Figure 2. 50-MHz (AC-200) ^{13}C shift-correlated 2D NMR contour plot of $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-C}\equiv CCH(CH_3)_2](\mu\text{-PPh}_2)$ (1). A $(90°\text{-}t_1\text{-}90°$ free induction decay)$_n$ pulse sequence was used employing a 16-step phase cycle. 16 FID's of 1 K data points were accumulated with a recycle delay of 2.5 s. A total of 256 t_1 values were used with a spectral width of 500 Hz (0.9 Hz/Pt) for a total acquisition time of 4.0 h. The complex was enriched to approximately 30% ^{13}CO in order to exploit the $^2J_{CC}$ coupling.

$^2J_{PMC}$ coupling constants are associated with mutually trans ligands and that the larger of the cis $^2J_{PMC}$ couplings arises from phosphorus and carbon nuclei which lie at approximately 90° to one another.[15]

We have examined the magnitudes and the signs of the $^2J_{PMC}$ coupling constants for three phosphido-bridged ruthenium systems and compared them with the available crystallographic data.[12,16] Our observations have led us to suggest that a viable stereochemical dependence does exist for $^2J_{PMC}$ in these systems (Table I). The coupling constants appear to depend, in part, on the geminal bond angle with a sign inversion occurring near angles of ~110°. In addition, the coupling constants appear to minimize at 90° and maximize at 180°.

Although several factors may influence the size and sign of $^2J_{PMC}$ such as the metal, its oxidation state, and the nature of the ligands, it is important to realize when comparing complexes of a similar nature that when a near zero geminal coupling constant is obtained that this may be the result of a bond angle of 110° not 90°.

The results presented herein demonstrate that the COSY method can lead to a clear determination of the relative signs of coupling constants in heteronuclear systems and that important stereochemical information can be readily obtained. We are presently investigating the application of this technique[17] to related systems in an effort to better understand the fundamental factors which affect geminal coupling constants in metal complexes.

(15) Substitution of two CO ligands of 1 by $Ph_2PCH_2PPh_2$ (dppm) affords a single isomer, $(CO)_2Ru[\mu\text{-}\eta^2\text{-C}\equiv CCH(CH_3)_2](\mu\text{-PPh}_2)(\mu\text{-dppm})Ru(CO)_2$ (4) which has been fully characterized by X-ray crystallography. The two CO groups trans to the phosphido bridge in 1 are replaced by phosphorus atoms of the μ-dppm ligand. The ^{13}CO NMR spectrum of 4 [^{13}C{^{1}H} δ 204.4 (m, CO), 201.0 (br s, CO)] at 300 K exhibits only two resonances with small (<6 Hz) $^2J_{PMC}$ couplings, the two resonances with large $^2J_{PMC}$ values in 1 having disappeared. The CO substitution product of 3 with PPh_3, $(PPh_3)(CO)_2Ru(\mu\text{-O}=CCHC(Ph)\text{-}NEt_2)(\mu\text{-PPh}_2)Ru(CO)_3$ (5), has also been fully characterized by X-ray diffraction. In 5 the PPh_3 ligand has displaced the CO group trans to the Ru–Ru bond and cis to the phosphido bridge in 3. The ^{13}C CO NMR spectrum of 5 [^{13}C{^{1}H} δ 252.0 (d, CO, $^2J_{PMC}$ = 10.0 Hz), 206.7 (dd, CO, $^2J_{PMC}$ = 2.5, 75.0 Hz), 206.6 (dd, CO, $^2J_{PMC}$ = 10.0, 8.0 Hz), 204.7 (d, CO, $^2J_{PMC}$ = 53.0 Hz), 201.2 (d, CO, $^2J_{PMC}$ = 11.0 Hz), 200.0 (dd, CO, $^2J_{PMC}$ = 5.0, 12.0 Hz)] at 300 K has five terminal ^{13}C CO resonances, two of which are doublets of doublets due to coupling to two phosphorus nuclei. The large coupling of 68.5 Hz in 3 is retained in 5 (75 Hz) while the resonance with $^2J_{PMC}$ = 0 Hz in 3 has disappeared. These data provide conclusive proof of the stereochemical dispositions of the CO ligands inferred in this paper.

