Synthesis and Reactivity of a Novel Palladium Germylene System

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The synthesis of three novel Pd germylene complexes is reported. $(Ph_3P)_2PdGe[N(SiMe_3)_2]_2$ (**1**) was synthesized by ligand substitution of $(Ph_3P)_4Pd$, whereas $(Et_3P)PdGe[N(SiMe_3)_2]_2$ (**2**) and $\{dppePdGe[N(SiMe_3)_2]_2\}_2$ (**3b**) (dppe = (diphenylphosphino)ethane) were synthesized by photolytic reduction of their corresponding phosphine oxalato complexes followed by addition of the germylene ligand. In solution, **3b** exists in equilibrium with the monomeric $dppePdGe[N(SiMe_3)_2]_2$ (**3a**). The germylene ligand of **2** was found to be 1 order of magnitude more labile than the analogous Pt system and 2 orders of magnitude less labile than the analogous Ni system. The reactivity of these new palladium germylenes toward O_2 is described.

Introduction

Germylenes are divalent germanium species. They contain a singlet lone pair capable of interacting with metals in a dative bonding sense, as well as an empty π-acidic p orbital localized on the Ge^{II} center.[1−6] The majority of the chemistry of the M−Ge bond has been studied in the context of Ge^{IV} species: germylation reactions utilizing a metal catalyst,[7−14] the metal-catalyzed formation of Ge-containing polymers,[15] or cross-coupling reactions.[16] However, the close proximity of the electron-rich metal and the Lewis acidic Ge^{II} suggests a variety of addition reactions should be

possible across the metal−germylene bond. This bond-forming reaction could occur with the breaking of the M−Ge bond, oxidation of the metal, and/or oxidation of the germanium center.

To study these addition reactions, we have explored the reactivity of the stable germylene ligands $Ge[N(SiMe_3)_2]_2$ and $Ge[CH(SiMe_3)_2]_2$, first reported by Lappert,[17,18] bound to nickel and platinum. Various small organic and inorganic molecules will react with platinum germylenes such as $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ to form four-membered rings. Subsequent insertion chemistry of these rings leads to the formation of novel five- and six-membered metallacyclic structures.[19,20] Reductive elimination of these metallacycles could be used to generate novel heteroatomic ring systems; however, thus far we have been unsuccessful in promoting such eliminations in the Pt system. We have also studied the reactivity of the analogous Ni germylene complexes. In this system the germylene ligand was found to be extremely labile.[21] This lability generally resulted in reagents reacting directly with the germylene ligand.[22]

On the basis of previous results using Pt and Ni, we decided to explore the analogous Pd system. Metallacycles formed from Pd complexes of the general structure $(R_3P)_2PdGeR'_2$ should be more prone to reductive elimination, allowing the heterocycles to be removed from the metal. In addition, four-membered metallacycles containing Pt−C bonds have not been amenable to additional insertions, whereas Pd−C bonds have a

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well-defined and facile insertion chemistry.[23-25] Finally, the Pd−Ge bond should be less labile than the Ni−Ge bond of the Ni complex, thus improving the chances for observing reactivity at the Pd−Ge nexus.

No direct Pd analogues of three-coordinate (R$_3$P)$_2$-MGeR'$_2$ systems exist. In fact, complexes of palladium with a germylene ligand are extremely rare, with only two examples in the literature. Lappert and co-workers reported the homoleptic complex Pd{Ge[N(SiMe$_3$)$_2$]$_2$}$_3$, which was found to react with CO to form the trinuclear cluster Pd$_3$(CO)$_3$(μ-Ge[N(SiMe$_3$)$_2$]$_2$)$_3$.[26,27] However, no additional reactivity of these species has been reported. There are no crystallographically characterized examples of palladium germylene complexes in the literature.

Herein the synthesis and spectroscopic and structural characterization of three novel palladium germylene complexes are reported. Two of the complexes are of the general formula (R$_3$P)$_2$PdGe[N(SiMe$_3$)$_2$]$_2$. The third contains a bidentate phosphine ligand. Such complexes may ultimately be important for controlling the desired reductive-elimination and insertion chemistry. As an initial test of the chemistry of these new complexes, the lability of the germylene ligand and the reactivity of the complexes with dioxygen was explored. These results were compared to previous studies using analogous Ni and Pt systems.[19,21]

Experimental Section

All manipulations of air-sensitive complexes were performed using air-free techniques. Benzene, toluene, THF, and benzene-d_6 were dried over sodium benzophenone ketyl and degassed. Acetonitrile was dried over 4 Å molecular sieves and degassed. PdCl$_2$, (PPh$_3$)$_4$Pd, PPh$_3$, PEt$_3$, and dppe were purchased from Strem and used as received. (cod)PdCl$_2$,[28] (dppe)PdCl$_2$,[29] (dppe)PdC$_2$O$_4$,[30] and Ge[N(SiMe$_3$)$_2$]$_2$[31] were prepared according to the literature procedures. An improved preparation for *trans*-(Et$_3$P)$_2$PdCl$_2$ is included.[32] The preparation for (Et$_3$P)$_2$-PdC$_2$O$_4$ was based upon the approach of Landis et al.,[33] omitting the refluxing step. Ag$_2$C$_2$O$_4$ (*Caution! explosive when heated*) was made by reaction of K$_2$C$_2$O$_4$ and AgCl$_2$ in water.[30] ^{1}H, ^{31}P, and ^{13}C NMR spectra were acquired on a Varian 400 MHz instrument (400, 161.9, and 100.6 MHz, respectively) or on a Varian 300 MHz instrument (300 MHz ^{1}H and 121.5 MHz ^{31}P). ^{31}P NMR spectra are referenced to H$_3$PO$_4$ by using an external secondary standard of PPh$_3$ in benzene-d_6 (assigned to −5.0 ppm).[34] Photolysis experiments were performed using a Blak-Ray long-wave (365 nm) ultraviolet lamp. All ger-

mylene-containing complexes are air and moisture sensitive to hydrolysis of the Ge−N bonds of the ligand.

