spectrum to −150 °C.[14] The infrared spectra of the two compounds are remarkably similar in the carbonyl stretching region (Figure 2). Cotton and Hunter[14] have proposed that $Fe_3(CO)_{12}$ adopts a continuum of different structures in solution and this is responsible for the broadness of the infrared absorptions (this interpretation has, however, recently been questioned[15]). Similar arguments could be used to rationalize the broad bands in the spectrum of 1.

It is conceivable that the CO exchange in 1 is so fast so as to cause the broadening of the absorptions in the infrared spectrum of the compound. The range in the chemical shifts of the ^{13}C NMR resonances of chemically different carbonyls in rigid osmium clusters is usually at least 10 ppm or ~1000 Hz at an operating frequency of 100.6 Hz. (For example, the chemical shift separation between the resonances of the axial and equatorial CO ligands in $Os_3(CO)_{12}$ is 11.9 ppm.[16]) For two sites undergoing fast exchange, the rate constant required to observe a detectable broadening (of 0.5 Hz) due to exchange is given by $\pi(\Delta\nu)^2$, where $\Delta\nu$ is the chemical shift difference between the two signals when the molecule is rigid.[17] The sharp singlet in the solution ^{13}C NMR spectrum of 1 at −130 °C therefore suggests that the carbonyls in the compound are undergoing exchange with a rate constant of at least 3×10^6 s^{-1} at this temperature.[18] If it is further assumed that the rate doubles with every ten degree rise in temperature, then a minimum rate of $\sim 2 \times 10^{11}$ s^{-1} is estimated for the CO exchange in 1 at 30 °C. This is a rate approaching that necessary to cause detectable broadening of infrared absorptions.[20] From the uncertainty principle, a rate necessary to cause a broadening of 5 cm^{-1} and thus coalesce two infrared peaks separated by this frequency is approximately 9.4×10^{11} s^{-1}. Dynamic rearrangement observable on the infrared time scale has recently been reported for some (η^4-diene)$Fe(CO)_3$ complexes.[22]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support. We also thank Professor W. A. G. Graham (University of Alberta) for valuable discussions.

Registry No. 1, 115227-28-6; $Os_4(CO)_{15}$, 110698-51-6.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles for 1 along with details of the data collection and refinement of the structure (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any masthead page.

---

(13) Shriver, D. F.; Whitmire, K. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, p 260 and references therein.

(14) Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* **1974**, *11*, L9.

(15) Binsted, N.; Evans, J.; Greaves, G. N.; Price, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1330.

(16) Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Robinson, B. H.; Jackson, W. G. *J. Chem. Soc., Chem. Commun.* **1974**, 1042.

(17) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; p 18.

(18) For $Fe_3(CO)_{12}$, the rate must be even faster at −150 °C since the ^{13}C NMR resonances of bridging carbonyls are typically 50 ppm to lower field of those due to terminal carbonyls in iron carbonyl derivatives.[19]

(19) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; p 172.

(20) (a) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 769. (b) Cohen, B.; Weiss, S. *J. Phys. Chem.* **1983**, *87*, 3606.

(21) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; p 86.

(22) Grevels, F. W.; Jacke, J.; Klotzbücher, W. E.; Krüger, C.; Seevogel, K.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 885.

Laser Photolysis of Aryl-Substituted Digermanes. Generation of Germyl Radicals and Germylenes

Kunio Mochida* and Masanobu Wakasa

Department of Chemistry, Faculty of Science
Gakushuin University
1-5-1 Mejiro, Tokyo 171, Japan

Yasuhiro Nakadaira

The University of Electro-Communications
1-5-1 Chofugaoka, Chofu, Tokyo 182, Japan

Yoshio Sakaguchi and Hisaharu Hayashi*

The Institute of Physical and Chemical Research
Wako, Saitama 351-01, Japan

Received March 16, 1988

Summary: Laser flash photolysis of the phenyl-substituted digermanes $(Ph_nMe_{3-n}Ge)_2$ results in Ge–Ge bond homolysis to give germyl radicals and probably a germylene.

