Photochemistry of Transition Metal Germylenes and Metallacycles

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Summary: Group 10 metal germylene complexes of general formula $(R_3P)_2MGeQ_2$ are found to be highly photosensitive. Ambient fluoresent lighting causes complete decomposition of nickel germylene species in less than one minute in the presence of germylene traps. The formation of metallacycle $(Et_3P)_2Pt(\mu\text{-}\eta^2\text{-}H_2CO)Ge[N(SiMe_3)_2]_2$ and the photochemical cycloreversion reaction are also reported.

Introduction

The importance of photochemical reaction mechanisms in the chemistry of M−ER$_2$ (E = Si, Ge, Sn) complexes was clearly demonstrated by Pannell in 1974.[1a] Photolysis of CpFe(CO)$_2$SiMe$_2$SiMe$_3$ was observed to proceed with the apparent ejection of :SiMe$_2$. This result has attracted considerable attention, and a great deal of effort has gone into understanding the details of this mechanism.[1−3] Turner et al. have proposed a photoinitiated loss of CO, followed by migration of −SiMe$_3$ to the iron center, resulting in an intermediate, CpFe(CO)(SiMe$_2$)(SiMe$_3$), containing both silyl and silylene ligands.[3] Spectroscopic evidence indicated that :SiMe$_2$ is lost via a second photolytic event; however, the :SiMe$_2$ itself could not be directly trapped. The proposal of the second photolytic event as the mechanism for the loss of :SiMe$_2$ provided new insight into the mechanism for this process. In other respects, Turner et al. concurred with the previous mechanisms proposed by Pannell et al.[1] and Tobita and Ogino et al.[2] Quantitative trapping of the silylene complexes has been difficult however, and rapid isomerization to species such as 1-methylsilene has been proposed to explain this apparent inconsistency. In a related germyl system studied by Satgé et al., photolytic dissociation of a proposed germylene intermediate was also observed and quantitative trapping could be achieved by quinone or dimethyl disulfide.[4] Similar chemistry appears to be operative in the transition metal catalyzed rearrangement of oligosilanes observed by Pannell et al.[1b] We are aware of one report of the photolytic dissociation of an isolable, stable complex containing a germylene or silylene ligand. Zybill et al. have isolated base-stabilized silylene complexes of iron and chromium and found that photolysis dissociates the silylene with the concomitant formation of polysilane.[5]

The reactivity reported for M−ER$_2$ systems upon exposure to intense UV irradiation from high-pressure mercury lamps raises the issue of the general sensitivity of such complexes to ambient light and the effects of this exposure on chemistry explored to date. For example, over 25 years ago Kumada et al. reported catalytic reactions using Ni and Pt closely related to those observed by Pannell. Given the recent studies discussed above, it now appears that this chemistry may involve photochemical dissociation of silylenes.[6] Another area of endeavor that has invoked silylenes and germylenes as potential intermediates is the area of dehydrocoupling to form polysilanes and polygermanes.[7] Other types of isomerizations and disproportionation reactions that could have important photochemical steps have also been observed.[8] The following related questions arise: (1) in general, how sensitive are M−ER$_2$ linkages to photolytic cleavage? (2) can and does this process act as an important mechanistic step under ambient light conditions? (3) how photosensitive are metallacycles generated from L$_2$M−ER$_2$ complexes?

Experimental Section

All manipulations were performed using air-free technique and dry, deoxygenated solvents. Toluene, pentane, and benzene were degassed and dried over sodium benzophenone ketyl. Acetonitrile was refluxed over P_2O_5 and distilled onto 4 Å molecular sieves. Paraformaldehyde and benzil were degassed in vacuo and stored under dinitrogen in a drybox. The following complexes were prepared according to previously published procedures: $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (**1**),[9] $(Et_3P)_2NiGe[N(SiMe_3)_2]_2$ (**2**),[10] and $Ge[N(SiMe_3)_2]_2$.[11] ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in the listed deuterated solvents

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on a Bruker AM-360 spectrometer (360.1, 90.6, and 145.8 MHz) and referenced to residual protons, solvent carbons, and external 85% H_3PO_4 in D_2O, respectively. IR spectra were recorded on a Nicolet 5DXB as Nujol mulls or KBr disks. All compounds reported are moisture sensitive to hydrolysis reactions of the $Ge[N(SiMe_3)_2]_2$ ligand.

