Studies of Germanium–Platinum Bonds in Bis(aryl-substituted Germyl)platinum Complexes by Laser Flash Photolysis and Chemical Trapping Experiments

Kunio Mochida,*[1] Yusuke Masukawa,[1] Atsuko Yamada,[1] Mai Yanaga,[1] Masato Nanjo,[1]
Hidekazu Arii,[1] Masao Gohdo,[2] and Masanobu Wakasa[2]
[1]*Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588*
[2]*Department of Chemsitry, Graduate School of Science & Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570*

(Received October 1, 2007; CL-071093; E-mail: kuniomochida@gakushuin.ac.jp)

The UV photolysis of bis(triaryl-substituted germyl)platinum complexes, $Pt(Ar_3Ge)_2(PMe_2Ph)_2$ (Ar = Ph, *p*-$C_6H_4SiMe_3$, and *p*-$C_6H_4C(CH_3)_3$) in THF at room temperature results in Ge–Pt bonds homolysis to give the corresponding germyl radicals.

Bis(silyl)- and bis(germyl)platinum(II) complexes are important intermediates in Pt-catalyzed synthetic reactions such as the bis-silylation and bis-germylation of C–C triple and double bonds and dehydrocoupling of group 14 element compounds.[1–4] These complexes also act as useful starting materials for group 14 element-containing compounds. Previously,[5] we reported on photoinduced trans–cis isomerization of *trans*-bis(germyl)platinum(II) at room temperature by irradiation with a xenon lamp ($h\nu > 450$ nm). As a part of our continuous study on germanium–transition metal bond, we have studied photochemical reactions of bis(triaryl-substituted germyl)platinum(II) complexes, $Pt(Ar_3Ge)_2(PMe_2Ph)_2$ (Ar = Ph (**1**),[6] *p*-$C_6H_4SiMe_3$ (**2**),[7] and *p*-$C_6H_4C(CH_3)_3$ (**3**)[8]) by laser flash photolysis and chemical trapping experiments.

Nanosecond laser flash photolysis[9] was performed on degassed solutions containing $Pt(Ph_3Ge)_2(PMe_2Ph)_2$ (**1**) (ca. 10^{-4} M) in THF at 298 K using the fourth-harmonic pulse of a nanosecond Nd:YAG laser as the exciting light source ($\lambda = 266$ nm).

The time profile of the transient absorption, $A(t)$, was measured with THF solutions containing **1**. The $A(t)$ curves were measured over the 300–600-nm wavelength region. The time resolution of the apparatus was about 10 ns. Transient absorption spectra with a peak at 330 nm were obtained (Figure 1). The transient peak at 330 nm decayed under second-order kinetics ($k/\varepsilon l = 8.0 \times 10^5$ at 330 nm) as is shown in Figure 1. Here, k is the rate constant for the second-order decay, ε is the molar extinction coefficient, and l is optical path length, $l = 0.5$ cm) The peak at 330 nm is further substantiated by quenching experiments with germyl radical trapping agents. The pseudo first-order rate constants (k_{obsd}) for decay depended linearly on the concentrations of such trapping agents (Figure 2). The rate constants for the disappearance of the transient at 330 nm obtained for these quenching experiments (oxygen, chloroform, and ethanol) were 1.7×10^9, 0.8×10^7 M^{-1} s^{-1}, and not quenched, respectively.

The experimentally determined decay constants of **1** are summarized in Table 1. The transient absorption at 330 nm is reasonably assigned to that of the triphenylgermyl radical $Ph_3Ge^{\bullet}$ from comparison of spectral characteristics with those of the germyl radical reported.[10]

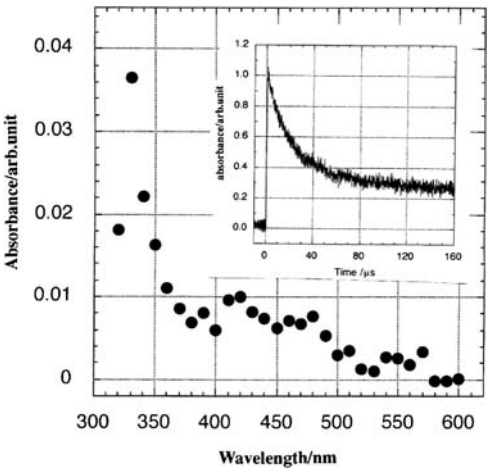

Figure 1. Transient absorption spectrum observed at 1 μs after photoexcitation of **1** (10^{-4} M) in degassed THF solution. Insert; $A(t)$ curve observed at 330 nm.

