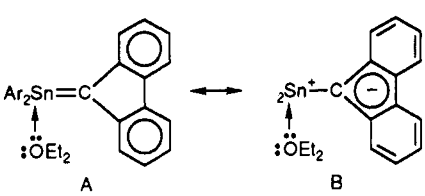
of tin with Et_2O (**1a**), as evidenced by the broad signals for the OCH_2 hydrogens in the ${}^{1}H$ NMR spectrum. Addition of THF to such a solution causes these signals to become sharper, whereas those due to THF become very broad, indicating a complexation of tin by THF (**1b**). Quenching with methanol sharpens up the THF signals.

Replacement of Et_2O by THF does not influence the ${}^{119}Sn$ chemical shift, which moves from 288.0 to 287.3 ppm (within experimental error). Such complexation of doubly-bonded group 14 metals by weak bases has already been observed in the case of silenes,[13] germenes,[7] and silaimines,[14] where, as in the stannenes, the metal is an electrophilic center, with a rather polarized double bond, $M^{\delta+}{=}C^{\delta-}$ or $Si^{\delta+}{=}NR^{\delta-}$.

In the ${}^{13}C$ NMR spectrum of **1a**, the Sn=C signal appears at 133.85 ppm, as expected for such a carbon: compare for example, stannenes **2a** and **2b**[2] (142 and 91 ppm, respectively). In the UV spectrum, the absorption due to the Sn=C double bond appears at 542 nm.

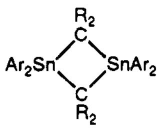
The representation of **1a** deserves some comment. One can imagine that the fluorenylidene group destabilizes the multiple bond by preferentially stabilizing the polarized resonance structure B. Thus, we can write the two limiting forms A and B for **1a**.



Form B would be an ylide of divalent tin. Calculations must be made to determine the most important contribution (form A or form B) for **1a**.

Note that the synthesis of stannene **1a** has until now been successful only in Et_2O, or in a mixture of solvents with at least about 10% of Et_2O. In toluene the formation of **1a** did not occur.

1a has rather good thermal stability. It was recovered unchanged after 1 month at −20 °C in Et_2O solution. At room temperature, it slowly converts to the head-to-tail dimer **7**[15] ($t_{1/2} \approx 1$ h). It is extremely air- and moisture-sensitive and cannot be isolated as yet in completely pure form. However, its structure, already evidenced by NMR spectroscopy, was given additional support by its chemical reactivity. For example, methanol adds very easily and quantitatively to the tin–carbon double bond to give **6**.[16] This reaction is regiospecific with, as expected, the oxygen atom bonded to tin due to the polarity ${}^{\delta+}Sn{=}C^{\delta-}$ of the double bond.



7

The study of the chemical behavior of the very reactive **1a** is in progress.

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[13] Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 35.

[14] Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

[15] Preparation of **7**: Violet solutions of **1a** in Et_2O slowly decolorized on standing at room temperature (about 2 h), whereupon crystals of the dimer $(Is_2Sn\text{-}CR_2)_2$ appeared. The latter can be recrystallized from Et_2O or from $CHCl_3$: mp 247 °C. ${}^{1}H$ NMR ($CDCl_3$): δ −0.5 and −0.42 (2 d, ${}^{3}J_{HH}$ = 6.8 Hz, 2 × 12 H, *o*-Me_2CH), 0.14 (d, ${}^{3}J_{HH}$ = 6.4 Hz, 12 H, *p*-Me_2CH), 1.02 and 1.05 (2 d, ${}^{3}J_{HH}$ = 6.8 Hz, 2 × 12 H, *o*-Me_2CH), 1.50 (d, ${}^{3}J_{HH}$ = 6.4 Hz, 12 H, *p*-Me_2CH), 2.63 (sept, ${}^{3}J_{HH}$ = 6.8 Hz, 8 H, *o*-C*H*Me_2), 3.00 (sept, ${}^{3}J_{HH}$ = 6.4 Hz, 4 H, *p*-C*H*Me_2), 6.29 and 6.30 (2 s*, 2 × 2 H, *m*-arom H, *p*-Ar, ${}^{4}J_{SnH}$ = 21.0 Hz), 6.84 and 6.85 (2 s*, 2 × 2 H, *m*-arom H, *o*-Ar, ${}^{4}J_{SnH}$ = 21.0 Hz), 6.84 and 6.98 (2 t, ${}^{3}J_{HH}$ = 8.0 Hz, 2 × 4 H, arom CR_2), 7.57 and 7.61 (2 d, ${}^{3}J_{HH}$ = 8.0 Hz, 2 × 4 H, arom CR_2). ${}^{13}C$ NMR ($CDCl_3$): δ 21.53, 22.99, 23.15, 23.81, 24.01, and 27.31 (Me_2CH), 33.76, 38.55, and 40.63 (*C*HMe_2), 70.63 (Sn–*C*–Sn), 118.64 (C_4C_5), 122.40, 122.59, 123.25, 123.51 ($C_1C_2C_3C_6C_7C_8$, *m*-C, Ar), 130.60 (*m*-C, Ar), 137.76 (*p*-C, Ar, ${}^{4}J_{SnC}$ = 8.8 Hz), 147.64 (*p*-C, Ar), 148.84 and 149.16 ($C_{10}C_{11}$-$C_{12}C_{13}$), 151.57 (*o*-C, Ar, ${}^{2}J_{SnC}$ = 23.8 Hz), 152.92 (*o*-C, Ar, ${}^{4}J_{SnC}$ = 21.6 Hz). ${}^{119}Sn$ = δ −6.0 (${}^{2}J_{{}^{119}Sn-{}^{117}Sn}$ = 210 Hz). The fact that each satellite peak is 5.1% as intense as that of the parent peak favors a dimeric structure (theoretical value for a dimer 3.8%). MS (DCI, CH_4): *m/z* 729 (M/2 + 41, 34), 619 (M/2 + 1, 100). Anal. Calcd: C, 74.92; H, 7.84. Found: C, 74.39; H, 8.02.