The photochemistry of organosilicon compounds having a σ(Si–Si)–π(C–C) conjugated system has been the subject of considerable interest in recent years.[1] However, there have been few reports on photochemical studies of the germanium analogue.[2] We describe herein the first laser photolysis studies on the aryl-substituted digermanes $(Ph_nMe_{3-n}Ge)_2$ (**1**–**3**, n = 1–3, respectively). Photolysis of the phenylated digermanes causes germanium–germanium bond homolysis which leads to the formation of a germyl radical and probably a germylene.

Laser flash photolysis[3] (λ = 266 nm, pulse width 5 ns, power 10 mJ/pulse) of **1**–**3** (10^{-3} M) in THF at 293 K gave two well-separated transient absorption bands as shown in Figure 1. Careful examination of the transient peak at shorter wavelength shows that this is composed of the two components (half-life in THF and hydrocarbon media, $t_{1/2} < 5$ μs and $t_{1/2} > 20$ μs, respectively). The former is reasonably assigned to that of the aryl-substituted germyl radical $Ph_nMe_{3-n}Ge^{\bullet}$ (n = 1–3) from comparison of spectral characteristics with those of the germyl radical reported.[4-6] The experimentally determined decay constants of these transient species are summarized in Table I and are dependent on the concentrations of the employed phenylated digermanes. This is reasonably attributed to the addition of the generated germyl radical to the aromatic ring on the germanium.[7,8] The assignment of the shorter lived tran-

---

(1) Vinyldisilane: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424. (b) Ishikawa, M.; Fuchigami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *117*, C58. Aryldisilane: (c) Ishikawa, M.; Fuchigami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923. (d) Ishikawa, M.; Fuchigami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139. (e) Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36. (f) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89. Ethynyldisilane: (g) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (h) Ishikawa, M.; Fuchigami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245. (i) Ishikawa, M.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 245.

(2) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1379.

(3) Sakaguchi, Y.; Hayashi, H.; Nagakura, S. *J. Phys. Chem.* **1982**, *86*, 3177.

(4) Hayashi, H.; Mochida, K. *Chem. Phys. Lett.* **1983**, *101*, 307.

(5) Chatgilialogu, C.; Ingold, K. U.; Lusztyk, J.; Narzan, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

(6) Mochida, K.; Wakasa, M.; Ishizaka, S.; Kotani, M.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1985**, 1709.

(7) Sakurai, H. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 25.

(8) Sakurai, H.; Nozue, I.; Hosomi, A. *J. Organomet. Chem.* **1974**, *80*, 71.

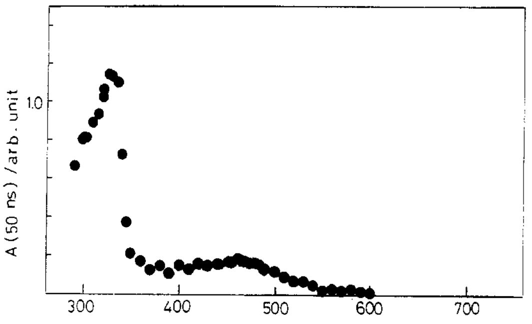


Figure 1. Transient absorption spectrum at 50 ns after photoexcitation of **3** (10^{-3} M) in degassed THF solution.

