effective scavenger than triethylsilane. This finding is supported by a recent gas-phase study which showed that oxygen was ca. 50 times less reactive than triethylsilane toward silylene (H₂Si:).[15] While we admit the experimental difficulties

(13) Sakurai, H.; Nakadaira, Y.; Kobayashi, T. *J. Am. Chem. Soc.* **1979**, *101*, 486.

(14) Gaspar, P. P.; Holten, D.; Konieczny, S., submitted for publication in *Acc. Chem. Res.*

(15) Eley, C. D.; Rowe, M. C. A.; Walsh, R. *Chem. Phys. Lett.* **1986**, *126*, 153.

of using oxygen as a scavenger and the possible errors that may be involved, it is more difficult to imagine that the ethanol:triethylsilane experiments are flawed, particularly when they have been confirmed elsewhere.[14]

There are two simple explanations for the discrepancies between the product and flash photolysis studies. First, the transient detected in the flash photolysis work may not have been methylphenylsilylene. In fact, product studies of the photolysis of 2-phenylheptamethyltrisilane[16] show that formation of a silene, IV (reaction 3), is about as efficient as silylene formation (eq 2). It has also been established that silenes of similar structure have absorption spectra in the critical 440-nm region.[17]

$$Me_3SiSiMe(Ph)SiMe_3 \xrightarrow{h\nu} \text{(structure)} \quad (3)$$

IV
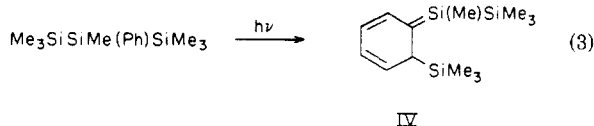
A second explanation can be invoked to rationalize all of the data. This explanation requires that methylphenylsilylene was indeed detected in the flash photolysis experiments but that its rapid reactions with oxygen and ethanol were reversible, so that the rate constants detected in the flash photolysis experiments need not necessarily have matched those of the product studies.

Which of these possibilities is correct remains unanswered. However, a resolution of these problems is only likely to come from more detailed studies of the photochemistry of silylene precursors.

Acknowledgment. We thank Professor P. P. Gaspar for many helpful discussions and for generously sharing unpublished flash photolysis data.

Registry No. I, 69545-85-3; II, 54731-53-2; III, 513-81-5; EtOH, 64-17-5; Et₃SiH, 617-86-7.

(16) Ishikawa, M.; Nakagawa, K.-I.; Enokida, R.; Kumada, M. *J. Organomet. Chem.* 1980, *201*, 151.

(17) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* 1985, *113*, 89.

Carbon–Hydrogen Bond Activation by Rhodium and Iridium Amides: Strategy vs. Serendipity

Michael D. Fryzuk,*† Patricia A. MacNeil, and Neil T. McManus

*Department of Chemistry, University of British Columbia Vancouver, British Columbia, Canada V6T 1Y6*

Received November 18, 1986

Summary: Iridium amide complexes selectively activate the aromatic C–H bonds of toluene while the analogous rhodium derivatives activate only the benzyl C–H bonds; a radical mechanism appears to be operative in the latter case.

Strategy. Prodded by the success of certain iridium complexes in carbon–hydrogen bond activation,[1] we examined the iridium(III) dihydride IrH₂[N-(SiMe₂CH₂PPh₂)₂] (1)[2] as a potential source of a reactive,

coordinatively unsaturated fragment. Our rationale was straightforward: if the formation of the 16-electron "CpIrL" (L = PMe₃ or CO; Cp = η⁵-C₅H₅ or η⁵-C₅Me₅) fragments can generate such intruiging results in C–H bond activation, then loss of H₂ from 1, either photochemically or thermally (by addition of t-BuCH=CH₂), would generate the 14-electron species "Ir[N-(SiMe₂CH₂PPh₂)₂]", capable of both C–H activation and further elaboration.[3] However, H₂ elimination from 1 proved futile by any technique (photolysis or dehydrogenation by t-BuCH=CH₂) that we tried. We also attempted the preparation of a presumed product of C–H activation, namely, the methyl hydride complex Ir(CH₃)-H[N(SiMe₂CH₂PPh₂)₂], in an effort to use this derivative in thermal C–H bond exchange;[4] addition of a variety of hydride reagents to the readily available methyl iodide derivative Ir(CH₃)I[N(SiMe₂CH₂PPh₂)₂][5] led to complicated mixtures of products, none of which corresponded to the desired methyl hydride species. Although we still had the option of replacing the phenyl sustituents on phosphorus with the more electron-rich and bulkier isopropyl groups and reexamining the strategy outlined above, we decided to abandon this project. However, in unrelated studies, we happened onto two systems that apparently activate C–H bonds under quite mild but very different conditions.