[16] Preparation of **6**: On addition of an excess of methanol, a violet Et_2O solution of **1** (0.42 mmol) immediately turned light yellow. Crystallization in pentane afforded light yellow crystals of **6** (70%); mp 127 °C. ${}^{1}H$ NMR ($CDCl_3$): δ 0.79 (d, ${}^{3}J_{HH}$ = 6.5 Hz, 24 H, *o*-Me), 1.15 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 12 H, *p*-Me), 2.44 (sept, ${}^{3}J_{HH}$ = 6.5 Hz, 4 H, *o*-CH), 2.79 (sept, ${}^{3}J_{HH}$ = 6.8 Hz, 2 H, *p*-CH), 3.72 (s*, ${}^{3}J_{SnH}$ = 43.0 Hz, 3 H, OMe), 4.80 (s*, ${}^{2}J_{SnH}$ = 123.0 Hz, 1 H, C*H*R_2), 6.88 (s*, ${}^{4}J_{SnH}$ = 11.0 Hz, 4 H, arom Ar), 7.17–7.94 (m, 8 H, CR_2). ${}^{13}C$ NMR ($CDCl_3$): δ 23.98, 24.30, 24.84 (*p*-CH_3 and *o*-CH_3), 34.29 (*p*-CH), 38.05 (${}^{3}J_{SnC}$ = 33.1 Hz, *o*-CH), 48.37 (*C*HR_2), 55.38 (OMe), 119.92 (C_4, C_5), 122.25 (${}^{3}J_{SnC}$ = 55.3 Hz, *m*-C Ar), 124.69, 125.58, 126.45 (C_1, C_2, C_3, C_6, C_7, C_8), 140.15, 140.42 (C_{12}, C_{13}), 144.69, 144.92 (C_{10}, C_{11}), 150.90 (*p*-C Ar), 154.84 (*o*-C Ar). ${}^{119}Sn$ NMR ($CDCl_3$): δ −32.0. MS (EI, 70 eV): *m/z* 691 (M^+ − OMe, 4), 557 (Ar_2SnOMe^+, 10), 525 (Ar_2Sn^+ − H, 11), 323 ($ArSn^+$, 6), 165 (R_2CH^+, 100).

Alkyl Group Substitution by Oxime-Bound Palladium(II) (the Shaw Reaction): Alkyl Group Selectivity and Deuterium Isotope Effects

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Summary: Alkyl group selectivity and kinetic deuterium isotope effects are presented for C–H palladation by oxime-bound palladium(II) (the Shaw reaction).

An attractive sequence for the functionalization of an "unactivated" equatorial methyl group in 2,2-dimethylcyclohexanone oximes involves Shaw palladation,[1] followed by oxidation or reduction of the C–Pd bond.[2,3] Steroidal systems respond well to this approach[2,3] (eq 1). Other than the requirement for a "near-coplanar" arrangement[3] of the oxime and "target" methyl group, few details on the Shaw reaction are available. In this report we provide infor-

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[1] Constable, A. G.; McDonald, W. G.; Sawkins, L. C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1978**, 1061; *J. Chem. Soc., Dalton Trans.* **1980**, 1992.

[2] Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227.

[3] Baldwin, J. E.; Najera, C.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1985**, 126. Baldwin, J. E.; Jones, R. H.; Najera, C.; Yus, M. *Tetrahedron* **1985**, *41*, 699. Shaw palladation–oxidation has also been applied to a gibberellin derivative (dihydro-GA_4) to provide the 18-acetate in moderate yield. (Mander, L. N. Private communication, Research School of Chemistry, Australian National University).