***trans*-(Et$_3$P)$_2$PdCl$_2$.** (cod)PdCl$_2$ (4.75 g, 0.017 mol) was dissolved in 200 mL of methylene chloride. PEt$_3$ (5 mL, 0.034 mol) was then added to the orange solution, which rapidly became yellow. The solution was stirred for 2 h, and then the volume was reduced in half. The solution was filtered, and the volatiles were evaporated from the filtrate, giving 6.28 g (92%) of shiny yellow microcrystals. ^{1}H NMR (CDCl$_3$): δ 1.19 (m, 18H, CH$_3$) 1.86 (m, CH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.16 (s).

(Ph$_3$P)$_2$PdGe[N(SiMe$_3$)$_2$]$_2$ (1). (Ph$_3$P)$_4$Pd (0.5 g, 0.43 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.170 g, 0.43 mmol) were stirred in 20 mL of benzene for 5 h. The volatiles were then evaporated, giving an orange-brown solid. Additional Ge[N(SiMe$_3$)$_2$]$_2$ (0.08 g, 0.20 mmol) was added to the crude product, and the mixture was then recrystallized from THF/acetonitrile to give 313 mg (71%) of orange microcrystalline **1**. ^{1}H NMR (C$_6$D$_6$): δ 0.48 (s, 36H, SiMe$_3$), 7.01 (m, 18H, Ph) 7.47 (m, 12H, Ph). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 28.84 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 5.95 (s, SiMe$_3$), 128.86 (s, Ph), 134.25 (t, J_{C-P} = 8.7 Hz), 138.02, (s, Ph). Anal. Calcd for C$_{48}$H$_{66}$GeN$_2$P$_2$PdSi$_4$: C, 56.28; H, 6.49; N, 2.73. Found: C, 56.15; H, 6.53; N, 2.59.

(Et$_3$P)$_2$PdGe[N(SiMe$_3$)$_2$]$_2$ (2). A two-necked 250 mL round-bottom flask was charged with (Et$_3$P)$_2$PdC$_2$O$_4$ (2.0 g, 4.6 mmol) and 80 mL of benzene. Excess PEt$_3$ (10 mL) was then added, and the flask was sealed with a rubber septum and a needle valve. The clear liquid with off-white solid suspension was frozen and the flask evacuated. After thawing the flask was irradiated while the contents were stirred in a water bath for 7 h. The solution gradually became yellow, with a yellow solid suspension. The solution was degassed three times during the photolysis and again at the end. A solution of Ge[N(SiMe$_3$)$_2$]$_2$ (2.012 g, 5.1 mmol) in 12 mL of benzene was then added via steel cannula. The solution was stirred for 16 h and gradually became red with no solids present. The solvent was evaporated, and the crude red-brown solid was recrystallized from THF/ acetonitrile to yield orange microcrystalline **2** (2.38 g, 70% yield). ^{1}H NMR (C$_6$D$_6$): δ 0.51 (s, 36H, SiMe$_3$), 1.05 (m, 18H, CH$_3$) 1.40 (m, 12H, CH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 15.31 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 5.95 (s, SiMe$_3$) 9.48 (s, CH$_3$) 21.84 (t, CH$_2$). Anal. Calcd for C$_{24}$H$_{66}$GeN$_2$P$_2$PdSi$_4$: C, 39.16; H, 9.04; N, 3.81. Found: C, 39.28; H, 9.14; N, 3.61.

{(dppe)PdGe[N(SiMe$_3$)$_2$]$_2$}$_2$ (3b). A 100 mL round-bottom flask was charged with dppePdC$_2$O$_4$ (120 mg, 0.23 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (81 mg, 0.21 mmol) in 20 mL of benzene. The solution was frozen and the flask evacuated. The solution was then thawed and irradiated for 6 h. The solution was degassed several times during photolysis. The volatiles were evaporated, leaving a sticky red-brown solid. The crude product was recrystallized from THF/acetonitrile, yielding 42 mg of a brown solid (23% yield). In benzene-d_6 solution, both the dimeric **3b** and the monomeric species (dppe)Pd Ge[N(SiMe$_3$)$_2$]$_2$ (**3a**) are observed. **3a**: ^{1}H NMR (C$_6$D$_6$) δ 0.48 (s, 36H, SiMe$_3$), 2.00 (d, 4H, CH$_2$, $^2J_{P-H}$ = 14.7 Hz), 7.11 (m, Ph), 7.58 (m, Ph); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 33.35 (s). **3b**: ^{1}H NMR (C$_6$D$_6$) δ 0.56 (s, 36H, SiMe$_3$), 2.71 (s, 4H, CH$_2$) 7.00 (m, Ph), 7.58 (m, Ph); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 22.47 (s). Elemental analysis was obtained on a crystal of **3b** grown from benzene-d_6 solution. Anal. Calcd for C$_{76}$H$_{120}$Ge$_2$N$_4$P$_4$Pd$_2$Si$_8$·C$_6$D$_6$: C, 52.37; H, 7.07; N, 2.98. Found: C, 52.37; H, 6.61; N, 2.74.

Benzil Trapping Experiments. A benzene-d_6 solution containing **2** (20 mg, 0.027 mmol) and 4 equiv of benzil (22.7 mg, 0.1 mmol) was placed in an NMR tube fitted with a Teflon valve. For experiments protected from light, the two solids were added to a tube containing frozen benzene-d_6. The tube was then sealed with a Teflon valve and immediately wrapped in foil. ^{1}H NMR spectra of the solutions were acquired over a period of several hours. The progress of the trapping reactions was followed by the growth of a singlet at 0.36 ppm in the ^{1}H NMR, the resonance for the trimethylsilyl protons of the product of the reaction of free germylene and benzil. The extent

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Table 1. Summary of Crystallographic Data for 1, 2, and 3b

