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Sequential Insertion of Formaldehyde and Carbon Monoxide into a Sulfide-Bridged Pd−Ge Bond Followed by Reductive Elimination To Form a [1,3,2]Oxathiagermolan-4-one

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The reaction of $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ (**2**) with paraformaldehyde under photolytic conditions results in the insertion of formaldehyde into the Pd−Ge bond, with bond cleavage, to give $(Et_3P)_2Pd(\mu\text{-}S)(\mu CH_2O)Ge[N(SiMe_3)_2]_2$ (**3**). Subsequent addition of CO to **3** results in migratory insertion into the Pd−C bond, followed by rapid reductive elimination to regenerate the Pd^0 metal center and give a unique five-membered organic heterocycle, $\overline{Ge[N(SiMe_3)_2]_2\text{-}SC(O)CH_2O}$ (**6**). The X-ray crystal structure of the dppe (dppe = bis(diphenylphosphino)ethane) derivative of **3**, $(dppe)Pd(\mu\text{-}S)(\mu CH_2O)Ge[N(SiMe_3)_2]_2$ (**4**), is reported.

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.[1−4] In late-metal−germylene complexes, the close proximity of the electron-rich metal and the Lewis acidic Ge^{II} suggests that a variety of addition reactions should be possible across the metal−germylene bond. This bond-forming reaction could occur with the addition of a substrate molecule in whole or in part across the M−Ge moiety, with oxidation of the metal and/or oxidation of the germanium center, or with direct insertion into the M−Ge moiety with M−Ge bond cleavage. Numerous stable σ-bonded metal germylene complexes have been synthesized in the last few decades;[5−28,41] however, comparatively fewer studies have emphasized the reactivity of the metal−germylene bond.[5,7,19,26,27,29−33,43,44]

To study the potential for cooperative reactivity of the M−Ge bond, we have explored the reactivity of the stable germylene ligand $Ge[N(SiMe_3)_2]_2$, first reported by Lappert,[34,35] bound to platinum. Various small organic and inorganic molecules, including O_2, CO_2, PhNO, and H_2CO, will react with platinum germylenes

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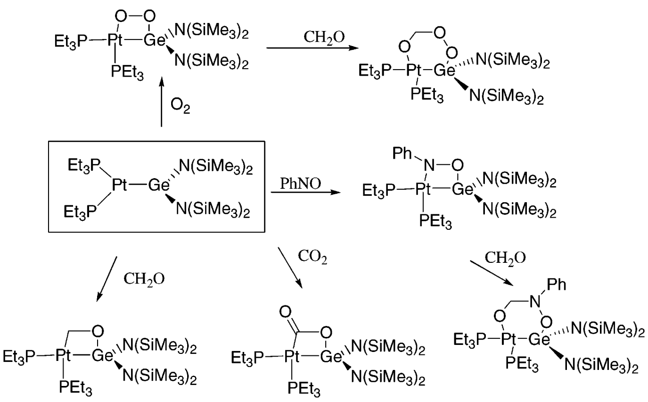
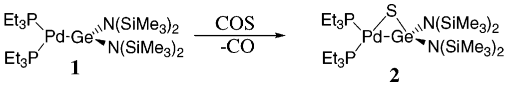
Scheme 1



such as $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$, without cleavage of the Pt−Ge bond, to form four-membered metallocycles.[7,29,30,36] Subsequent insertion chemistry of these rings at the Pt−O or Pt−N bond leads to the formation of novel five- and six-membered metallacyclic structures, demonstrating the ability to effect new bond-forming reactions with metal−germylene complexes (Scheme 1).[29,30,36] No insertion chemistry was observed for the Pt−C bonds or at the Pt−Ge bond. Reductive elimination of these metallacycles could be used to generate novel heteroatomic ring systems. However, we were unsuccessful in promoting such eliminations from the Pt complexes.