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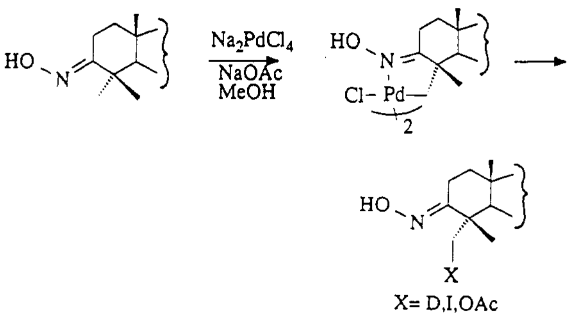
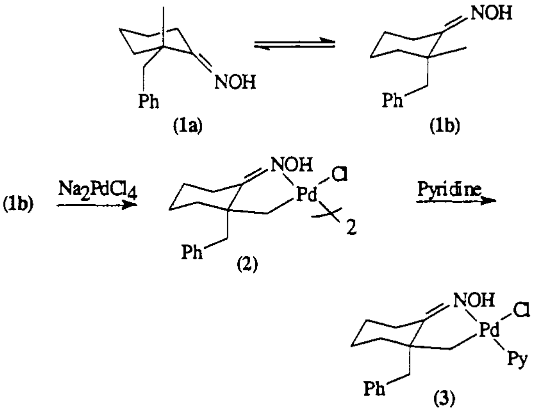


(1)

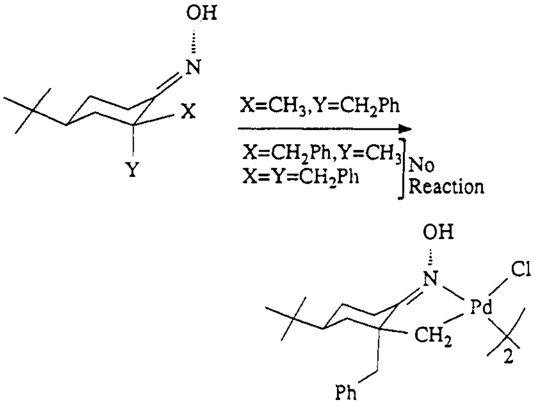
mation on alkyl group selectivity and the likely nature of the transition state.

Treatment of the oxime of 2-benzyl-2-methylcyclohexanone (1) under Shaw conditions provided a yellow product in high yield (>90%) which was fully characterized[4] as the chloro-bridged dimer 2 and as the monomeric pyridine adduct 3 (eq 2). Within the limits of detection



(2)

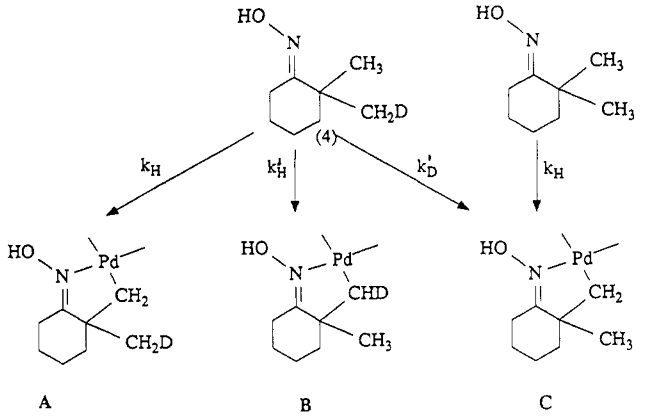
(high-field ^1H and ^{13}C NMR spectroscopy), palladation of the methyl group was exclusive. Although operation of $A^{(1,3)}$ strain[5] presumably would favor conformation **1b** over **1a**, thus disfavoring benzylic palladation,[6] this cannot be the explanation, as an enforced *equatorial* orientation of the benzyl group does not lead to palladation (eq 3).



(3)

These results imply a transition state reflecting in part the strength of the Pd–C bond being formed (benzyl–metal σ-bonds are weaker than alkyl–metal bonds)[7,8] rather than the weakness of the C–H bond being broken.[9] This led to a study of deuterium isotope effects for palladation.