	1	**2**	**3b·$^1/_2$THF**
empirical formula	$C_{48}H_{66}GeN_2P_2PdSi_4$	$C_{24}H_{66}GeN_2P_2PdSi_4$	$C_{78}H_{124}Ge_2N_4 O_{0.50}P_4Pd_2 Si_8$
fw	1024.32	736.08	1832.39
temp, K	178(2)	158(2)	158(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
unit cell dimens			
a, Å	13.9430(10)	15.9735(15) Å	13.437(2)
α, deg	90	90	114.446(3)
b, Å	18.3100(10)	21.595(2)	19.872(3)
β, deg	107.330(10)	91.851(2)	90.181(3)
c, Å	21.383(2)	11.1049(11)	20.924(3)
γ, deg	90	90	109.656(2)
V, Å^3; Z	5211.2(7); 4	3828.7(6); 4	4723.4(13); 2
density (calcd), Mg/m^3	1.306	1.277	1.288
abs coeff, mm^{-1}	1.108	1.479	1.214
$F(000)$	2128	1552	1904
cryst size, mm	$0.20 \times 0.20 \times 0.18$	$0.04 \times 0.24 \times 0.34$	$0.18 \times 0.06 \times 0.01$
θ range, deg	2.70−26.00	1.59−26.39	1.22−23.25
limiting indices	$-17 \leq h \leq 16$, $0 \leq k \leq 22$, $0 \leq l \leq 26$	$-19 \leq h \leq 19$, $-26 \leq k \leq 26$, $-13 \leq l \leq 13$	$-14 \leq h \leq 14$, $-22 \leq k \leq 20$, $-3 \leq l \leq 23$
no. of rflns collected/unique	12 674/10 236(R(int) = 0.0459)	37 605/3914 (R(int) = 0.0426)	42 030/13 562 (R(int) = 0.1343)
abs cor	ψ scans	semiempirical from equivalents	semiempirical from equivalents
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	10 232/0/537	3914/0/167	13 562/30/936
goodness of fit on F^2	0.848	1.068	0.999
final R indices ($I > 2\sigma(I)$)			
R1	0.0342	0.0287	0.0625
wR2	0.0718	0.0701	0.1330
R indices (all data)			
R1	0.0613	0.0372	0.1456
wR2	0.0759	0.0738	0.1659
largest diff peak and hole, e Å^{-3}	0.672 and −0.698	0.358 and −0.409	0.904 and −0.548

of conversion to trapped product was determined by comparing the integration of this singlet with the resonance of the trimethylsilyl protons of the remaining **2** at 0.51 ppm.

Oxygen Experiments. A solution of **1**−**3** or **5** in benzene-d_6 was added to an NMR tube fitted with a Teflon valve. The solution was degassed and then frozen. One equivalent of O_2 was then added. The tubes were either kept in ambient light or wrapped in foil to protect them from ambient light. ^{1}H and ^{31}P NMR spectra were acquired periodically over several days to monitor the progress of the reactions.

Structure Determination of 1. A colorless, rectangular block of **1** of dimensions $0.20 \times 0.20 \times 0.18$ mm was coated with Paratone-N oil and transferred directly to the cold stream of the diffractometer. Single-crystal X-ray diffraction experiments were performed on a Siemens R3/v automated diffactometer equipped with an LT-2 low-temperature apparatus at −95 °C and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Additional details: scan method $\theta/2\theta$, scan rate variable 2−5° min^{-1}, background-to-scan ratio 0.5, 2θ scan range 5−52° (h, −17 to +16; k, 0−22; l, 0−26), 12 674 reflections measured, merged to 10 236 unique reflections, R_{int} = 0.0459, absorption correction via ψ scans. The structure was solved by direct methods, and 537 parameters were refined in a full matrix with the program SHELXTL PLUS.[35] All non-hydrogen atoms were refined anisotropically with hydrogen atoms placed in idealized positions. Neutral atom scattering factors and corrections for anomalous dispersion were taken from published values.[36] See Table 1 for additional details.

Structure Determination of 2. Yellow plates of **2** were crystallized from THF/acetonitrile at 10 °C. A crystal of dimensions $0.34 \times 0.24 \times 0.04$ mm was cut from a larger crystal and mounted on a standard Bruker SMART CCD based

X-ray diffractometer equipped with an LT-2 low-temperature device and normal focus Mo-target X-ray tube (λ = 0.710 73 Å) operated at a power of 2000 W (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K. The detector was placed at a distance 4.939 cm from the crystal. A total of 2322 frames were collected with a scan width of 0.3° in ω and ψ with an exposure time of 30 s/frame. The frames were integrated with the Bruker SAINT software package[37] with a narrow-frame algorithm. The integration of the data yielded a total of 37 605 reflections to a maximum 2θ value of 52.80°, of which 3914 were independent and 3377 were greater that $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 4245 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[38] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package,[39] using the space group $C2/c$ with Z = 4 for the formula $C_{24}H_{66}N_2Si_4P_2GePd$. The molecule occupies a 2-fold rotation axis in the crystal lattice coincident with the Pd−Ge bond. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0287 and wR2 = 0.0701 (based on $I > 2\sigma(I)$) and at R1 = 0.0372 and wR2 = 0.0738 for all data. Additional details are presented in Table 1.

Structure Determination of 3b. Yellow plates of **3b** were crystallized from a THF/acetonitrile solution at room temperature. A crystal of dimensions $0.18 \times 0.06 \times 0.01$ mm was mounted as for **2**. A total of 2408 frames were collected with a scan width of 0.3° in ω and ψ with an exposure time of 30

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s/frame. The frames were integrated with the Bruker SAINT[37] software package with a narrow-frame algorithm. The integration of the data yielded a total of 42 030 reflections to a maximum 2θ value of 49.8°. Due to the lack of high-angle data, resolution was limited during refinement to 0.90 A, which yielded 13 562 unique data and 7461 data greater that $2\sigma(I)$. The final cell constants (Table 1) were based on the *xyz* centroids of 2347 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[38] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package,[39] using the space group $P\bar{1}$ with $Z = 2$ for the formula $C_{76}H_{120}N_4P_4Si_8Ge_2Pd_2 \cdot 0.5THF$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms located on a difference Fourier map and refined isotropically or placed in idealized positions. Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0625 and wR2 = 0.1330 (based on $I > 2\sigma(I)$) and at R1 = 0.1456 and wR2 = 0.1659 for all data. Additional details are presented in Table 1.

Results and Discussion

Synthesis of $(R_3P)_2PdGe[N(SiMe_3)_2]_2$. Several different approaches were used to synthesize and isolate Pd germylene complexes. The first was simple ligand substitution using a Pd^0 species. The commercial availability of Pd^0 is limited to $(Ph_3P)_4Pd$ and $Pd_2(dba)_3$ (dba = dibenzylidineacetone). The latter was found to be an undesirable starting material, due to the tendency of the germylene to preferentially react with the dba ligand in solution. Germylenes are known to undergo $2 + 4$ additions with unsaturated systems, including α,β-unsaturated ketones.[40,41] NMR and IR spectra of the reaction of $Ge[N(SiMe_3)_2]_2$ with $Pd_2(dba)_3$ are consistent with the addition of the germylene to the carbonyl and one of the double bonds of the dba ligand. However, the reaction of the germylene ligand with $(Ph_3P)_4Pd$ resulted in the displacement of two PPh_3 ligands to generate complex **1** quantitatively by NMR (eq 1).