Table I. Rate Constants for Disappearance of the Shorter Lived Transients at Shorter Wavelength in the Photolysis of 1, 2, and 3 in THF (10^{-3} M)[a]

trapping agent	1	2	3
none (s^{-1})	4.3×10^5	3.2×10^5	1.9×10^5
CCl_4 (s^{-1} M^{-1})	2.2×10^8	4.7×10^8	5.8×10^8
O_2 (s^{-1} M^{-1})	5.3×10^9	4.0×10^9	3.8×10^9
2,3-dimethylbutadiene	*b*	*b*	*b*

[a] Absorption maxima: 315 nm for **1**, 325 nm for **2**, and 330 nm for **3**. [b] The transient decays too fast to be observed.

sient is further substantiated by quenching experiments with carbon tetrachloride, oxygen, and 2,3-dimethylbutadiene. Addition of carbon tetrachloride, an effective germyl radical scavenger,[9] quenched the transient absorption as shown in Table I.

$$Ph_nMe_{3-n}Ge^\bullet + CCl_4 \xrightarrow{k_{Cl}} Ph_nMe_{3-n}GeCl + {}^\bullet CCl_3$$

The quenching rate constants observed agree with the value reported for germyl radicals nicely.[4,9] Similarly, oxygen quenched the shorter lived transient very fast as shown in Table I.[7]

What is the latter carrier of the longer lived transient at the shorter wavelength? The concentration of this species appeared to correlate with that of the shorter lived species assigned to germyl radical and also with that of the longer wavelength transient arising probably from the germylene described below. Furthermore, the intensity of the transient in isooctane tends to increase in more viscous solvents such as *n*-dodecane. This implies that this transient species may be a product of the radicals escaped from the cage. Accordingly, the longer lived species may be assigned tentatively to either a germene, **7**, or a coupling product, **8**, of germyl radicals at the ipso position as described in Scheme I.[10]

On the other hand, the transient at the longer wavelength in Table II is tentatively assigned to that of a germylene by comparing its spectral and chemical properties with those reported.[11,12] These transients arising **2** and **3** in THF decayed with first-order kinetics. However, the transient arising from **1** in THF is too weak to measure its decay constant. These kinetic behaviors imply that the germylene reacts with THF in a similar manner as the silylene.[13] In constant inert solvents such as isooctane, the transient decayed with second-order kinetics, suggesting the formation of digermenes.[14] This is substantiated further by quenching experiments with a germylene trapping agent, 2,3-dimethylbutadiene, which gives the corresponding germacyclopentene **10** as shown.[15] The transient from **2** and **3** in THF in the presence of large excess amounts of the diene decayed with pseudo-first-order kinetics, and the rate constants obtained are shown in Table II. These transient species were quenched with oxygen. However, the transient was not quenched by ethanol,[16] and this is in accord with the chemical property observed.

Scheme I

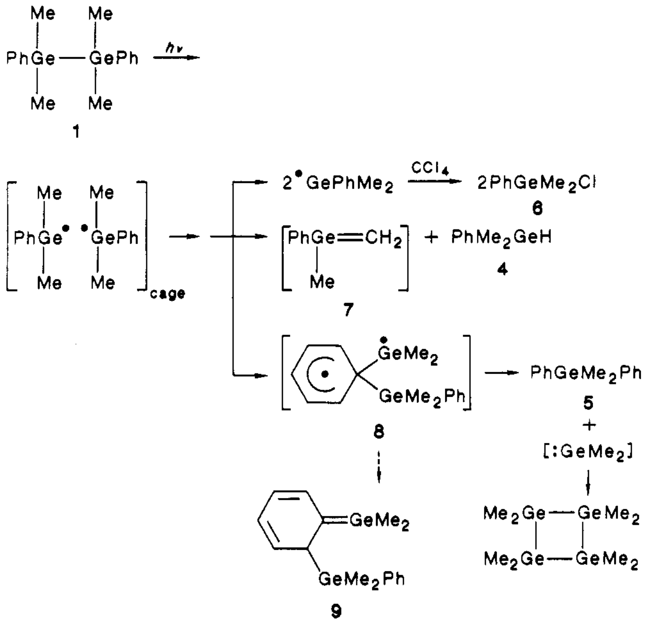
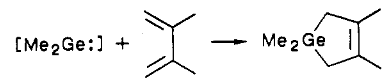