Scheme I



$$A : B : C = (3x92)k_H : (2x92)k'_H : (92k'_D + \{6x8\}k_H)$$

$$= 276k_H : 184k'_H : (92k'_D + 48k_H)$$

Initially we examined the oxime of 2-(methyl-$^2H_3$)-2-methylcyclohexanone,[10] and it was clear that palladation occurred preferentially at a C–H bond with an apparent k_H/k_D value of 3.0–3.5. To minimize complications associated with the conformational preferences of CH_3 and CD_3[11] and multiple isotope effects etc., examination of $-CH_3$ versus $-CH_2D$ was undertaken, with the required starting material 4–^{2}*H* (92% (together with unlabeled 4 (8%)) (Scheme I) being obtained by borodeuteride reduction[3] of the Shaw product from the oxime of 2,2-dimethylcyclohexanone.[3] The palladation product was examined as both the chloro-bridged dimer and the pyridine adduct by high-field ^1H, ^2H, and ^{13}C NMR spectroscopy. The kinetic analysis, which ignores γ-isotope effects, is shown in Scheme I and, with the appropriate assays of the reaction mixture, permits calculation of the primary and secondary (α) deuterium kinetic isotope effects.

The 76.77-MHz ^2H NMR spectrum of the pyridine adduct showed signals for CH_2D (representing A in Scheme I) at δ 1.27 and equally intense signals for the epimeric CHD– systems in B at δ 2.11 and 2.47. The ratio A:B = 1.8:1.00, which represents $3k_H$:$2k^1_H$ (Scheme I), and hence $k_H/k^1_H = 1.20$, a large positive secondary deuterium KIE. Palladation of the C–D bond is not monitored by the ^2H NMR spectrum, and a measure of C relative to A and B (Scheme I) is required and is available for example from the C–Pd (~44 ppm) and C–CH_3 (~26.5 ppm) regions of the 125.77-MHz ^{13}C NMR spectrum.[12] Intensity measurements provide A:B:C = 4:2.2:1, and from Scheme I this leads to $k_H/k^1_H = 1.21$ and $k_H/k^1_D = 4.3$, the primary deuterium KIE. On the basis of various measures of A:B:C, $k_H/k^1_H = 1.20 \pm 0.05$ and $k_H/k^1_D = 4.0 \pm 0.5$, although we

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[4] All new compounds were characterized by high-field ^1H and ^{13}C NMR spectra, FAB mass spectra, and C, H, and N analyses where appropriate.

[5] Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

[6] There was no evidence for the formation of (η^1-benzyl)- or (η^3-benzyl)palladium complexes, which are known as stable species, or for a nitrogen–arene complex derived from 1a, which would hinder benzylic palladation. See: Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845. Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99 and references therein. We are grateful to a reviewer for raising these possibilities.

[7] Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91 and references therein.

[8] Lavin, M.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 99.

[9] For a general discussion of these and related subjects, see: Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989.

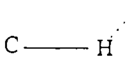
[10] This compound was formed by alkylation of the enolate of 2-methylcyclohexanone with perdeuteriomethyl iodide.

[11] See, for example: Anet, F. A. L.; Basus, V. J.; Hewett, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945. A CD_3, group relative to CH_3, prefers the *axial* position by ca. 25 cal/mol.

[12] In the C–Pd region (ca. 44 ppm), A is represented by a singlet at 44.29 ppm ($^3\Delta = -34$ ppb), B by a doublet of triplets (for two epimers of B) at 43.95 ppm ($^1\Delta = -380$ ppb, $J_{C-D} = 20.6$ Hz), and unlabeled C by a singlet at 44.32 ppm. In the C–CH_3 region, A is represented by a C–D triplet at 26.53 ppm ($J_{C-D} = 20$ Hz, $^1\Delta = -300$ ppb), B by singlets at 26.74 ($^3\Delta = -59$ ppb) and 26.81 ppm ($^3\Delta = -21$ ppb) (for the –CHD epimers), and unlabeled C at 26.83 ppm.

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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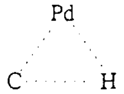

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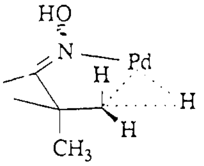

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With respect to stereochemistry,[17] **7** may imply retention at carbon and the conventional view[14] of a significant positive secondary KIE would be consistent with retention over inversion of configuration at carbon for Shaw palladation. Stereochemical 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_2D would be an *intermolecular* effect relating to complex formation. The effect from competing C-H vs C-D within a single CH_2D 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.

(14) Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific and Technical: Harlow, Essex, U.K., 1987; Chapter 7. See also: Gilliom, R. D. *Introduction to Physical Organic Chemistry*; Addison-Wesley: Reading, MA, 1970; Chapter 8.

(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 $-CH_2X$ 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 $-CH_2D$ 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.

(17) Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177. Olszowy, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1676.

(18) Nishiyama, H.; Matsumoto, M.; Matsukura, T.; Miura, R.; Itoh, K. *Organometallics* **1985**, *4*, 1911.

(19) Anal. Calcd for $C_{32}H_{58}O_4N_4Pd$: 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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(1) West, R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, New York, Toronto, Sydney, Frankfurt, 1982; Vol. 2, Chapter 9.4.

(2) Sakurai, H. *Synthesis and Application of Organopolysilanes*; CMC: Tokyo, 1989.