On the basis of the previous results using Pt, we decided to explore the analogous Pd system. Metallacycles formed from the analogous Pd complexes should be more prone to reductive elimination,[37] allowing the heterocycles to detach 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 well-defined and facile insertion chemistry.[38−40] However, with the notable exception of O_2, the analogous Pd complexes failed to reproduce any of the addition chemistry noted for Pt[41] and the direct reactions with various substrates, including CH_2O, were unsuccessful.[42]

We recently demonstrated the reactivity of $(Et_3P)_2PdGe[N(SiMe_3)_2]_2$ (**1**) with COS to extrude S atoms and form the sulfide-bridged species $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ (**2**) (eq 1).[43] Interestingly, the presence of the sulfide bridge in complex **2** dramatically improved our ability to observe cooperative reactivity of the Pd−Ge bond. Clean insertion products can be isolated from reaction with the sulfide-bridged complex.[44] The reactivity of the Pd−Ge bond in the sulfide-bridged complexes was surprising, since none of the previous Pt−Ge metallacycles had exhibited clean, cooperative reactivity at the Pt−Ge bond nexus.



(1)

Herein we report the insertion of formaldehyde into the Pd−Ge bond of complex **2** with bond scission to give a five-membered metallacycle. Subsequent reaction of this metallacycle with CO results in migratory insertion into the newly generated Pd−C bond. Insertion is followed by rapid, facile reductive elimination to form a new C−S bond and generate 2,2-bis(1,1,1,3,3,3-hexamethyldisilazan-2-yl)[1,3,2]oxathiagermolan-4-one (**6**), a novel five-membered organic heterocycle comprised of four different elements.

Experimental Section

All manipulations of metal-containing species were performed using air-free techniques. Benzene, toluene, THF, pentane, and benzene-d_6 were dried over sodium benzophenone ketyl and degassed. Acetonitrile was dried over 4 Å molecular sieves and degassed. Paraformaldehyde, CuCl, dppe, and PPh_3 were purchased commercially (Aldrich, Strem) and used as received. $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$[43] (**2**) was made according to literature procedures. Photolysis experiments were performed using a Blak-Ray long-wave (365 nm) ultraviolet lamp. ^1H, ^{31}P, and ^{13}C NMR spectra were acquired on a Varian 400 MHz instrument (400, 161.9, and 100.6 MHz, respectively). ^{31}P NMR spectra are referenced to H_3PO_4 by using an external secondary standard of PPh_3 in benzene-d_6 (assigned to −5.0 ppm).[45] Mass spectra were acquired on a VG (Micromass) 70-250-S magnetic sector mass spectrometer. IR spectra were acquired on a Perkin-Elmer Spectrum BX.

$(Et_3P)_2Pd(\mu\text{-}S)(\mu\text{-}CH_2O)Ge[N(SiMe_3)_2]_2$ (3). Complex **2** (1.2 g, 1.6 mmol) and paraformaldehyde (600 mg, 20 mmol) were added to 100 mL of THF. The light brown solution with white precipitate was placed in a water bath and stirred under a UV lamp for 4 days. The solution gradually darkened. The volatiles were evaporated, and the resulting brown solid was dissolved in toluene and filtered to remove excess formaldehyde. The toluene was evaporated, and the resulting brown solid was recrystallized from THF/MeCN to give 725 mg (58% yield) of **3** as a tan-brown solid. ^1H NMR (C_6D_6): δ 0.68 (s, 36H, $SiCH_3$), 0.75 (m, 9H, CH_2CH_3), 0.88 (m, 9H, CH_2CH_3), 1.13 (m, 6H, CH_2CH_3), 1.52 (m, 6H, CH_2CH_3), 5.01 (dd, J_{H-P} = 8.4 and 0.8 Hz, 2H, CH_2O). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.07 (d, $^2J_{P-P}$ = 42.1 Hz), 20.5 (d, $^2J_{P-P}$ = 42.1 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.58 (s, $SiCH_3$), 8.23 (s, CH_2CH_3), 8.34 (s, CH_2CH_3), 15.66 (d, J_{P-C} = 24.4 Hz, CH_2CH_3), 17.31 (d, J_{P-C} = 14.5 Hz, CH_2CH_3), 74.41 (d, trans J_{P-C} = 107.5 Hz, cis-J_{P-C} too small to observe, CH_2O). IR (KBr pellet): 1032 cm^{-1} (ν(C−O)). Anal. Calcd for $C_{25}H_{68}GeN_2OP_2PdSSi_4$: C, 37.62; H, 8.59; N, 3.51. Found: C, 37.63; H, 8.61; N, 3.29.