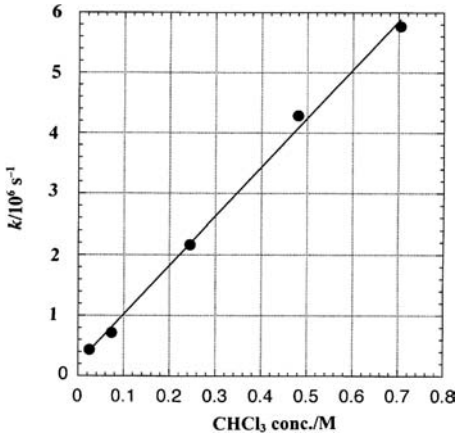

Figure 2. Quenching rate constants for the disappearance at 330 nm in **1** containing various concentrations of chloroform.

Laser flash photolysis studies of **2** and **3** were also carried out. Transient peaks observed and their experimentally determined rate constants are summarized in Table 1.

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 30 min under argon in THF. The photolysis of **1** containing chloroform[11] as a germyl radical trapping reagent gave triphenylchlorogermane in 84% yield together with tetrachloroethane (35% yield).

Table 1. Quenching rate constants for disappearance of the transient at 330 nm in the photolysis of **1–3** in THF (10^{-4} M)[a]

Complex	λ_{max}/nm	$(k/\varepsilon l)/s^{-1}$[b]	Rate constant/s^{-1} M^{-1}		
			O_2	$CHCl_3$	EtOH
1	330	8.0×10^5	1.7×10^9	0.8×10^7	NQ (34–696 mM)
2	340	3.0×10^5	5.4×10^9	1.3×10^7	NQ (19–699 mM)
3	340	7.9×10^5	6.4×10^9	1.3×10^7	NQ (18–698 mM)

[a]Measured in THF. [b]k is the rate constant of second-order decay, ε is the corresponding molar extinction coefficient, and l is optical peth length.

The formation of tetrachloroethane is a result of the dimerization of dichloromethyl radical produced by abstraction of chlorine atoms from chloroform with germyl radicals (eqs 1 and 2).

$$\mathbf{1} \xrightarrow{h\nu} Ph_3Ge\cdot \quad (1)$$

$$Ph_3Ge\cdot + CHCl_3 \longrightarrow Ph_3GeCl + \cdot CHCl_2 \quad (2)$$

This paper is dedicated to the memory of Professor Yoshihiko Ito.

References and Notes

1 a) R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359. b) I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435. c) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221.

2 a) R. West, in *Comprehensive Organometallic Chemistry*, ed. by G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, New York, **1982**, Vol. 2, p. 376. b) R. West, in *Comprehensive Organometallic Chemistry*, ed. by G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, New York, **1995**, Vol. 2, p. 77. c) I. Ojima, in *The Chemsitry of Organic Silicon Compounds*, ed. by S. Patai, Z. Rappoport, John Wiley & Sons, New York, **1989**. d) T. D. Tilley, in *The Silicon-heteroatom Bond*, ed. by S. Patai, Z. Rappoport, John Wiley & Sons, Chichester, **1991**. Chapt. 9. e) S, Murai, N. Chatani, *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 421 and references cited therein. f) H. Yamashita, M. Tanaka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 403 and references cited therein. g) M. Suginome, H. Oike, S.-S. Park, Y. Ito, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289 and references cited therein. h) M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *685*, 218. i) H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita, A. Kunai, *J. Am. Chem. Soc.* **2003**, *125*, 6638. j) J. Terao, A. Oda, N. Kambe, *Org. Lett.* **2004**, *6*, 3341.

