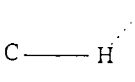
recognize that the former value, which is large for a secondary KIE with hydrogen as the leaving group, may be less reliable because of the NMR integration method used. There was no evidence for H–D scrambling in this system. The above calculation of isotope effects is based on an assumption of a single-step insertion of palladium into the C–H or C–D bond, and a different treatment and interpretation would be required for a more complex multistep pathway.[13]

We presume that palladation originates from oxime-bonded Pd(II) that is sufficiently electrophilic to interact with a C–H bond of the *equatorial* methyl group. Whether the trajectory[8,9] of this interaction is "end-on" (**5**) or "side-on" (**6**), this two-electron, three-center Pd–H–C interaction will enhance the acidity of the C–H bond, thus facilitating proton removal by a base. If the initial interaction is close to end-on, i.e. with a large Pd–H–C angle, the transition state must be located further along the reaction coordinate (reduced MHC angle) to reflect developing Pd–C bond formation. The substantial primary KIE requires advanced C–H bond rupture and the secondary KIE a movement toward sp^2 hybridization and carbenium ion character at the carbon center.[14-16]



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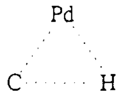

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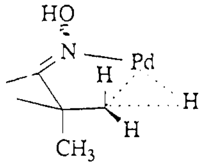

7

With respect to stereochemistry,[17] **7** may imply retention at carbon and the conventional view[14] of a significant positive secondary KIE would be consistent with retention over inversion of configuration at carbon for Shaw palladation. Stereochemical studies of the related pallado-destannylation in an acyclic system were inconclusive,[18] probably because of β-hydride removal and readdition.

Reaction of the oxime of cyclooctanone under Shaw conditions led to no trans-annular product. However, a complex was isolated that was formulated, on the basis of ^{1}H and ^{13}C NMR spectra[19] and microanalysis, as bis(cyclooctanone oxime)bis(cyclooctanone oximato)palladium(II) (**8**).[20] The X-ray crystal structure[21] shows a square-planar ligand array about Pd, but with some alternation (87 and 93°) of the angles in the square plane, presumably in response to the O···H···O moieties.

Acknowledgment. We are grateful to the Australian Research Council for financial support and for a scholarship to A.P.W. and to Dr. Peter Wells, The University of Queensland, and Professor V. J. Shiner, Jr., Indiana University, for helpful comments.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compound **3**, ^{2}H and ^{13}C NMR spectra for the product from **4**, a table of selected microanalytical and FAB mass spectra, and tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **8** (22 pages). Ordering information is given on any current masthead page.

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(13) An alternative would be a two-step mechanism involving an alkane complex, and the isotope effect from competing CH$_3$ vs CH$_2$D would be an *intermolecular* effect relating to complex formation. The effect from competing C–H vs C–D within a single CH$_2$D group would be an *intramolecular* effect, characterizing the conversion of the complex to the oxidative-addition product. This latter effect would be observable irrespective of which step was rate-determining. In this hypothetical two-step mechanism, the two isotope effects are separate, and the analysis in Scheme I to calculate primary and secondary effects is inapplicable. We are very grateful to a reviewer for incisive comments on this matter. In this connection see ref 6 and: Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

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(15) Baldwin[3] has observed that a methyl group is palladated in preference to acetoxymethyl and attributed this selectivity to the "smaller" methyl group preferentially occupying the *equatorial* position ($A^{1,3}$ strain). However, the *A* values of –CH$_3$ and –CH$_2$X are very similar (Kitching, W.; Olszowy, H. A.; Adcock, W. *Org. Magn. Reson.* **1981**, *46*, 563). Alternatively, development of sp^2 (carbenium ion) character in the transition state would be disfavored by the acetoxy group.

(16) The proposed transition state, being nonlinear and incorporating a heavy atom, makes detailed discussion of the magnitudes of the KIE's difficult. Special interactions of a type not treated in the normal derivation of secondary KIE's may occur between Pd and the –CH$_2$D group, and there may be "hyperconjugative" effects involving C–H (or C–D) and Pd orbitals, although the degree of matching and any overlap in unclear. See ref 7, particularly Chapter 5. See also: Chiao, W. B.; Saunders, W. H. *J. Am. Chem. Soc.* **1978**, *100*, 2802. For recent determinations of some β-deuterium isotope effects on organometallic oxidative-addition reactions see: Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 787.