Serendipity. The oxidative addition of both iodo- and bromomethane to the iridium(I) cyclooctene complex Ir-(η²-C₈H₁₄)[N(SiMe₂CH₂PPh₂)₂] (2) proceeds smoothly in toluene to generate the corresponding methyl halide complexes Ir(CH₃)X[N(SiMe₂CH₂PPh₂)₂] (X = I, 3a; X = Br, 3b).[5] With chloromethane no reaction is observed at room temperature. If, however, a mixture of 2 and CH₃Cl (approximately 100 equiv) in toluene is heated to 80 °C for 12 h, 2 is completely converted to a 4:1 mixture of *m*- and *p*-tolyl chloride complexes Ir(C₆H₄CH₃)Cl[N-(SiMe₂CH₂PPh₂)₂] (4c);[6] the desired methyl chloride species is formed in only trace quantities (<5%) (eq 1).

$$\text{(reaction scheme)} \quad (1)$$
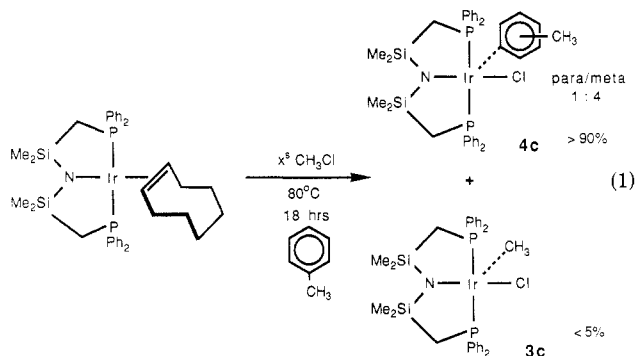
If the temperature is lowered to 60 °C and the reaction time extended to approximately 3 days, then the methyl chloride complex 3c is formed in a 3:2 ratio (by ¹H NMR)

† Fellow of the Alfred P. Sloan Foundation (1984–1987).

(1) (a) Janowicz, A.; Bergman, R. G. *J. Am. Chem. Soc.* 1982, *104*, 352. (b) Bergman, R. G.; Janowicz, A. *J. Am. Chem. Soc.* 1983, *105*, 3929. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* 1982, *104*, 3723. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, *105*, 7190. (e) Crabtree, R. H. *Chem. Rev.* 1985, *85*, 245 and references therein.

(2) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* 1983, *2*, 682.

(3) The anticipated products of C–H activation would be the 16-electron species Ir(R)H[N(SiMe₂CH₂PPh₂)₂] capable of undergoing insertion by CO, olefins, or acetylenes. A related 14e fragment can be formed by dehydrohalogenation of Rh(H)Cl[C₆H₃-o,o'-(CH₂P-t-Bu₂)₂]; see: Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* 1983, *2*, 1442.

(4) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1984, *106*, 1121.

(5) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* 1986, *5*, 2469.

(6) 4c: ¹H NMR (C₆D₆, ppm): meta isomer, Si(CH₃)₂, 0.53, -0.12 (s); PCH₂Si, 1.63 (dt, J_gem = 14.0, J_app = 6.1 Hz), 1.53 (dt, J_app = 5.4 Hz); C₆H₄CH₃, 1.81 (s); C₆H₄CH₃, 6.76 (d, J = 8.0 Hz, ortho), 6.62 (s, ortho), 6.36 (d, para), 6.31 (t, meta); P(C₆H₅)₂, 7.05, 6.94 (m, para/meta), 7.63, 7.98 (m, ortho); para isomer; Si(CH₃)₂, 0.54, -0.13 (s); PCH₂Si, same as the meta isomer; C₆H₄CH₃, 2.01 (s); C₆H₄CH₃, 6.82 (d, J = 8.0 Hz, ortho), 6.21 (d, meta); P(C₆H₅)₂, same as the meta isomer. C, H, and N analyses.