$Ph_2C_2O_2Ge[N(SiMe_3)_2]_2$ (2). Benzil (0.261 g, 0.1.24 mmol) was added to a stirred solution of $Ge[N(SiMe_3)_2]_2$ (0.489 g, 1.24 mmol) in 20 mL of benzene. After 2 h, the benzene was removed in vacuo. The ^1H NMR spectrum revealed quantitative formation of **2**. Analytically pure material of this highly soluble compound was obtained by recrystallization from cold pentane, resulting in 80 mg of off-white crystals (11% yield). ^1H NMR (C_6D_6): δ 7.67 (d, 4H, *o*-C_6H_5), 7.07 (pseudo-t, 4H, *m*-C_6H_5), 6.96 (t, 2H, *p*-C_6H_5), 0.37 (s, 36H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.89 (Ph*C*), 135.91 (*i*-C_6H_6), 128.89, 128.55, 127.85, 5.29 (CH_3). MS (70 eV, EI): *m/z* (%) 604 (100) [M^+]. Anal. Calcd for $C_{26}H_{46}GeN_2O_2Si_4$: C, 51.74; H, 7.68; N, 4.64. Found: C, 51.84; H, 7.54; N, 4.56.

$(Et_3P)_2Pt(\mu\text{-}\eta^2\text{-}H_2CO)Ge[N(SiMe_3)_2]_2$ (5). $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (250 mg, 0.30 mmol) and paraformaldehyde (11 mg, 0.37 mmol) were dissolved in 5 mL of benzene. After stirring the solution for 4 h, the excess paraformaldehyde was removed by filtration and all volatiles were removed in vacuo. The solid was washed with two 0.5 mL portions of acetonitrile, resulting in 179 mg of an off-white powder (69% yield). ^1H NMR (C_6D_6): δ 0.68 (s, 36H, $Si(CH_3)_3$), 0.74 (m, 9H, CH_2CH_3), 0.86 (m, 9H, CH_2CH_3), 1.21 (m, 6H, CH_2CH_3), 1.64 (m, 6H, CH_2CH_3), 4.87 (dd w/ ^{195}Pt satellites, $^3J_{P-H} = 2.70$ Hz, $^3J_{P-H} = 4.20$ Hz, $^2J_{Pt-H} = 39$ Hz, 2H, H_2CO). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 52.9 (dd w/^{195}Pt satellites, $^2J_{P-C} = 4.9$ Hz, $^2J_{P-C} = 81.0$ Hz, $^1J_{Pt-C} = 800$ Hz, $Pt-CH_2O$), 21.1 (m, CH_2CH_3), 16.2 (m, CH_2CH_3), 9.10 (m, CH_2CH_3), 7.73 (m, CH_2CH_3), 7.20 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.40 (d w/^{195}Pt satellites, $^2J_{P-P} = 9.3$ Hz, $^1J_{Pt-P} = 2183$ Hz), 4.80 (d w/^{195}Pt satellites, $^2J_{P-P} = 9.3$ Hz, $^1J_{Pt-P} = 1687$ Hz). Anal. Calcd for $C_{25}H_{68}GeN_2OP_2PtSi_4$: C, 35.13; H, 8.02; N, 3.28. Found: C, 34.85; H, 8.04; N, 3.22.

X-ray Crystal Structure Determination of 5. A yellow, multifaceted crystal of dimensions 0.40 × 0.40 × 0.36 was mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 153(2) K; the detector was placed at a distance of 5.059 cm from the crystal. A full sphere of data consisting of a total of 2132 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s/frame. The frames were integrated with the Siemens SAINT software package with a narrow frame algorithm. The integration of the data using a primitive monoclinic unit cell yielded a total of 79 643 reflections to a maximum 2θ value of 58.9°, of which 20 336 were independent. The final cell constants $a = 22.4453(2)$ Å, $b = 15.6770(2)$ Å, $c = 23.31870(10)$ Å, and $\beta = 110.84°$ were based on the *xyz* centroids of 8192 reflection above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption using SADABS. The structure was solved and refined with the Siemens SHELXTL (version 5.03) software package, using the space group $P2(1)/n$ with $Z = 8$ for the formula $C_{25}H_{68}N_2O_4P_2Si_4GePt$. A check for additional crystallographic symmetry was performed with the assistance of the PLATON suite of programs. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The final full matrix refinement based on F^2 converged at R1 = 0.0227 and wR2 = 0.0495 (based on $I > 2\sigma$ data); R1 = 0.0292 and wR2 = 0.0531 (based on all data). The largest peak/hole in the final difference map was $+1.53/-1.05$ e/Å^3, associated with Pt.