Table II. Rate Constants for Disappearance of the Transient at Longer Wavelength in the Photolysis of 1, 2, and 3 in THF (10^{-3} M)[a,b]

trapping agent	2	3
none (s^{-1})	1.1×10^5	2.0×10^5
2,3-dimethylbutadiene (s^{-1} M^{-1})	4.5×10^6	1.0×10^6
O_2 (s^{-1} M^{-1})	2.3×10^8	1.8×10^8

[a] Absorption maxima: 440 nm for **1**, 450 nm for **2**, and 470 nm for **3**. [b] The absorption of **1** is too weak to determine rate constants.



10

Along with laser flash photolysis experiments, product studies were carried out by photolyzing **1** (0.04 M) with a 110-W medium-pressure Hg arc lamp at room temperature for 3 h under argon in cyclohexane. Together with high-boiling unidentified products containing germanium, phenyldimethylgermane (**4**, 11%), dimethyldiphenylgermane (**5**, 15%), and octamethylcyclotetragermane (4%)[2] were identified in the photolysate by means of GC–MS. The photolysis in THF containing carbon tetrachloride

---

(9) Sakurai, H.; Mochida, K. *J. Chem. Soc. D* **1971**, 1581.

(10) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.

(11) Ando, W.; Tumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, 317.

(12) Konieczny, S.; Jacobs, S. J.; Wilking, J. K. B.; Gasper, P. P. *J. Organomet. Chem.* **1988**, *341*, C17.

(13) (a) Vancik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 4097. (b) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617.

(14) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 1281.

gave phenyldimethylchlorogermane (**6**) quantitatively. As expected, photolysis of **1** in cyclohexane containing a large excess of 2,3-dimethylbutadiene gave the corresponding germylene trapped product 1,1,3,4-tetramethyl-1-germacyclopent-3-ene (**10**, 1%) together with **4** (11%) and **5** (17%).[15] These results are best rationalized by a diradical path described in Scheme I. A similar mechanism has been proposed for the photolysis of the silicon analogue aryldisilane.[1c,e] In contrast to the case of the disilane, we obtained no concrete evidence for the presence of a formal 1,3-germyl migration product, **9**, in the photolysis of **1**. As described above, the transient at 440 nm is more reasonably assigned to that from a germylene rather that from **9**.[17] These differences in photochemical behaviors between the phenylated digermane and disilane may be accounted for by following reasons. The bond dissociation energy of a Ge–C bond is less than that of a Si–C bond,[18] and π-bonding of carbon must be formed more effectively with a silicon atom than with germanium atom. In addition, germylene is virtually more thermodynamically stable than silylene. All these factors favor formation of germylene and **5** over that of **9** in the germanium analogue.

---

(15) Schriewer, M.; Neuman, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

(16) If the transient at 440 nm is due to **9**, this should be quenched by ethanol effectively.

(17) Kira, M.; Sugiyama, H.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 6436.

(18) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.

The Conversion of Chelated η^6-Arene to σ-Aryl Coordination at Tungsten Metal Centers

Judith L. Kerschner and Ian P. Rothwell*[,1]

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

John C. Huffman and William E. Streib

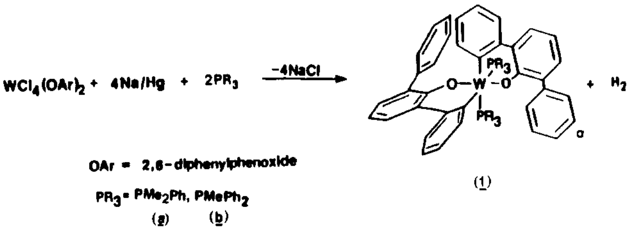
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405

Received March 14, 1988

Summary: Reduction of the mixed chloro–aryloxide *cis*-W(OAr-2,6-Ph$_2$)$_2$Cl$_4$ (OAr-2,6-Ph = 2,6-diphenylphenoxide) with Na/Hg (4 equiv) in the presence of PMePh$_2$ leads to the green, η^6-arene compound W(OAr-2-Ph-6-η^6-C$_6$H$_5$)(OAr-2,6-Ph$_2$)(PMePh$_2$) which converts smoothly on addition of PMePh$_2$ to the bis-cyclometalated compound W(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(PMePh$_2$)$_2$ and H$_2$.