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(19) Anal. Calcd for C$_{32}$H$_{58}$O$_4$N$_4$Pd: C, 57.49; H, 8.68; N, 8.38. Found: C, 57.25; H, 8.94; N, 8.29. ^{13}C NMR (δ; CDCl$_3$, 125.77 MHz): 23.81, 24.83, 25.42, 26.10, 27.46, 29.68, 34.66, 166.85. ^{1}H MNR (δ; CDCl$_3$, 500 MHz): 1.05–1.29 (ring proton), 4.35 (br, OH).

(20) For a discussion of structures of this general type, see: Imamura, S.; Kajimoto, T.; Kitano, Y.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 805.

(21) Full discussion of the structure will be presented elsewhere (Wells, A. P.; Kitching, W.; Kennard, C. H. L. To be submitted for publication. Wells, A. P. Ph.D. Thesis, University of Queensland, 1992).

Laser Flash Photolysis of Octaisopropylcyclotetragermane. Generation of Digermenes and Germylenes

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Received April 23, 1992

Summary: **Laser flash photolysis of octaisopropylcyclotetragermane involves both formation of hexaisopropylcyclotrigermane with extrusion of diisopropylgermylene and conversion to tetraisopropyldigermene.**

The chemistry of polysilanes, especially cyclopolysilanes, has been a subject of interest in recent years because of their unique physical and chemical properties arising from electronic delocalization in the Si–Si σ framework.[1-6]

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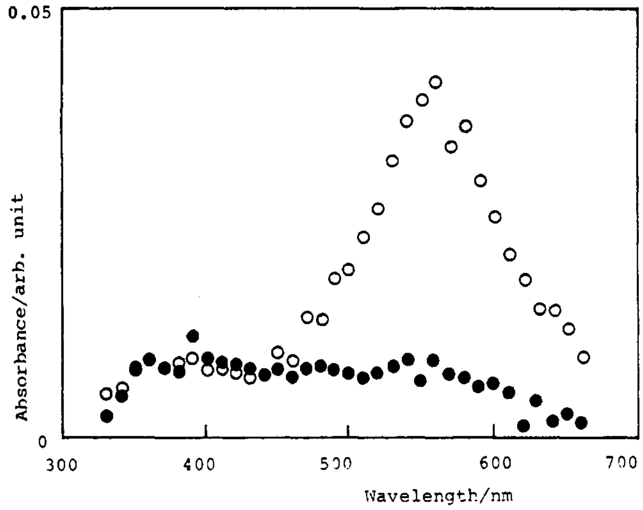

Figure 1. Transient absorption spectra after photoexcitation of octaisopropylcyclotetragermane (1) at 293 K: (○) 80 ns; (●) 200 ns.

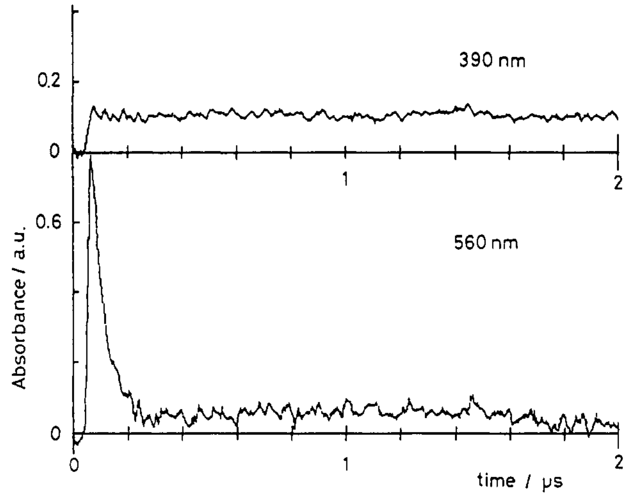

Figure 2. Plots of the absorbance at 390 and 560 nm against time observed with the cyclohexane solution of octaisopropylcyclotetragermane (1).

However, there have been few reports on photochemical studies of the germanium analogue.[7-12] We describe herein the first laser flash photolysis studies on the cyclotetragermane. Photolysis of octaisopropylcyclotetragermane, [^{i}Pr$_2$Ge]$_4$, involves both ring contraction to hexaisopropylcyclotrigermane with extrusion of diisopropylgermylene and conversion to tetraisopropyldigermene.