(16) $Ru_2(CO)_6[\mu\text{-CHC(Ph)NEt}_2](\mu\text{-PPh}_2)$ (2) and $Ru_2(CO)_6[\mu\text{-O}=CCHC(Ph)NEt_2](\mu\text{-PPh}_2)$ (3) were prepared as previously described. See: (a) Cherkas, A. A.; Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Yule, J. E.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 1115. (b) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189.

(17) The carbon–carbon coupling constants in the above compounds are on the order of 5 Hz for cis stereochemistries and 20 Hz for trans geometries. Since the "long-range" COSY sequence with fixed delays before and after the mixing pulse compensates for low Hz/point values (when compared to the size of the coupling constant), this sequence may prove to be more routinely applicable. Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *42*, 164.

The Rate of Ring Closure of 1,1-Dimethyl-2-phenyl-1-silabuta-1,3-diene to 1,1-Dimethyl-2-phenyl-1-silacyclobutene

Robert T. Conlin,*,† **Shizhong Zhang,**† **Mohammad Namavari,**† **Kevin L. Bobbitt,**† **and Mark J. Fink***,‡

Center for Organometallic Research and Education Department of Chemistry, University of North Texas Denton, Texas 76203, and Department of Chemistry, Tulane University New Orleans, Louisiana 70118

Summary: Irradiation of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene in a 3-methylpentane glass at 77 K yields 1,1-dimethyl-2-phenyl-1-silabuta-1,3-diene whose UV spectrum displays a λ_{max} at 338 nm. Flash photolysis of the silacyclobutene in a cyclohexane solution at 298 K produces the same reactive siladiene, λ_{max} which cyclizes to the starting ring structure with an activation barrier of ≈9.4 kcal/mol. Trapping studies with methoxytrimethylsilane support both the kinetic and spectral assignments.

Recent observation of transient silenes by matrix isolation spectroscopy and of stable silenes by conventional methods has revealed much of the structural and electronic details of π-bonded silicon.[1] The property that first drew

†University of North Texas.
‡Tulane University.

(1) (a) Michl, J.; Raabe, G. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, in press.

attention to this novel type of bonding between carbon and silicon was its extraordinary reactivity. Yet still very little is known about the mechanisms and rates of these silene reactions.[2,3] Herein we report the UV matrix spectrum of a 1-silabutadiene at 77 K, rate of closure to a 1-sila-cyclobut-2-ene at ambient temperature, and rate of reaction of the siladiene with methoxytrimethylsilane.

The 254-nm photolysis of 1,1-dimethyl-2-phenyl-1-sila-cyclobutene (1) in methanol, a non-absorbing solvent, is known to yield three products whose origin has been attributed to capture of the transient 1,1-dimethyl-1-sila-2-phenyl-1,3-butadiene (2).[4] We find that irradiation of 1 (10^{-2} M) with methoxytrimethylsilane (0.1 M in cyclohexane), an effective trapping agent of photogenerated silenes,[5,6] yielded the 1,2-adduct 3 exclusively and quantitatively.[7]
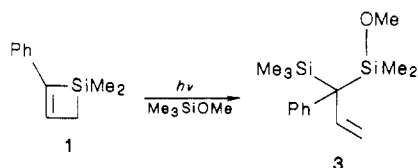
Irradiation of 1 (10^{-4} M) at 254 nm in a 3-methylpentane glass frozen at 77 K quickly gave rise to a new species: λ_{max} = 338 nm. Upon annealing the glass (ca. 100 K), the 338 nm signal rapidly disappeared and a GC/MS analysis of the solution indicated only trace (<5%) amounts of starting 1. The remainder of photoconverted 1 was isolated as an involatile and insoluble polymeric material. We have assigned the UV absorption at 338 nm to 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (2) and the involatile material to the polymerization product of 2.[8]