(1)
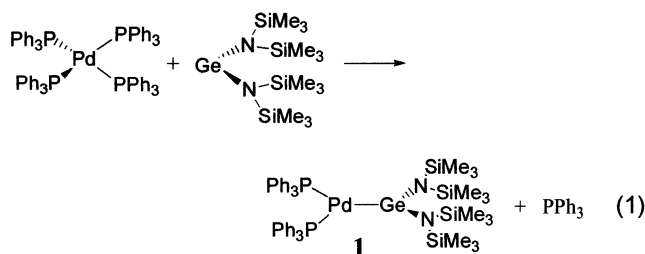
Separation of the 2 equiv of free PPh_3 from this reaction mixture without also causing the decomposition of **1** proved to be quite challenging. Attempts to use CuCl to precipitate out copper phosphines did not remove all of the PPh_3 and caused decomposition upon extended stirring with crude **1**. An interesting result was observed in our attempts to sublime away the PPh_3 under vacuum. At temperatures above 55 °C, PPh_3 was deposited on the cold finger of the sublimator; however, NMR spectroscopy of the material left in the bottom of the apparatus revealed a mixture of **1** and newly formed $(PPh_3)_4Pd$, with no free germylene present. The white solid on the cold finger was found to contain only PPh_3.

It appears that, under these conditions, the germylene ligand is labile enough to separate from the metal in the solid state and is then volatile enough to be removed in vacuo. The tetrakis(phosphine) complex is subsequently re-formed from the remaining excess phosphine present, either in the solid state or upon dissolution in the NMR solvent. Addition of more germylene to this material resulted in complete conversion of the $(Ph_3P)_4Pd$ present to complex to **1** and free PPh_3. Recrystallization of crude **1** from THF and acetonitrile removed PPh_3 and also resulted in the formation of 10−20% $(Ph_3P)_4Pd$. This is likely due to the lability of the germylene ligand (see discussion below), leading to it being separated from **1** in solution as the less soluble Pd species precipitate out. The remaining "−$(Ph_3P)_2Pd^0$" fragment can then be stabilized by some of the remaining excess PPh_3. Recrystallization in the presence of excess germylene eliminated this problem, generating analytically pure **1**.

To generate complexes with phosphine ligands other than PPh_3, a synthetic procedure involving the reduction of a Pd^{II} species similar to the synthesis of the analogous Pt complex was followed.[42] Photolysis of $(R_3P)_2PdC_2O_4$ generates a "$(R_3P)_2Pd^0$" fragment as well as 2 equiv of CO_2.[30] Attempts to perform the photolysis of $(Et_3P)_2PdC_2O_4$ in the presence of germylene ligand produced very low yields of **2** due to much of the germylene being consumed by a side reaction with CO_2.[43] Many other side products were generated by the in situ photolysis, presumably the result of the highly reactive "$(Et_3P)_2Pd$" fragment having no other ligands to stabilize it. Pure **2** could not be isolated from this mixture. The photolysis was then performed without germylene, but in the presence of a large excess of PEt_3 to trap the Pd^0 species as it was being formed. The reaction mixture was then degassed before addition of a germylene solution (eq 2). The excess PEt_3 could then

(2)
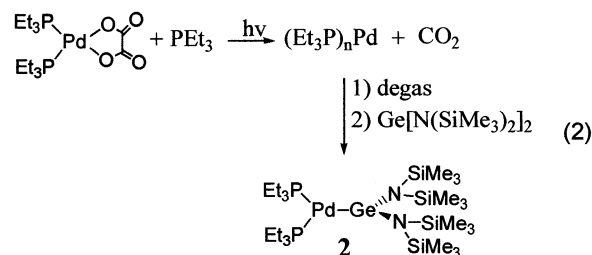
be removed in vacuo. This method cleanly generated high yields of **2** after recrystallization.

To the best of our knowledge, there is only one example of a terminal germylene ligand bound to palladium in the literature. In 1985, Lappert and co-workers reported the formation of the homoleptic Pd germylene $Pd[Ge[N(SiMe_3)_2]_2]_3$[26] from the reaction of $Pd(cod)Cl_2$ (cod = 1,5 cyclooctadiene) with 5 equiv of germylene. The complex was characterized as being red with a melting point of 210−212 °C. Crude **2** is sometimes red, but recrystallization removes a red oil comprised of various unidentified germylene side products. Pure **2** is then obtained as a bright orange microcrys-

(40) Neuman, W. P. *Chem. Rev.* **1991**, *91*, 311−334.
(41) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178−180*, 593−622.
(42) Litz, K. E.; Henderson, K.; Gourley, R. W.; Banaszak Holl, M. M. *Organometallics* **1995**, *14*, 5008−5010.
(43) Sita, L. R.; Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912−10913.

talline powder. Complexes **1** and the **3a/3b** mixture discussed below are also observed to be orange to brown.

The approaches toward the generation of Pd germylene species presented here have not yielded any complexes containing multiple germylene ligands bound to one metal. In the ligand substitution reaction utilized to make **1**, the only products of the reaction are **1** and free PPh₃, as observed in the ¹H NMR and ³¹P NMR spectra of this reaction. There is no evidence for further displacement of PPh₃ to generate a bis- or tris(germylene) complex. Furthermore, the ³¹P NMR spectra do not show any broadening or shifting as might be expected in the event of an equilibrium with (PPh₃)₄-Pd. Likewise, complex **2** also appears to be stable in solution for several days, without any further rearrangement. Addition of 10 equiv of germylene to a solution of **2** did not result in any displacement of the phosphine ligands on the Pd. This implies that a bis-(phosphine) mono(germylene) configuration is electronically favored and/or that there may be a significant steric barrier to the addition of more germylene ligands. The reaction of **2** and CO was also attempted. One atmosphere of the gas was added to a benzene-d_6 solution of the palladium germylene; however, no reaction was observed over a period of 24 h at 20 °C.