$(dppe)Pd(\mu\text{-}S)(\mu\text{-}CH_2O)Ge[N(SiMe_3)_2]_2$ (4). A 25 mL round-bottom flask was charged with **3** (50 mg, 0.06 mmol) and dppe (25 mg, 0.06 mmol). An 8 mL portion of benzene was distilled in, and the pale brown solution was stirred for 1 h. The volatiles were then removed and the resulting brown oil was left under dynamic vacuum for 1.5 h, while standing in a warm water bath. The oil began to solidify gradually while under vacuum. The product was dissolved in benzene and left to evaporate slowly over several days, yielding 28 mg (47% yield) of tan crystals of **4**. ^1H NMR (C_6D_6): δ 0.68 (s, 36H, $SiCH_3$), 1.66 (m, 1H, CH_2), 1.72 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.93

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(m, 1H, CH_2), 5.21 (dd, $J_{H-P} = 8.0$ and 1.4 Hz, 2H, CH_2O), 7.00 (m, 8H, Ph), 7.10 (m, 4H, Ph), 7.42 (m, 4H, Ph), 7.91 (m, 4H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 34.0 (d, $^2J_{P-P} = 33.8$ Hz), 51.5 (d, $^2J_{P-P} = 33.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.54 (s, SiCH_3), 25.0 (m, CH_2), 29.6 (m, CH_2), 75.75 (d, trans-$^2J_{P-C} =$ 109.83 Hz, cis-$^2J_{P-C}$ too small to observe, CH_2O), 128.77, 128.86, 128.88, 128.98 (*o* or *m*, Ph), 129.77, 130.18 (*i*, Ph), 130.55, 130.58, 131.06, 131.08, (*p*, Ph) 132.82, 133.09 (*i*, Ph), 133.40, 133.52, 133.69, 133.82 (*o* or *m*, Ph). Ipso and para assignments are based upon relative intensities. Anal. Calcd for $C_{39}H_{62}GeN_2OP_2PdSSi_4$: C, 48.78; H, 6.51; N, 2.92. Found: C, 48.73; H, 6.33; N, 2.82. IR (KBr pellet): 1104 cm^{-1} (ν_{asym}-(C−O−Ge)).

$\overline{Ge[N(SiMe_3)_2]_2SC(O)CH_2O}$ (6). A Pyrex bomb reactor was charged with **3** (400 mg, 0.5 mmol) and PPh_3 (523 mg, 2.0 mmol) and evacuated. Toluene (~40 mL) was distilled in, and 1 atm of CO was added. The solution was stirred vigorously and changed color slowly from a dark brown to a lighter brown. After 8 days the volatiles were evaporated and NMR spectra indicated that the reaction was less than half complete. The NMR solution was returned to the bomb, and the volatiles were removed. Toluene (~40 mL) was again distilled in and 1 atm of CO added. The solution was stirred vigorously for another 12 days, and the volatiles were removed. Pentane (~40 mL) was then added. The resulting slurry was filtered to separate the green-yellow solid $(PPh_3)_4Pd$ from the pale yellow filtrate. The volatiles were removed from the filtrate, giving a pale yellow oil that contained **6** and free PPh_3. This oil was redissolved in 15 mL of benzene, and CuCl (260 mg, 2.6 mmol) was added to precipitate the PPh_3. The solution was stirred for 15 min and slowly became more reddish. The volatiles were removed, and the resulting solid was suspended in 15 mL of pentane. The solution was filtered, and the volatiles were removed from the filtrate, leaving a yellow oil. This oil was redissolved in benzene and passed through a silica gel column, giving a faintly yellow eluent. The volatiles were removed, giving 31 mg of **6** as a faintly yellow oil (13% yield). ^1H NMR (C_6D_6): δ 0.24 (s, 36H, SiCH_3), 4.12 (s, 2H, CH_2O). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 5.23 (s, SiCH_3), 71.55 (s, CH_2O), 203.06 (s, C=O). IR (thin film on NaCl plate): 1706 cm^{-1} (ν(C=O)), 1111 cm^{-1} (ν_{asym}(C−O−Ge)). EI/MS (*m*/*z*): [M]$^+$ 484.5, [M − O=CCH$_2$O]$^+$ 426.4. EI/HRMS (*m*/*z*): [M]$^+$ 484.0941.