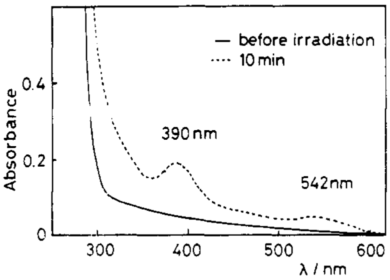

Figure 3. UV absorption of octaisopropylcyclotetragermane in a 3-methylpentane glass at 77 K.

Laser flash photolysis[13] (λ = 266 nm, pulse width 5 ns, power 10 mJ/pulse) of [^{i}Pr$_2$Ge]$_4$ (1; 2.8×10^{-3} M) in cyclohexane at 293 K gave two separated transient bands at 390 and 560 nm, as shown in Figure 1. The transient peak at 390 nm appears very rapidly within the duration of the laser pulse, suggesting that the photolysis originates from the excited singlet state of 1. The 390-nm transient is stable, since no change in absorbance is observed within the observable time limit of the laser system. The time dependence of absorbance $A(t)$ is shown in Figure 2. The peak at 390 nm is reasonably assigned to that of tetraisopropyldigermene, ^{i}Pr$_2$Ge=Ge^{i}Pr$_2$ (2), from comparison of its spectral characteristics with those of similar germenes reported.[10,12] Tetramethyldigermene has been reported to disappear with second-order kinetics (k/ϵ = ca. 10^6), resulting in the formation of octamethylcyclotetragermane.[10,12] The stability of 2 can apparently be ascribed to the steric hindrance of the isopropyl group.

On the other hand, the transient peak at 560 nm for 1 appears very rapidly just after laser pulsing and decays single-exponentially with a lifetime of 56 ns (error limit of 10%) as shown in Figure 2. The transient at 560 nm as shown in Figure 1 is safely assigned to that of diisopropylgermylene, ^{i}Pr$_2$Ge: (3), by comparing its spectral characteristics with those reported for similar germylenes.[10,12,14] The value of λ_{max} (560 nm) for diisopropylgermylene observed in this study was relatively red-shifted. This may be due to a conformational change in the C–Ge–C bond angle between the ground and lowest excited singlet states of 2. The 560-nm transient in cyclohexane decayed with first-order kinetics. Laser flash photolysis of germylenes has been shown to decay with second-order kinetics (k/ϵ = ca. 10^7), resulting in the formation of the corresponding digermenes.[10,12,14] This route for the germylene 3 is not the main decay. Tentatively, the unimolecular reaction of germylene 3 is ascribable to photochemical isomerization to 2-germapropene, followed by polymerization. A similar photochemical isomerization of dimethylsilylene to 2-silapropene has been reported.[15] The intramolecular shift of the α-hydrogen atom of isopropyl groups seems to be much faster than that of the methyl groups of dimethylgermylene.

The photolysis of 1 at 254 nm was also carried out in a 3-methylpentane (3-MP) glass at 77 K. UV irradiation of 1 (10^{-4} M) produced a yellow glass with two broad bands at 390 and 542 nm as shown in Figure 3. The yellow species at λ_{max} = 390 and 542 nm obtained in this study can be assigned to the corresponding digermene 2 and

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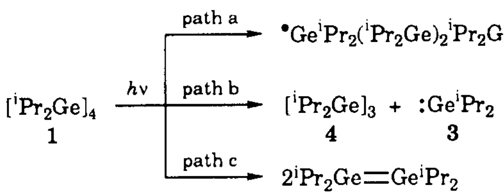
Scheme I



germylene 3, respectively, on the basis of trapping experiments and from a comparison of their spectral characteristics with those of such species previously reported.[10,12,14] No change in absorbance was observed over a 77–143 K temperature range.