Synthesis of {(dppe)PdGe[N(SiMe₃)₂]₂}₂ (3b). We are interested in studying the effects of bidentate phosphine ligands on these palladium germylene systems. The more constrained geometry about the Pd center afforded by the bidentate ligand could bring about a greater reactivity toward activations, and also a greater propensity toward reductive elimination of activated metallacycles. No such bidentate analogues have been made in the Pt or Ni systems.

Attempts to perform photolysis of (dppe)PdC₂O₄ in the presence of excess PEt₃, analogous to the synthesis of **2**, were unsuccessful. The resulting product mixtures contained Pd species with different combinations of phosphine ligands, including (dppe)₂Pd, with no formation of the desired palladium germylene complex. Fortunately, photolysis of (dppe)PdC₂O₄ in the presence of slightly less than 1 equiv of germylene (eq 3) was somewhat cleaner than for the synthesis of **2**, and clean products could be isolated from these reaction mixtures, albeit in relatively low yields.
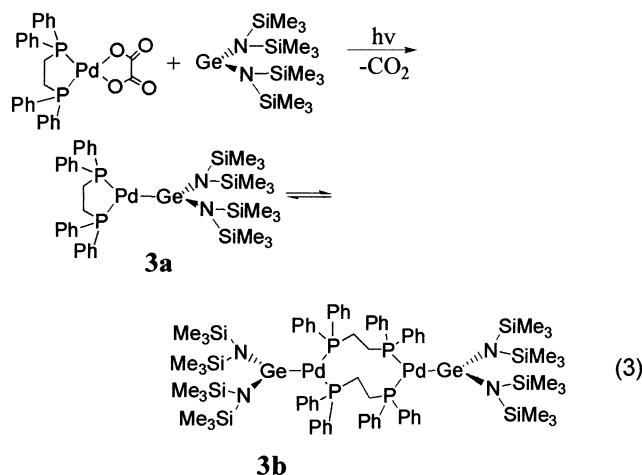
The progress of the photolysis of (dppe)PdC₂O₄ in the presence of germylene was monitored by the NMR

chemical shifts of the trimethylsilyl protons on the germylene ligand. Two main products appeared in this region. The first is a large singlet at 0.48 ppm, assigned to the monomeric form of the product, **3a**. A much smaller peak corresponding to the dimeric form **3b** grew in more slowly at 0.56 ppm. After recrystallization, the two species could be observed in the NMR spectra with their relative concentrations varying as a function of the concentration of the NMR sample. At a concentration of 8.8 mM, the ratio of dimer to monomer was 2:3. The relative percentage of **3b** was observed to decrease as the sample was diluted, though traces of the dimer could be observed until the solution was so dilute that the NMR signal was too weak to be a reliable measure of the species in solution. Crystals grown from this mixture were those of **3b**.

The ³¹P NMR chemical shifts of the monomeric versus the dimeric species are consistent with expected values. **3b** appears as a singlet at 22.5 ppm, which is intermediate between complex **1** (δ 28.8 ppm) and **2** (δ 15.3 ppm). However, the monomeric species has a resonance markedly downfield at 33.3 ppm, suggesting a very different electronic environment about the P in **3a.** Such a downfield shift is expected for ethyl-bridged phosphines upon a change in binding mode from bridging two metals to chelating one metal center.[44]

The formation of the dimeric species **3b** clearly relieves the steric strain that would arise from a small-bite-angle bidentate ligand chelated to the metal. Portnoy and Milstein have reported the P−Pd−P angle for (dippe)₂Pd (dippe = 1,2-bis(diisopropylphosphino)ethane) to be 87.05(3)°.[45] Hitchcock and co-workers reported the P−Pd−P angle for the depe ligand of Pd(depe)(dppe) to be 85.7(2)° (dppp = bis(diphenylphosphino)propane).[29] It is likely that the bite angle of dppe in **3a** would be very similar. The P−Pd−P angle of the dimer **3b** is 111.6(1)°. This is very close to that of **1**, giving a steric environment similar to that of the monodentate phosphine complex. However, if this dimeric species were substantially lower in energy than the monomeric form, a monomer−dimer equilibrium should not be observed. The presence of this equilibrium suggests that neither species **3a** nor **3b** is significantly more thermodynamically favored than the other. It is also an indication of the lability of the phosphine ligands in these complexes.

Attempts to synthesize bidentate phosphine palladium germylene species by displacing monodentate phosphine ligands of **1** and **2** with a bidentate phosphine were unsuccessful. Though the germylene ligand is observed to displace PPh₃ and PEt₃, as noted above, to give the three-coordinate bis(phosphine) complexes, the germylene itself can be quickly displaced by a bidentate phosphine ligand. Reaction of **1** with depe (depe = 1,2-bis(diethylphosphino)ethane) resulted in the formation of the bis bidentate species (depe)₂Pd and the liberation of free germylene and free PPh₃, as observed by ¹H and ³¹P NMR spectroscopy. This germylene displacement is also observed in the slow conversion of the **3a/3b** mixture to (dppe)₂Pd. Stirring of this mixture for several days in tetrahydrofuran gave rise to free germylene, as

(44) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.
(45) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655−1664.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, and 3b

	1	2	3b[a]
Pd−Ge	2.3281(4)	2.330(5)	2.337(2)
Pd−P$_1$	2.3013(9)	2.3173(7)	2.307(4)
Ge−N$_1$	1.867(2)	1.893(2)	1.89(1)
P$_1$−Pd−P$_2$	112.85(3)	119.45(4)	111.6(1)
N$_1$−Ge−N$_2$	106.09(11)	105.59(12)	106.2(4)
Ge−Pd−P$_1$	125.66(2)	120.276(19)	124.0(1)
P$_1$−Pd−Ge−N$_1$	−74.68(11)	99.60(8)	71.3(4)
P$_1$−Pd−Ge−N$_2$	103.43(11)	−80.40(8)	−108.3(4)