3 a) J. Chatt, C. Eaborn, P. N. Kappor, *J. Chem. Soc. A* **1970**, 881. b) J. Chatt, C. Eaborn, S. D. Ibekwe, P. N. Kappoor, *J. Chem. Soc. A* **1970**, 1343. c) C. Eaborn, T. N. Metham, A. Pidcock, *J. Organomet. Chem.* **1977**, *131*, 377. d) T. Kobayashi, T. Hayashi, H. Yamashita, M. Tanaka, *Chem. Lett.* **1988**, 1411. e) T. Kobayashi, T. Hayashi, H. Yamashita, M. Tanaka, *Chem. Lett.* **1989**, 467. f) H. Yamashita, T. Kobayashi, T. Hayashi, M. Tanaka, *Chem. Lett.* **1990**, 1447. g) M. Tanaka, Y. Uchimaru, H. J. Lautenschlager, *Organometallics* **1991**, *10*, 16. h) S. L. Grundy, R. D. Holmes-Smith, S. R. Stobart, M. A. Williams, *Inorg. Chem.* **1991**, *30*, 3333. i) H. Yamashita, M. Tanaka, M. Goto, *Organometallics* **1992**, *11*, 3227. j) R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 1917. k) M. J. Michalczyk, C. A. Recatto, J. C. Calabrese, M. J. Fink, *J. Am. Chem. Soc.* **1992**, *114*, 7955. l) S. Sakaki, M. Ieki, *J. Am. Chem. Soc.* **1993**, *115*, 2373. m) T. Hikida, K. Onitsuka, K. Sonogashira, T. Hayashi, F. Ozawa, *Chem. Lett.* **1995**, 985. n) F. Ozawa, T. Hikida, *Organometallics* **1996**, *15*, 4501. o) F. Ozawa, T. Hikida, K. Hasebe, T. Mori, *Organometallics* **1998**, *17*, 1018. p) F. Ozawa, J. Kamite, *Organometallics* **1998**, *17*, 5630. q) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, H. Maciejewski, *Organometallics* **1998**, *17*, 5599. r) Y. Kang, S. O. Kang, J. Ko, *Organometallics* **1999**, *18*, 1818. s) F. Ozawa, *J. Organomet. Chem.* **2000**, *611*, 332. t) D. Kalt, U. Schubert, *Inorg. Chim. Acta* **2000**, *306*, 211. u) M. Tanabe, K. Osakada, *J. Am. Chem. Soc.* **2002**, *124*, 4550. v) Y.-J. Kim, E.-H. Choi, S. W. Lee, *Organometallics* **2003**, *22*, 3316.

4 a) H. Yamashita, T. Kobayashi, M. Tanaka, J. A. Samuels, W. E. Streib, *Organometallics* **1992**, *11*, 2330. b) H. Komoriya, M. Kako, Y. Nakadaira, K. Mochida, *Organometallics* **1996**, *15*, 2014. c) H. Komoriya, M. Kako, Y. Nakadaira, K. Mochida, *J. Organomet. Chem.* **2000**, *611*, 420. d) K. Mochida, T. Wada, W. Hatanaka, M. Nanjo, A. Sikine, Y. Ohashi, M. Sakamoto, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 123. e) K. Mochida, K. Hirakue, K. Suzuki, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1023. f) K. Mochida, H. Karube, M. Nanjo, Y. Nakadaira, *J. Organomet. Chem.* **2005**, *690*, 2967. g) K. Mochida, H. Karube, M. Nanjo, Y. Nakadaira, *Organometallics* **2005**, *24*, 4734.

5 K. Mochida, T. Fukushima, M. Suzuki, W. Hatanaka, M. Takayama, Y. Usui, M. Nanjo, K. Akasaka, T. Kudo, S. Komiya, *J. Organomet. Chem.* **2007**, *692*, 395.

6 K. Mochida, T. Wada, K. Suzuki, W. Hatanaka, Y. Nishiyama, M. Nanjo, A. Sekine, Y. Ohashi, M. Sakamoto, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 123.

7 **2** (trans isomer/cis isomer = 8/1) ^{1}H NMR (δ, C_6D_6) 0.22 (s), 0.27 (s), 0.89 (d), 1.28 (vt), 7.16–7.89 (m); ^{31}P NMR (δ, C_6D_6) −10.52 (J_{Pt-P} = 2555.1 Hz), −12.43 (J_{Pt-P} = 2020.5 Hz).

8 Trans isomer **3**: ^{1}H NMR (δ, C_6D_6) 0.39 (s, 6H), 1.26 (s, 9H), 7.19 (s, 5H), 7.22–7.72 (m, 4H); ^{31}P NMR (δ, C_6D_6) −10.34 (J_{Pt-P} = 2650 Hz).

9 M. Wakasa, *J. Phys. Chem. B* **2007**, *111*, 9434.

10 K. Mochida, M. Wakasa, Y. Sakaguchi, H. Hayashi, *J. Am. Chem. Soc.* **1987**, *109*, 7942.

11 H. Sakurai, K. Mochida, *J. Chem. Soc. D* **1971**, 1581.

Published on the web (Advance View) December 15, 2007; doi:10.1246/cl.2008.62