Reaction of 2 with $[CH_2O]_3$ Protected from Light. Two round-bottomed flasks were charged with a THF solution of complex **2** (20 mg, 0.026 mmol) and paraformaldehyde (8 mg, 0.26 mmol). One flask was wrapped in foil and left stirring inside of a cabinet to protect the reaction from ambient light. For a direct comparison to this dark reaction, the other flask was placed in a water bath and stirred under a UV lamp. After 23 h the volatiles were removed from both flasks and the products were dissolved in benzene-d_6 for NMR analysis.

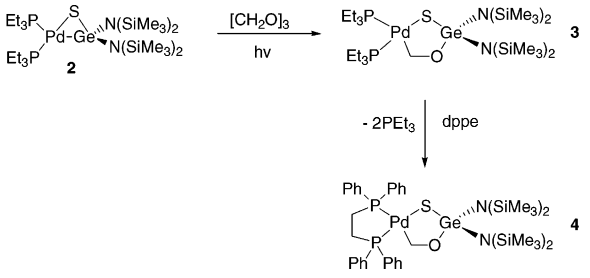
Structure Determination of 4. Colorless plates of **4** were grown from a benzene/toluene solution at 22 °C. A crystal of dimensions 0.36 × 0.24 × 0.16 mm was mounted as on a standard Bruker SMART CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.710\,73$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 118(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 2223 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[46] with a narrow frame algorithm. The integration of the data yielded a total of 40 894 reflections to a maximum 2θ value of 43.94°, of which 11 581 were independent and 9725 were greater than 2σ(I). The final cell constants were based on the *xyz* centroids of 6467 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[47] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package,[48] using the space group $P\bar{1}$ with $Z = 4$ for the formula $C_{39}H_{62}N_2OSi_4P_2$-SGePd. 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 = 0.0583 and wR2 = 0.1534 (based on $I > 2\sigma(I)$); R1 = 0.0785 and wR2 = 0.1735 for all data. A summary of crystallographic data is given in Table 1.

Table 1. Summary of Crystallographic Data for 4

empirical formula	$C_{39}H_{62}GeN_2OP_2PdSSi_4$
formula wt	960.26
temp	118(2) K
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimens	
a	14.115(2) Å
b	17.175(2) Å
c	21.180(3) Å
α	68.090(4)°
β	89.880(5)°
γ	88.499(5)°
V	4761.9(11) Å^3
Z, calcd density	4, 1.339 Mg/m^3
abs coeff	1.251 mm^{-1}
λ	0.710 73 Å
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0583, wR2 = 0.1534
R indices (all data)	R1 = 0.0785, wR2 = 0.1735

Results

Photolysis of THF solutions of $(Et_3P)_2Pd(\mu\text{-}S)Ge[N(SiMe_3)_2]_2$ (**2**) in the presence of paraformaldehyde yields the insertion of formaldehyde into the Pd−Ge bond to give $(Et_3P)_2Pd(\mu\text{-}S)(\mu\text{-}CH_2O)Ge[N(SiMe_3)_2]_2$ (**3**) (eq 2). Characterization of this complex by ^{31}P NMR and ^1H NMR spectroscopy indicates the presence of two inequivalent phosphine ligands. The ^{13}C NMR spectrum contains a resonance at 74.1 ppm with a trans-J_{P-C} coupling constant of 107 Hz, consistent with a Pd-bound methylene.[49] The trimethylsilyl protons of the germylene appear as a singlet at 0.68 ppm, shifted downfield from the starting material, and the methylene protons appear as a doublet of doublets at 5.01 ppm. The IR spectrum of this complex contains a ν(C−O−Ge) band at 1032 cm^{-1}.