General Conditions for UV Lamp Photolysis Reactions. Samples in Pyrex glassware were placed 15 cm from a long-wavelength UV lamp, model B-100 AP purchased from UVP, Upland, CA. This lamps emits radiation between 320 and 400 nm with a maxima of emission at 365 nm.

Calculational Methods. Density functional calculations were performed using standard routines included in Spartan 5.0 (BP86/DN**) and Jaguar 3.5 (pseudospectral BP86/LACVP**).[12,13] BP86 is a nonlocal functional that employs Becke's 1988 gradient correction[14] to Slater's exchange functional,[15] and Perdew's 1986 gradient correction[16] to the Perdew−Zunger local correlation functional.[17] DN** is a numerical all-electron basis set of split-valence + polarization quality (all atoms). LACVP** is a split valence + polarization basis set that employs an effective core potential for Ni (Ne core)[18] and Ge (Ar core)[19] and uses the 6-31G** basis for all remaining atoms.[20]

Results and Discussion

The syntheses of three-coordinate group 10 metallogermylene complexes of the general stoichiometry $(R_3P)_{3-x}M(GeR'_2)_x$ ($x = 1, 3$) have been reported by a number of research groups.[21,22] Over the past several years, we have expanded upon this foundation by exploring the reaction chemistry of group 10 transition metal germylenes of general formula $(R_3P)_2MGeQ_2$ (R = Et, Ph; Q = $N(SiMe_3)_2$, $CH(SiMe_3)_2$, $(2,4,6\text{-}(CF_3)_3-C_6H_2)$; M = Ni, Pd, Pt).[9,10,23,24] $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (**1**) has been found to have a very versatile chemistry, ranging from reversible additions of hydrogen and carbon dioxide to dehydrocoupling reactions of germanes. **1** is thermally stable in a wide variety of organic solvents, including ethers, and is fairly stable to stoichiometric equivalents of germylene traps such as benzil,[25] indicating that the germylene ligand is not thermally labile at 20 °C. In the presence of 4 equiv of benzil, a 0.24 mmol toluene solution of **1** in Pyrex glassware carefully protected from light requires 113 h before 50% of the germylene has been trapped as $Ph_2C_2O_2Ge[N(SiMe_3)_2]_2$ (**2**) (eq 1). The observed thermal reaction rate is dependent on the benzil concentration, suggesting that the trapping is base-assisted and/or that

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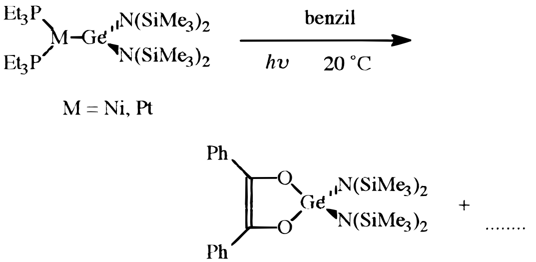
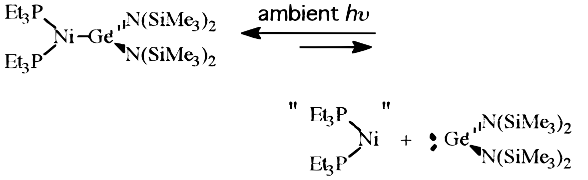


2 (1)

the $(Et_3P)_2Pt$ fragment and benzil compete for the free germylene in solution. However, exposure of the reaction to ambient light (34 W fluorescent laboratory lighting) results in 91% conversion to trapped germylene after 94 h. Photolysis using a long-wavelength UV lamp did not increase the rate of reaction over that observed from the ambient laboratory light.