Flash photolysis of 1 (10^{-4} M in cyclohexane) at 298 K with 266 nm light from a Nd:YAG laser produced a transient species with an absorption envelope ($\lambda_{max} \approx 335 \pm 3$ nm) nearly identical with that observed in the matrix experiments. The rate constant for decay of the signal was $(1.19 \pm 0.06) \times 10^5$ s^{-1}. The same rate constant was also obtained by monitoring the disappearance of the new absorption at 300 nm. The rate of decay was examined at four different concentrations (c) of 1 [$k/10^5$ s^{-1} ($c/10^{-4}$ M)]: 1.20 (2.06), 1.13 (1.03), 1.24 (0.52), 1.20 (4.12). Since the decay of the absorption provides the same first-order rate constant independent of the concentration of 1, reaction of siladiene 2 with its precursor, 1, does not occur in these experiments.[9] The rate of decay of 2 is very likely the unimolecular return to the starting silacyclobutene. If the

entropic requirements of the transition state for ring closure are about the same for the siladiene as for other 1,3-dienes,[10] the significance of the rate constant, via the Arrhenius equation, can be extended to an activation energy for the siladiene ring closure. Assuming that $\Delta S \neq$ −5.6 cal mol^{-1} deg^{-1}, log $A = 12^{10}$ and the activation enthalpy is $\approx$9.4 kcal/mol.[11]
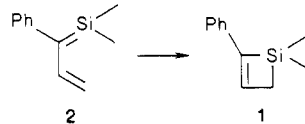
An interesting consequence of these Arrhenius parameters is that the rate of ring closure at $\approx$100 K, the melting range of the 3-MP glass, is many orders of magnitude slower than the rate of polymerization. For ring closure, substitution of the values of A and E_a from above gives $k_{rc} < 10^{-8}$ s^{-1} at 100 K. The maximum *rate* of closure of 2 at low concentration and temperature is $k_{rc}[2] = 10^{-12}$ mol dm^{-3} s^{-1}. In comparison, k_{poly} is very likely to be near the encounter control rate constant, 10^9 dm^3 mol^{-1} s^{-1}. Again with [2] $\approx 10^{-4}$ mol dm^{-3}, the *rate* of polymerization is expected to be 10 mol dm^{-3} s^{-1}. The activation enthalpy for reclosure thus renders this pathway prohibitively slow reactive to polymerization at low temperature.

An additional test of these assumptions is the kinetic behavior of the signal in the presence of a trapping agent. Varied concentrations of methoxytrimethylsilane, under pseudo-first-order conditions, yield kinetic data that support both our spectral assignment and the kinetic interpretation. The rate of decay of the 335 nm absorption, at 298 K and with three different concentrations (c) of methoxytrimethylsilane, provides the pseudo-first-order rate values [$k/10^6$ s^{-1} ($c/10^{-1}$ M)]: 0.729 (2.00), 1.17 (3.09), 1.27 (3.67). The least-squares slope of this line, (3.40 ± 0.56) × 10^7 M^{-1} s^{-1}, is the bimolecular rate constant for addition of the silicon–oxygen bond to the sila diene.[12] The intercept of such a pseudo-first-order plot, i.e. no methoxysilane trapping agent present, is the rate constant of the unimolecular cyclization. From the plot, the intercept, 0.68×10^5 s^{-1}, is in reasonable accord with the value, 1.19×10^5 s^{-1}, obtained in the absence of a trap.