[a] For **3b** average values are provided from the two crystallographically independent molecules.
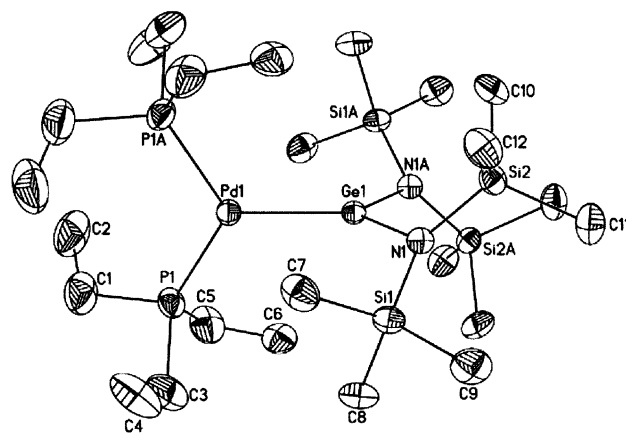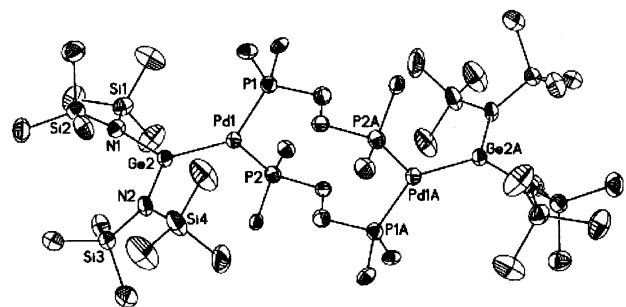
Table 3. Selected Bond Lengths (Å) and Angles (deg) of Other Group 10 Metal Germylene Complexes

	4[48]	5[42]
M−Ge	2.2064(6)	2.304(1)
M−P	2.157(1), 2.164(1)	2.263(3), 2.261(3)
Ge−N	1.867(2), 1.885(3)	1.867(7), 1.874(7)
P−M−P	113.81(4)	115.0(1)
N−Ge−N	105.05(11)	106.3(3)

judged by the ^{1}H NMR spectrum, and a small amount of a new species, (dppe)$_2$Pd, at 31.24 ppm in the ^{31}P NMR spectrum. The basicities of these bidentate phosphines should be very similar to those of their monodentate analogues; therefore, it is likely that the chelate effect plays an important role in this displacement phenomenon.

Crystal Structures. The crystal structures of the complexes presented here appear to be the first crystallographic documentation of a germylene bound to palladium. A search of the Cambridge Crystallographic Database found only one complex containing a Pd−Ge bond. Ito and co-workers have reported the structure of a bis(organogermyl)palladium(II) complex containing two palladium−germyl bonds, with Pd−Ge distances of 2.427(2) and 2.404(2) Å.[46] The three structures presented here all have similar Pd−Ge bond lengths (see Table 2 for selected bond lengths and angles). These lengths are somewhat shorter than those reported for the germyl ligands. With no other crystal structures for comparison, it is unclear how much of this shortening is due to some double-bond character of the metal−ligand bond[47] or due to the change in coordination number of the Pd from 4 to 3. There is also the potential for a competitive Fisher type interaction of the N atoms bound to the Ge center. These Pd−Ge lengths are somewhat longer than the Pt−Ge bond of (Et$_3$P)$_2$PtGe-[N(SiMe$_3$)$_2$]$_2$ (**5**) (2.3039(10) Å)[42] and the Ni−Ge bond of (Ph$_3$P)NiGe[N(SiMe$_3$)$_2$]$_2$ (**4**) (2.2064(6) Å) (Table 3).[48]

In addition to the Pd−Ge bond length, the P−Pd−P angle is an important parameter to analyze. Crystal structures of complexes **1**, **2**, and **3b** show a trigonal geometry about the Pd metal center (Figures 1 and 2). However only **2** exhibits a near-perfect trigonal plane with P−Pd−Ge and P−Pd−P angles of 120.276(19) and 119.45(4)°, respectively. In complexes **1** and **3b** the P−Pd−P angles are approximately 112°. This does not

(46) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *J. Organomet. Chem.* **1996**, *521*, 405−408.
(47) Bender, J. E., IV; Shusterman, A. J.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **1999**, *18*, 1547−1552.
(48) Litz, K. E.; Bender, J. E.; Kampf, J. W.; Banaszak Holl, M. M. *Angew. Chem., Int. Ed.* **1997**, *36*, 496−498.

Figure 1. ORTEP diagram of (Et$_3$P)$_2$PdGe[N(SiMe$_3$)$_2$]$_2$ (**2**)-(50% probability).

Figure 2. ORTEP diagram of {(dppe)PdGe[N(SiMe$_3$)$_2$]$_2$}$_2$ (**3b**) (50% probability). Only ipso carbons of the phenyl rings are shown for clarity.

follow the simple trend of cone angles (PPh$_3$, 145°; PEt$_3$, 132°; dppe, 125°)[49] of the three phosphine ligands and is an indication of the influence of the substantial steric bulk of the germylene ligand. The trimethylsilyl groups of the germylene extend forward on both sides in the plane of the Pd−Ge bond, where they approach the alkyl groups attached to the phosphine ligand that are also protruding forward. In both **1** and **3b**, the two phenyl-substituted phosphine ligands are squeezed closer together to accommodate the germylene, resulting in a smaller P−Pd−P angle. In complex **2**, the ethyl groups also protrude forward but are themselves much smaller than the phenyl rings of the other complexes, and thus a more trigonal conformation can be attained.