Along with laser flash photolysis and matrix isolation experiments, product studies were carried out by photolyzing 1 (0.04 M) with a 110-W low-pressure Hg arc lamp at room temperature for 1 h under argon in cyclohexane. Together with high-boiling unidentified products containing germanium, octaisopropyltetragermane, $(\mathrm{H}{}^i\mathrm{Pr}_2\mathrm{Ge}{}^i\mathrm{Pr}_2\mathrm{Ge})_2$ (13%), hexaisopropyltrigermane, $(\mathrm{H}{}^i\mathrm{Pr}_2\mathrm{Ge})_2\mathrm{Ge}{}^i\mathrm{Pr}_2$ (2%), and tetraisopropyldigermane, $(\mathrm{H}{}^i\mathrm{Pr}_2\mathrm{Ge})_2$ (4%), were carefully identified in the photolysate by means of GC–MS and NMR methods. The dihydrotetragermane is likely to arise from the cyclotetragermane 1, which undergoes ring opening to form the intermediate tetragermyl diradical. The tetragermyl diradical in turn abstracts hydrogen from hydrogen sources such as the solvent used in this study and the isopropyl group on the germanium atom. The dihydrotrigermane is explained by the intermediacy of the trigermyl diradical. The trigermyl diradical, which forms from ring opening of the cyclotrigermane $[{}^i\mathrm{Pr}_2\mathrm{Ge}]_3$ (4) or from the tetragermyl diradical by α-elimination of a germylene, abstracts hydrogen. No formation of a germylene by α-elimination of polygermyl radical has been reported.[14] The dihydrodigermane seems to arise from the intermediacy of the digermene 2 abstracting hydrogen. In order to obtain more information on possible reactive intermediates, cyclohexane solutions of 1 containing carbon tetrachloride were similarly irradiated. Diisopropyldichlorogermane (50%) and 1,2-dichlorotetraisopropyldigermane (45%) were obtained as the main products. The formation of dichlorogermane and dichlorodigermane seems to indicate the intermediacy of the germylene 3 and digermene 2.[16,17] This may be further substantiated by the presence of 1,1-diisopropyl-3,4-dimethyl-1-germacyclopent-3-ene (3%) and 1,1,2,2-tetraisopropyl-4,5-dimethyl-1,2-digermacyclohex-4-ene (1%) for the photolysis of 1 in cyclohexane containing a large amount of 2,3-dimethylbutadiene.[17,18] Photochemically generated germylene species are not trapped effectively by 2,3-dimethylbutadiene.[10,12,14] In the presence of ethanol and 2,2-dimethylpropanol, photolysis of 1 in cyclohexane afforded 1,1,2,2-tetraisopropylethoxydigermane (4%) and 1,1,2,2-tetraisopropyl-*tert*-butoxydigermane (3%), respectively. It is well-known that digermene species can be trapped efficiently by alcohol.[17] On the other hand, photochemically generated germylene species do not react with alcohol.[10,12,14]

These results are best rationalized by three paths described in Scheme I: (a) ring opening of 1 to form the tetragermyl diradical, (b) ring contraction of 1 to give cyclotrigermane 4 with extrusion of germylene 3, and (c) conversion to digermene 2. A route to digermene with sucessive α-elimination of germylene has been proposed in the photodecomposition of octaethylcyclotetragermane.[9] These laser photolysis studies show another route to digermene in the photolysis of octaisopropylcyclotetragermane.

Acknowledgment. We thank Drs. Hisaharu Hayashi and Masanobu Wakasa of the Institute of Physical and Chemical Research for making laser flash photolysis instruments available for our use and for helpful discussion. This research was partly supported by the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research No. 03215228).

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(19) All new compounds were characterized by ^{1}H NMR and GC–MS methods.

Cationic and Neutral 50-Electron Triruthenium Carbonyl Clusters Containing Three Bridging Diphenylphosphido Ligands

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Summary: The reaction of $\mathrm{RuCl_3 \cdot \mathit{n}H_2O}$ with CO in refluxing 2-methoxyethanol and subsequent treatment of the obtained solution with $\mathrm{PPh_2H}$ (Ru:P = 1:1), zinc, and CO gives the cationic 50-electron triruthenium complex $[\mathrm{Ru_3(\mu\text{-}PPh_2)_3(CO)_9}]\mathrm{Cl}$ (1) in 32% yield. Complex 1 undergoes CO elimination upon UV irradiation to give quantitatively the neutral derivative $[\mathrm{Ru_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_3(CO)_7}]$ (2). Compounds 1 and 2 react with refluxing propan-2-ol to give the 48-electron hydrido complex $[\mathrm{Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7}]$ (3). The molecular structure of complex 2 is reported.

Significant chemistry of diphenylphosphido-bridged organometallics has been developed over the past decade.[1-7] For ruthenium, many trinuclear carbonyl deriv-

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