The photosensitivity of analogous nickel germylene complexes was also explored. A 0.24 mmol toluene solution of $(Et_3P)_2NiGe[N(SiMe_3)_2]_2$ (**3**) containing 4 equiv of benzil was stirred for 1 h while exposed to ambient light; Quantitative conversion to **2** was observed by ^1H NMR. Over the same time period, a control reaction protected from light showed a 40% conversion. An NMR tube charged with the same ratio of reactants and 0.5 mL of frozen toluene-d_8 was thawed in a darkened room and placed in an NMR spectrometer. Under these conditions, a 40% conversion to trapped germylene was also observed. Upon exposing the NMR tube to room light (fluorescent lights) for 20 s, the reaction immediately proceeded to completion.

The above experiment demonstrates that complex **3** is highly photosensitive. Even ambient room light can set up a rapid equilibrium in which free germylene is generated in solution (eq 2).



4 (2)

Recombination of the germylene with the metal center occurs very rapidly, and no buildup of germylene is observed by ^1H NMR spectroscopy. The bis(trimethylsilyl)amide substitution stabilizes the germylene in the free form, $Ge[N(SiMe_3)_2]_2$ (**4**). Thus, in the absence of germylene traps, complex **3** is stable in solution and can be isolated by routine methods despite the presence of the rapid equilibrium. However, the presence of the rapid equilibrium dominates the observed chemistry of **3**, and reactions of $(Et_3P)_2Ni$ and $Ge[N(SiMe_3)_2]_2$ occur instead of chemistry at the Ni–Ge nexus when reactions are run at 20 °C while exposed to ambient light.

UV–vis spectra of complexes **1** and **3** were obtained to explore the origin of the photosensitivity. Three broad transitions were observed for **1** at 290 nm ($\epsilon = 7600$), 329 nm ($\epsilon = 6100$), and 400 nm ($\epsilon = 1600$). Complex **3** exhibits a similar set of transitions, some of which are shifted to lower energy, namely, 290 nm ($\epsilon = 7800$) and 384 nm ($\epsilon = 8030$). The peak at 384 nm is quite asymmetric with a long tail extending to ~500 nm. Generally for D_{3h} ML_3 d^{10} complexes,[26] the transitions are assigned as n(d) to $(n+1)$p transitions. Electrons in the filled metal d orbitals are excited into the metal p_z LUMO. The transitions observed for **1** are very similar to those observed for the ML_3 complex $Pt(PPh_3)_3$ in terms of both energy and extinction coefficient. However, the LUMO calculated for **1** using PM3 level semiempirical calculations or for the model complex $(H_3P)_2NiGe[N(SiH_3)_2]_2$ using density-functional calculations (pBP-DN**) is a π-antibonding hybrid of metal p and d with the empty Ge p orbital.[27] Transitions to the LUMO likely arise from the filled, nonbonding metal d orbitals, in analogy to the D_{3h} ML_3 d^{10} complexes, weakening the M–Ge bond and increasing the likelihood of dissociation. The greater sensitivity of the nickel complex may be explained by the initially weaker M–Ge bond strength of the first-row metal and the shift of the transitions into the visible region.

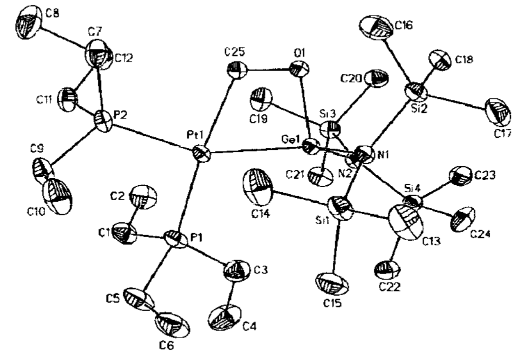


Figure 1. ORTEP diagram for **5** showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Pt(1)–C(25), 2.109(2); Pt(1)–P(1), 2.3241(6); Pt(1)–P(2), 2.3032(6); Pt(1)–Ge(1) 2.4368(3); Ge(1)–O(1), 1.834(2); C(25)–O(1), 1.445(3); Ge(1)–N(1), 1.894(2); Ge(1)–N(2), 1.889(2); Ge(1)–Pt(1)–C(25), 64.75(6); Pt(1)–C(25)–O(1), 109.3(2); C(25)–O(1)–Ge(1), 95.97(13); O(1)–Ge(1)–Pt(1), 85.22(5); P(1)–Pt(1)–Pt(2), 96.94(2); N(1)–Ge(1)–N(2), 108.44(9).