(2)

We wished to confirm the presence of the sulfide bridge and the connectivity of the formaldehyde bridge

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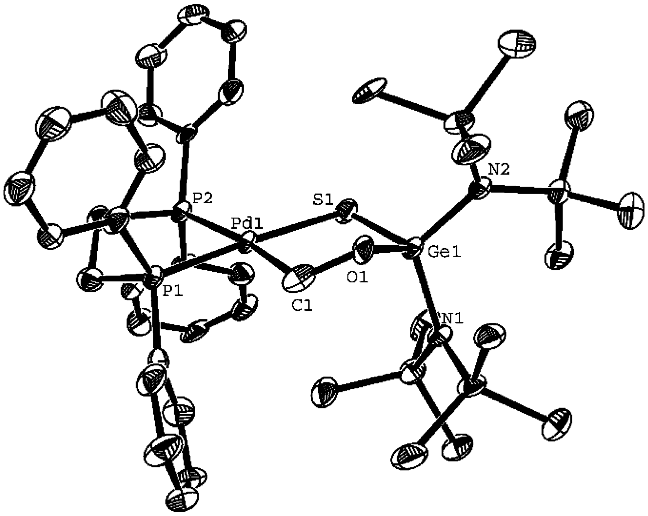


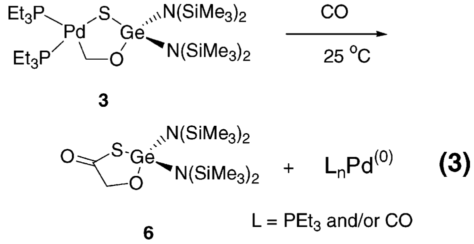
Figure 1. ORTEP representation (50% probability) of (dppe)Pd(μ-S)(μ-CH_2O)Ge[$N(SiMe_3)_2$]$_2$ (**4**). Selected bond lengths (Å) and angles (deg): Pd1−S1 = 2.389(3), Pd1−C1 = 2.166(11), O1−C1 = 1.383(14), Ge1−O1 = 1.785(6), Ge1−S1 = 2.182(3), Pd(1)−P(1) = 2.230(3), Ge(1)−N(2) = 1.848(8), P(2)−Pd(1)−S(1) = 97.10(10), O(1)−Ge(1)−N(2) = 101.3(3), C(1)−O(1)−Ge(1) = 114.6(6), O(1)−C(1)−Pd-(1) = 115.2(7), S1−Pd1−C1 = 91.7(3), Ge1−S1−Pd1 = 95.72(10), S1−Ge1−O1 = 103.7(3), N2−Ge1−N1 = 116.0(3), P2−Pd1−P1 = 85.57(10).

of **3** crystallographically. However, suitable crystals could not be grown. To facilitate crystallization, the bis(diphenylphosphino)ethane (dppe) derivative was prepared by ligand substitution. NMR spectroscopy confirmed the displacement of the two PEt_3 ligands of **3** with the dppe to give (dppe)Pd(μ-S)(μ-CH_2O)Ge[N(SiMe$_3$)$_2$]$_2$ (**4**) (eq 2).

The crystal structure of **4** (Figure 1) confirms the presence of the sulfide bridge and the binding mode of the inserted formaldehyde. Attempts to refine the structure with the C−O moiety reversed, Pd−O−CH_2−Ge, resulted in nonpositive-definite thermal displacement parameters for C and unrealistically large thermal displacement for O. The Ge−O bond length of 1.785(6) Å and the Pd−C bond length of 2.166(11) Å are consistent with literature values.[50,51] The C−O bond length of the bridge is 1.383(14) Å. The palladium metal center is square planar, and the Ge center has a tetrahedral geometry.