The homogeneous activation of aromatic CH bonds (both inter- and intramolecularly) by transition-metal compounds has received extensive synthetic study over the last 20 years.[2-4] An important mechanistic question that has been the focus of much attention involves the possible importance of η^2-arene intermediates prior to the oxidative addition of aromatic CH bonds at low-valent, electron-rich metal centers.[5-7] Although in some situations the activation of the CH bonds of benzene has been shown to proceed via an η^2-benzene complex,[5] the activation of CH bonds of ethylene has been shown to occur in related systems without prior π-coordination of the olefin.[7] Recently we had reported that the use of the ligand 2,6-diphenylphenoxide (OAr-2,6-Ph$_2$) attached to group 6 metal centers resulted in bonding modes in which the ligand could be chelated to the metal either via an η^6-interaction or else through a metal–carbon σ-bond to the arene side groups.[8,9] In this communication we wish to report our observation of the direct interconversion of these two types of bonding as well as some insights into the mechanism of this interconversion.

Scheme I



(1)

Reduction of toluene solutions of the bis(aryloxide) substrate *cis*-W(OAr-2,6-Ph$_2$)$_2$Cl$_4$[10] with sodium amalgam in the presence of added phosphine donor ligands can lead to a variety of mononuclear products (Scheme I).[11] In the presence of 4 equiv of Na/Hg and PMe$_2$Ph (2 equiv), the reaction proceeds to produce the orange bis-cyclometalated W(IV) compound **1a** in moderate yields.[11,12] The spectroscopic properties of **1a** are consistent with the geometry

---

[1] Camille and Henry Dreyfus Teacher–Scholar, 1985–1990. Fellow of the Alfred P. Sloan Foundation, 1986–1990.

(2) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984.

(3) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113; **1970**, *3*, 139. (c) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (d) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (e) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.

(4) Thompson, M. E.; Baxter, S. M.; Bulb, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(5) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305. (b) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73.

(6) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(7) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(8) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 5840.

(9) (a) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019. (b) Chesnut, R. W.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1988**, *7*, xxxx.

(10) (a) Quignard, F.; Leconte, M.; Bassett, J. M.; Hsu, L-Y.; Alexander, J. J.; Shone, S. G. *Inorg. Chem.* **1987**, *26*, 4272. (b) Quignard, F.; Leconte, M.; Bassett, J. M. *J. Mol. Catal.* **1986**, *36*, 13.

(11) Two intermediates in the reduction of stoichiometry W(OAr-2,6-Ph$_2$)$_2$Cl$_3$(PMe$_2$Ph) and W(OAr-2,6-Ph$_2$)$_2$Cl$_2$(PMe$_2$Ph)$_2$ have been identified and characterized (supplementary material). The reduction of mixed chloro–aryloxides of the type W(OAr)$_4$Cl$_2$ and W(OAr)$_3$Cl$_3$ in the absence of added ligand has been shown to lead to mononuclear and dinuclear compounds of stoichiometries [W(OAr)$_4$]$_n$ and [W(OAr)$_3$]$_n$; n = 1 or 2 depending on the bulk of OAr; see: (a) Schavarien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2161.

(12) Anal. Calcd for WC$_{52}$O$_2$P$_2$H$_{46}$ (**1a**): C, 65.69; H, 5.09; P, 6.52. Found: C, 65.31; H, 5.00; P, 5.89.

0276-7333/88/2307-1871$01.50/0