Interestingly, the closely related silylene complexes, $(Cy_3P)_2Pt{=}SiMes_2$ and $(^iPr_3P)_2Pt{=}SiMes_2$, are generated via a *photochemical* reaction.[22] Unlike $Ge[N(SiMe_3)_2]_2$ present in **1** and **2**, $:SiMes_2$ is not itself a stable compound. Thus, if the new platinum silylenes are photochemically active and the Pt–Si bond is broken, the recombination rate with the L_2Pt fragment must be much faster than other possible decomposition reactions of the $:SiMes_2$ fragment. The observed decomposition of both silyene complexes over time in solution is very similar to the behavior of the metal germylene complexes in the presence of a germylene trap.

Elucidation of the photochemistry for complexes **1** and **3** shed considerable light on the binding and decomposition reactions of formaldehyde noted in this system.[28] **1** was found to react with 1/3 equiv of paraformaldehyde to yield the four-membered metallacycle $(Et_3P)_2Pt(\mu\text{-}\eta^2\text{-}H_2CO)Ge[N(SiMe_3)_2]_2$ (**5**) (Figure 1). This is a rare example of a μ-η^2-formaldehyde complex in which a metal–metal bond exists and is the first example where

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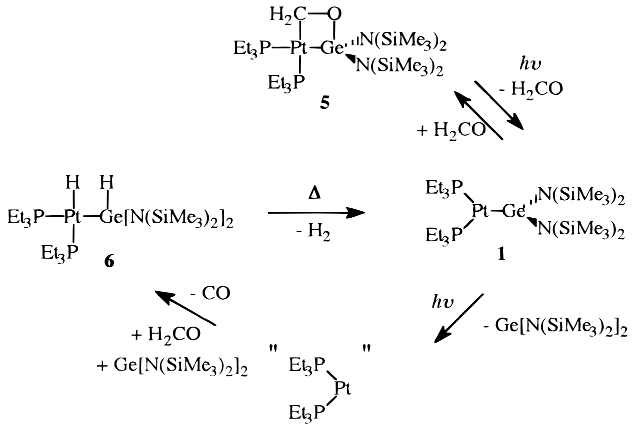
the metal bound to oxygen is not zirconium.[29,30] **5** was observed to decompose very slowly in solution when exposed to ambient light, yielding **1**, $(Et_3P)_2Pt(H)Ge(H)[N(SiMe_3)_2]_2$ (**6**), H_2, and CO. However, upon exposure to a long-wavelength UV lamp, **5** rapidly converted to a mixture of **1**, $(Et_3P)_2Pt(H)Ge(H)[N(SiMe_3)_2]_2$ (**6**), H_2, and CO. The use of long-wavelength UV light does not enhance the rate of Pt−Ge bond breaking in **1** over that observed under ambient light, so the observed rate enhancement must be related to greater sensitivity of the metallacycle in **5**. If **5** is photolyzed in a sealed system, the CO partial pressure can rise high enough to induce the formation of $(Et_3P)_2Pt(CO)_2$ and $H_2Ge[N(SiMe_3)_2]_2$ from **6**.[10] When this experiment was performed in the presence of the germylene trap benzil, **2** was observed in addition to **1** and **6**, indicative of a competition between formaldehyde and benzil for the reactive fragments generated from the photodissociation of the Pt−Ge bond. Scheme 1 summarizes the proposed pathway for the photodecomposition of **5**. The chemistry observed is reminiscent of the photocleavage of 1,2-digermacyclobutanes recently reported by Apeloig et al.[31]

In summary, the first evidence that transition metal germylenes can be highly photosensitive to fluorescent laboratory light is reported. The implications for this type of light sensitivity are wide ranging. For example, isolation of transition metal complexes containing unstable ER_2 (E = Si, Ge) species would be impossible to achieve under ambient light conditions if the $M-ER_2$ are highly photosensitive. In addition, a variety of transition metal catalyzed reactions of silanes and germanes have been proposed to proceed via $M-ER_2$ intermediates. Clearly, these intermediates could be photosensitive, leading to loss of ER_2 in key mechanistic steps. Finally, attempts to use metal germylenes,[32] silylenes,[33] and stannylenes[34] to activate and modify organic substrates need to take into account, and ideally exploit, the type of cycloreversion reactions demonstrated for complex **5**.

Scheme 1. Proposed Pathway for Photolytic Decomposition of 5



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Supporting Information Available: Crystallographic data for **1** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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