A similar trend is observed in the dihedral angles of these complexes. Complex **2** displays an almost orthogonal arrangement of the P−Pd−P plane versus the N−Ge−N plane with a dihedral angle of 80.40(8)° (P$_1$−Ge−Pd−N$_2$). There is substantially less orthogonality present for complexes **1** and **3b**, with dihedral angles of 74.68(11) and 71.3(4)°, respectively. This is also due to steric constraints. A view of these structures down the Pd−Ge bond reveals that, in **1** and **3b**, the phenyl rings of the phosphine are staggered with respect to the alkyl groups of the germylene. A rotation of the ligands toward greater orthogonality would lead to a more eclipsed conformation and greater steric repulsions.
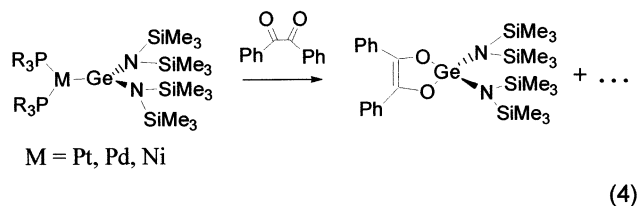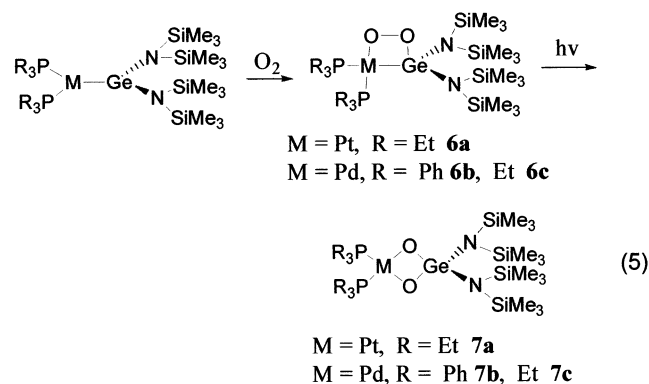
Lability of the Germylene Ligand. Free germylene ligand can be trapped with benzil as shown in eq 4.[21]

(49) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(4)

Table 4. ^{31}P NMR Chemical Shifts (ppm) for Reactions of 1−3 and 5 with O_2

complex	δ(starting material)	δ(**6**) [J_{P-P}, Hz]	δ(**7**)	δ(oxidized phosphine)
1	28.8	16.4 (d), 41.5 (d) [33]	26.4 (s)	25.2 (s)
2	15.3	23.2 (d), 26.7 (d) [40]	25.3 (s)	45.8 (s), 53.1 (s)
3	33.4 (**3a**), 22.5 (**3b**)	45.3 (d), 50.9 (d) [34]	44.0 (s)	29.5 (s)
5	38.2	−5.0 (d), 16.5 (d) [11]	2.1 (s)	not obsd

The length of time necessary to completely trap the ligand is used as an indicator of the lability of the germylene ligand in a particular complex. The addition of 4 equiv of benzil to a solution of (Ph$_3$P)NiGe-[N(SiMe$_3$)$_2$]$_2$ (**4**) resulted in complete trapping of the germylene ligand in less than a few minutes in ambient light. When a frozen solution of **4** and benzil was thawed in a darkened room and placed into an NMR spectrometer, 40% conversion to trapped product could be observed. When the NMR tube was exposed to ambient light for 20 s, the reaction immediately proceeded to completion.[21] Reaction of (Et$_3$P)PtGe[N(SiMe$_3$)$_2$]$_2$ (**5**) with benzil showed 91% conversion to the trapped form after 94 h in ambient light and 50% conversion after 113 h for a solution that had been shielded from light.[21]

The lability of the germylene ligand bound to Pd appears to follow the expected trend of being intermediate between its two group 10 neighbors. A solution of **2** with 4 equiv of benzil was allowed to react in ambient light. After 30 min, ~50% of the germylene had been trapped, and after 4 h, ~90% had been converted to trapped product. Thus, in ambient light the germylene ligand bound to **2** is 1 order of magnitude more labile than on the analogous Pt system and 2 orders of magnitude less labile than the similar Ni system. Trapping reactions that were protected from light resulted in ~30% conversion to trapped product after 30 min and ~75% conversion after 4 h. These results suggest that the Pd germylene system will display reactivity closer to that observed for the Pt germylene complex and that the germylene ligand may not be too labile for reactivity across the Pd−Ge bond. Thus, the lability of the germylene ligand in the Pd system in the dark is not substantially greater than in the presence of ambient light, indicating that the thermal and photochemical labilities are on the same order of magnitude.

Reaction with O_2. Complex **5** will react with O_2 to give a side-bridged peroxide species (**6a**), as shown in eq 5.[19] Complex **6a** will photochemically rearrange in

(5)

ambient light to insert oxygen across the Pt−Ge bond,

generating species **7a**.[19] Both species **6a** and **7a** are stable complexes that have been isolated and crystallographically characterized. To probe the reactivity of the palladium germylene system with oxygen, reactions of complexes **1**, **2**, and the **3a/3b** mixture with 1 equiv of O_2 were followed by NMR.

The Pd species formed orange solutions in benzene-d_6. Upon addition of oxygen, they slowly changed color over a period of several hours to a dark brown and eventually turned black. In all three reactions, the starting materials are completely consumed and appear to form both a peroxide species (**6**) and germanate species (**7**). Both of these products could be observed in the ^{31}P NMR (see Table 4). Peaks corresponding to oxidized phosphine ligands were also observed within minutes of O_2 addition for reactions with **2** and **3** and within the first 1 h for reaction with **1**. ^{31}P NMR spectra were generally clean, with only the two products **6** and **7** and the oxidized phosphine resonances. The reaction with **2** produced trace amounts of other P-containing complexes. The reaction with **1** was the only reaction to generate another substantial P-containing species with some, though not all, spectra, displaying a broad resonance at approximately 22 ppm. ^{1}H NMR spectra contained downfield-shifted singlets in the trimethylsilyl region, consistent with shifts observed in the Pt system. The ^{1}H NMR also contained other smaller peaks in this region that were difficult to assign and grew as the reactions progressed and the products decomposed. However, none of the ^{1}H NMR spectra contained peaks at 0.47 ppm, the resonance for [Ge[N(SiMe$_3$)$_2$]$_2$(μ-O)]$_2$, which is the product of the reaction of free germylene with O_2.[50] This indicates that free germylene did not react directly with oxygen.

The reactivity of O_2 with the Pt system was also followed by NMR for comparison to the Pd reactions. Complex **5** forms a bright yellow solution in benzene-d_6 that slowly becomes lighter in color after addition of O_2. The pale yellow color of the solution remains unchanged for several weeks with no metallic precipitation and no observed decomposition in solution. This reaction produced products **6a** and **7a** cleanly without any observed formation of oxidized phosphine species even after many days in solution. The ^{31}P NMR spectrum contained only the signals for the two products with no other resonances observed.

Unlike the fairly stable Pt system, the Pd reactions with O_2 resulted in the steady decomposition of the Pd species in solution as time progressed. This decomposition was characterized by the decrease in the amount

(50) Ellis, D.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1992**, 3397−3398.