The insertion of CH_2O into the Pd−Ge bond of **2** is observed to require photolytic conditions.[52] THF solutions of **2** with excess $[CH_2O]_3$ that were protected from light showed no reaction after 1 day of stirring. By way of contrast, 60% conversion to **3** can be observed in solutions that have been stirring for 1 day with UV irradiation. Very slow conversion to **3** can also be observed under ambient (fluorescent) light, with approximately 15% conversion to **3** after 5 days of stirring.

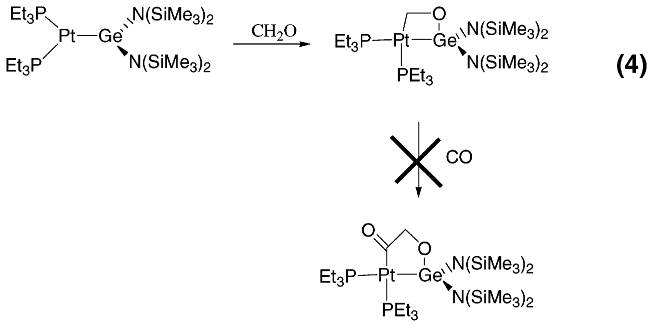
The addition of 1 atm of CO to benzene solutions of **3** results in the formation of [1,3,2]oxathiagermolan-4-one (**6**), with reduction of the Pd metal center (eq 3). The ^{1}H NMR spectrum of **6** contains a singlet in the trimethylsilyl region at 0.24 ppm, consistent with similar Ge^{IV} species.[53−55] The two methylene protons appear as a singlet at 4.12 ppm. The presence of the carbonyl moiety is evident in the ^{13}C NMR spectrum with a resonance at 203.1 ppm and in the IR with a ν(C=O) band at 1706 cm^{-1}. The asymmetric C−O−Ge stretch is also observed at 1111 cm^{-1}. High-resolution mass spectroscopy gives a parent peak at *m*/*z* 484.1 with isotopic distribution pattern matching the calculated spectrum for **6**. The next heaviest fragment at *m*/*z* 426.4 is consistent with the loss of a O=CCH_2O moiety from the parent complex. Complex **4** is stable in the presence of CO and does not form an analogous insertion product.



The formation of **6** occurs cleanly and quantitatively, as long as the solution contains ligands to trap the free Pd^0 fragment also formed in the reaction. Once the overpressure of CO is removed from the reaction, the Pd metal center is no longer stabilized and partial decomposition of the product is observed. However, reactions run in the presence of PPh_3 result in clean conversion to **6** and $(Ph_3P)_4Pd$ with no subsequent decomposition observed upon removal of volatiles.

Discussion

The reactivity of the Pd−Ge bond with formaldehyde differs markedly from the chemistry observed in our studies of Pt−Ge chemistry. $(Et_3P)_2$PtGe[N(SiMe$_3$)$_2$]$_2$ reacts with paraformaldehyde to give a four-membered metallacycle (eq 4).[36] Reactions of the Pd analogue, $(Et_3P)_2$PdGe[N(SiMe$_3$)$_2$]$_2$ (**1**), with paraformaldehyde were unsuccessful and decomposition of the Pd complex was observed.[42] The presence of a sulfide bridge between the Pd and Ge centers was necessary in order to observe cooperative reactivity of the Pd−Ge bond with CH_2O.