The connection between the absorptions at 338 nm in the 3-MP matrix and the 335 nm in solution would be identical reactivity toward a trapping agent, in this case methoxytrimethylsilane. Such a parallel requires, however, that mechanisms of both the matrix and liquid phase reaction of the silicon–oxygen bond with the siladiene follow the same course. Instead, matrix-isolated 2, which provides a confirmation of the kinetically monitored electronic spectrum, reacts with the methoxysilane to produce three isomers of 3 detected by GC/MS. In the same concentrations, but in solution, 2 reacts with the methoxysilane to give 3. Changes in reaction mechanisms of and hence products from reactive molecules in matrices from what might be expected in fluid media have been described frequently.[13,14]

(2) A variety of silene reaction rates have been estimated. See: Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc., Chem. Commun.* 1982, 550. Frey, H. M.; Kashoulis, A.; Ling, L. M.; Lodge, S. P.; Pidgeon, I. M.; Walsh, R. *J. Chem. Soc., Chem. Commun.* 1981, 915.

(3) Reaction rates of divalent silicon have recently been reported from a variety of different precursors, for examples, see: Gaspar, P. P.; Holten, D. H.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* 1987, 20, 329. Levin, G.; Das, P. K.; Lee, C. L. *Organometallics* 1988, 7, 1231. Jasinski, J. *J. Phys. Chem.* 1986, 90, 555.

(4) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* 1981, 219, 153.

(5) Conlin, R. T.; Bobbitt, K. L. *Organometallics* 1987, 6, 1406.

(6) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* 1988, 110, 1315.

(7) Satisfactory spectroscopic, mass spectrometric, and analytical data were obtained for 3 (see supplementary material).

(8) Attempts to obtain spectra of the polymer of 2, a thin white film coating the inside of the cell, have been unsuccessful.

(9) In the gas phase and at higher temperatures, the more volatile 1,1-dimethylsilabuta-1,3-diene dimerizes and reacts with its thermal precursor, the silacyclobutene, to yield several products. Conlin, R. T.; Namavari, M. submitted for publication. In solution, however, at ambient temperature, prolonged 254-nm photolysis of repeatedly purified 1 in a cyclohexane solution (10^{-2} M) effects no change in composition.

(10) The only other 1,3-diene for which the entropy of ring closure has been measured is perfluoro-1,3-butadiene, see: Schlag, E. W.; Peatman, W. B. *J. Am. Chem. Soc.* 1964, 86, 1674.

(11) If log A is as high as 14, E_a becomes 12.2 kcal/mol. For comparison, the activation enthalpy for ring closure of buta-1,3-diene to cyclobutene is $\approx$22.6 kcal/mol from thermochemical data. Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(12) In ref 3, it has been reported that the bimolecular rate constant for a silene photogenerated from 2-phenylheptamethyltrisilane and methanol is 5.4×10^7 M^{-1} s^{-1}.

(13) For a discussion of a "matrix effect" on carbene reactions see: Platz, M. S. *Acc. Chem. Res.* 1988, 21, 236.

Supplementary Material Available: Spectroscopic data (^{13}C NMR, ^{1}H NMR, and mass spectra) and low-temperature and time-resolved UV-difference spectra (3 pages). Ordering information is given on any current masthead page.

(14) Matrices alter the mechanism of 1-methylsilene trapping reactions. Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

Additions and Corrections

Judith C. Gallucci, Bernard Gautheron,* Melinda Gugelchuk, Philippe Meunier, and Leo A. Paquette*: Bis-(isodicyclopentadienyl) Complexes of the Group 4 Transition Metals. Stereoselective Synthesis and Crystal Structures of the Titanocene and Zirconocene Dichloride Derivatives. **1987**, *6*, 15.

The names given to compounds **4**, **5**, and **6** in the Experimental Section are incorrectly reported as η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trien-6-yl systems. As indicated correctly in the formulas and elsewhere in the text, these complexes are of the η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5-dienyl type.

William J. Evans* and Donald K. Drummond: Reactivity of Isocyanides with (C$_5$Me$_5$)$_2$Sm(THF)$_2$: Synthesis and Structure of Trimeric [(C$_5$Me$_5$)$_2$Sm(CNC$_6$H$_{11}$)(μ-CN)]$_3$. **1988**, *7*, 797–802.

In Table II, the y coordinates for C(19), C(31), and C(34) should be 0.0797 (19), -0.1397 (17), and -0.1795 (9), respectively.