Scheme 1
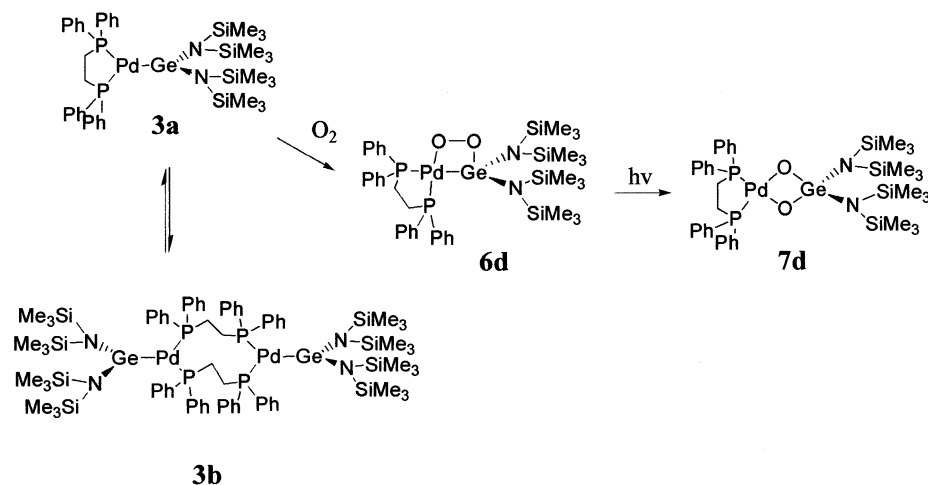
of material present in solution, as gauged by the decrease in the signal-to-noise ratio of the ^{31}P NMR spectra over time. Visually, the solutions darkened over the course of a few hours, and eventually precipitated black solid coated the walls of the NMR tube with a black metallic material, presumably metallic Pd. Decomposition of these species is related to the formation of phosphine oxide, which serves to remove the phosphine ligands required to stabilize the Pd metal center. In the ^{31}P NMR spectrum the resonances corresponding to oxidized phosphine grew and the signals from the products decreased over a period of several days, and in the case of **3**, the oxidized phosphine eventually became the only P species in solution. To test if these oxidized phosphines were the result of a side reaction of dissociated phosphine ligand with O_2, a solution of **1** was stirred with 1 equiv of O_2 and then the volatiles were removed. NMR spectra showed that all of **1** had been consumed, though no signal for oxidized phosphine was yet present. This material was redissolved in benzene, and stirring was continued. Unlike the chemistry observed for Pt, species **6b** does not convert cleanly under thermal or photolytic conditions to **7b**. Instead, slow decomposition to form OPPh$_3$ and insoluble black, Pd-containing precipitates occurred.

The reactions of **1** and **2** were also performed shielded from light, to study the influence of photolytic reactions on this system. No significant differences were observed in the rates of reactivity or of decomposition of the species in solution for the reactions kept in the dark. Both species **6b** and **7b** and **6c** and **7c** were observed in the solution, indicating that conversion from **6** to **7** occurs even in the absence of light. This result is markedly different than what is observed for the Pt system. Complex **6a** can be isolated without the formation of **7a** if the reaction with oxygen is performed in the absence of light.[19] The peroxide product converted cleanly to **7a** with prolonged stirring in the light or by UV irradiation. In the Pd system, the thermal reaction dominates and protection from light does not prevent rearrangement of peroxide **6** to germanate **7**.

The reactivity of the **3a/3b** mixture with O_2 is particularly interesting. This reaction begins with both monomeric and dimeric starting materials, but only two products are observed in the ^{31}P NMR spectrum: one singlet and one pair of doublets. These are assigned to

the formation of products **6d** and **7d** (see Scheme 1). The reaction with O_2 appears to occur solely with **3a**, on the basis of the rapid disappearance of the monomeric species as the reaction progresses. An initial solution concentration of approximately 30 mM containing a 1:1 ratio of **3a** and **3b** was exposed to 1 equiv of O_2. After 10 min the solution contained no **3a**, as assessed by ^{1}H and ^{31}P NMR spectroscopy. Products **6d** and **7d** had formed in a 1:1 ratio and together comprised ~70% of the P-containing species in solution. Complex **3b** could also be observed and accounted for ~20% of the P species in solution, whereas oxidized phosphine was integrated to be ~10% of the P present. After 30 min, a small amount of **3b** (~5% of the P species) remained in solution. The products **6d** and **7d** together were ~75% of the species in solution, and the amount of oxidized phosphine had grown to ~20%. All of the starting materials were consumed after 1.5 h. Thus, **3a** was consumed rapidly, and **3b** persisted in solution, presumably converting slowly to **3a**. The monomer was then consumed as it was being formed, to give the two oxidized products.

Species **6d** and **7d** should have a more constrained geometry about the Pd center and, thus, would be expected to be more reactive than the analogous monodentate phosphine complexes. Of the three Pd reactions, the products **6d** and **7d** were the fastest to decompose, with only oxidized phosphine observed in the NMR after 4 days. In contrast, for the reactions with **1** and **2**, the oxygen products were still approximately 20% and 57%, respectively, of the P-containing species in solution after 4 days.

Conclusions

Three novel palladium germylene complexes containing monodentate and bidentate phosphine ligands have been synthesized. The crystal structures of these complexes show a trigonal geometry about the metal with the germylene ligand tilted orthogonally to the plane of the phosphines. The lability of the germylene on Pd was found to be intermediate between similar Ni and Pt systems, though more similar to Pt. Unlike the Pt and Ni systems, the photochemical lability of the Pd system does not dramatically affect the overall lability of the ligand. Initial studies of the reactivity of the Pd system with O_2 suggest that these complexes react in a

manner similar to that of the Pt system, only with increased reactivity. However, unlike the Pt system, shielding the reactions from light does not affect the reactivity. The use of bidentate phosphine ligands appears to increase reactivity, possibly enabling reactions to be tuned. The increased reactivity and differing photochemistry of the Pd system as well as the use of bidentate ligands could be exploited in future reactions to give products that could not be attained with the Pt complexes. We are currently investigating other reactivity of this novel system.

Supporting Information Available: X-ray crystallographic data for **1**, **2,** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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