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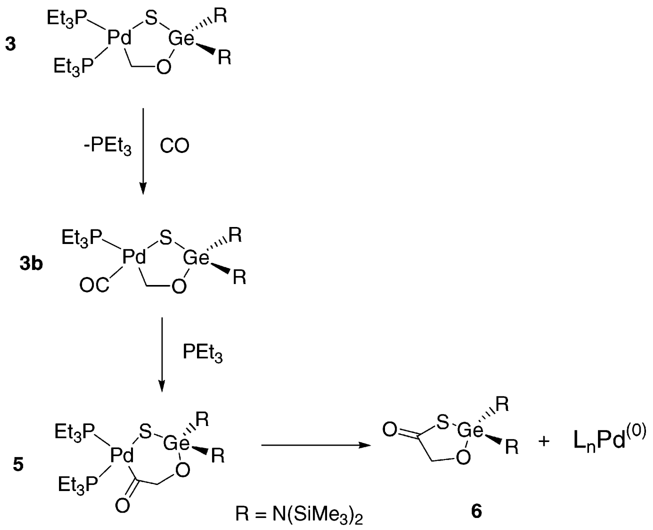
Scheme 2



This cooperative reactivity exhibited in the formation of **3** is different from any of the addition and insertion reactions observed in the Pt system. The Pd−Ge bond is broken in the formation of the insertion product. In the Pt chemistries, reaction of $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ with various substrate molecules resulted in four-membered metallacycles with preservation of the Pt−Ge bond.[7,29,30,36] Subsequent reactivity (Scheme 1) resulted in insertions into the Pt−X bond (X = O, N), without the Pt−Ge bond cleavage. The reactions with the Pt−Ge and Pd−Ge bonds are similar in that the connectivities of the insertion products are the same, $M-CH_2-O-Ge$.

The formation of complex **3** is, to our knowledge, the first example of an insertion of formaldehyde into a M−Ge bond with concomitant M−Ge bond cleavage. Formaldehyde is known to insert into M−C[56−58] and M−Si[59] bonds. The metal carbon insertion products display a $M-O-CH_2-R$ connectivity for both early transition metals (Ta) and late transition metals (Ni, Cu). Insertions of formaldehyde into early-metal (Ta) silicon bonds also give this connectivity.[59] However, aldehyde insertions into M−Si bonds of electron-rich or low-valent metals generate $M-CR_2-O-Si$ insertion isomers.[59] This latter connectivity is observed in **3** and is consistent with the trend observed for M−Si insertions.

Complex **3** reacts further with CO to form a new organic heterocycle and a Pd^0 fragment (eq 3). A formal mechanism for this reaction can be postulated (see Scheme 2). The first step is ligand substitution of PEt_3 with CO, to give the cis coordination necessary for concerted migration.[60] In complex **4**, where a bidentate phosphine ligand blocks access to this coordination site, no reactivity with CO is observed. Species **3b** and **5** are not observed in NMR spectra of these reactions, suggesting that conversion from **3b** to **5** and from **5** to **6** is rapid. Thus, the loss of PEt_3 from **3** is most likely the rate-determining step in this reaction.

Because species **5** has not been observed spectroscopically, we have no direct evidence as to its structure. We believe that migratory insertion of CO into the Pd−C bond and not the Pd−S bond is most likely occurring. Insertions of CO into Pd−C bonds are well precedented.[60,61] Pd is used industrially to polymerize CO and alkenes to make polyketones.[62]

In contrast, there are very few examples of CO insertion into M−S bonds in the literature. CO has been observed to desulfurize thiols on Co to give Co−alkyl complexes and COS.[63−67] There has been one report in which the insertion of CO into Pd−S−Ar bonds has been proposed as a possible intermediate in the Pd-catalyzed transformation of sulfenamides ($RSNR'_2$) to thiocarbamates ($RSC(O)NR'_2$).[68] However, in this example the two possible migratory insertion pathways are into the Pd−S bond versus into the Pd−N bond and not a Pd−S bond versus a Pd−C bond. In our system we have observed that the reaction of $(Et_3P)_2PdGe[N(SiMe_3)_2]_2$ (**1**) with COS generates complex **2** and CO (eq 1).[43] Complex **2** is stable for days in the presence of excess CO at room temperature and does not undergo subsequent insertion or desulfurization. Thus, the Pd−S−Ge moiety appears to be unreactive to carbonylation of the Pd−S bond under our conditions.

Reductive elimination to generate C−S bonds has been reported in the literature.[69−71] Insertions of CO into S−C bonds followed by C−S bond forming reductive eliminations can be used to catalytically generate thioesters on Co, Rh, and Pd. However, these reactions require forcing conditions (~60 atm of CO, 125−180 °C).[69] Stoichiometric C−S-forming reductive eliminations on Pd have been reported under milder conditions (50−95 °C).[71] In our system, the precursor to reductive elimination, complex **5**, is not observed spectroscopically, indicating that reductive elimination is rapid and facile at room temperature. The rates of C−S bond-forming reductive eliminations on Pd are accelerated by an electron-deficient carbon center and by the presence of a π system in the product that can coordinate and stabilize the reductive elimination transition state.[71] Both of these elements are present in the carbonyl moiety of **5** that gives rise to the cyclic thioester **6** and may be facilitating reductive elimination.

The insertion of CO into the Pd−C bond of **3** and subsequent reductive elimination illustrates two desirable modes of reactivity of the Pd−Ge system not observed in the Pt−Ge heterocyclic chemistry. The first

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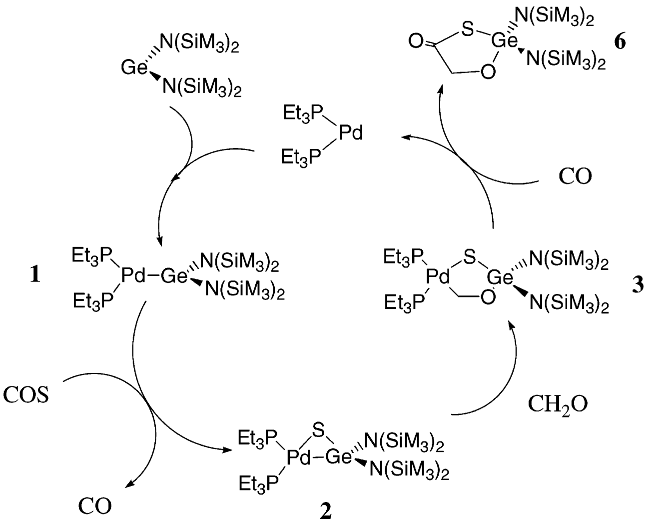
Scheme 3



is the insertion into a M−C bond. Although insertions into Pt−N and Pt−O bonds could be observed,[29,30] we have been unsuccessful in effecting insertions into the Pt−C bond of complexes such as $(Et_3P)_2Pt(\mu CH_2O)Ge[N(SiMe_3)_2]_2$[36] (eq 4) and $(Et_3P)_2Pt(\mu C(O)O)Ge[N(SiMe_3)_2]_2$.[7,36] Finally, reductive elimination of Pt metallacycles could not be induced, yet elimination is rapid and facile for Pd.

Scheme 3 summarizes the overall process for the synthesis of **6** beginning from complex **1**.[41] Three different substrate molecules can be coupled together in a controlled manner to generate four new bonds: Ge−S, Ge−O, C−C, and C−S. Compound **6** is a unique heterocyclic ring, in which only two atoms are of the same type.

Conclusions

Novel cooperative reactivity of the Pd−Ge bond is reported. A sulfide bridging the Pd and Ge centers enables insertion of formaldehyde into the Pd−Ge bond with bond cleavage. The resulting metallacycle undergoes further insertion chemistry with the migratory insertion of CO into the newly formed Pd−C bond. Subsequent reductive elimination generates a unique organic heterocycle. These reactions demonstrate the capacity of the Pd system to couple multiple organic and inorganic substrates together in a controlled manner on one metal center.

The chemistries reported here further develop the chemistry of group 10 metal germylene and germyl complexes. Three novel modes of reactivity not observed in the Pt−Ge chemistry are reported. Direct insertion of a substrate into the M−Ge bond with bond cleavage is observed. This is followed by insertion of a substrate molecule into the M−C bond and reductive elimination of metallacycles from the metal center.

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Supporting Information Available: Tables giving X-ray crystallographic data and files in CIF form for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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