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Article

Insertion of SO_2 into a Sulfide-Bridged M–Ge Bond: Synthesis, Characterization, and Reactivity of the *O*-Germyl-*S*-sulfoxylate

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Addition of SO_2 to $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ (**1**) results in the insertion of SO_2 into the Pd–Ge bond to give the *O*-germyl-*S*-sulfoxylate insertion isomer $(Et_3P)_2Pd(\mu\text{-}S)S(O)OGe[N(SiMe_3)_2]_2$ (**2**). Heating solutions of **2** results in the formation of $(Et_3P)Pd(SGe[N(SiMe_3)_2]_2OSOGe[N(SiMe_3)_2]_2S)$ (**3**) and a $L_nPd(0)$ fragment. X-ray crystal structures of **2** and **3** are reported.

Introduction

The insertion of SO_2 into M−R (R = C, Si, Ge, Sn) bonds is a fundamental organometallic insertion reaction,[1−3] transforming M−R σ-bonded compounds into various sulfinate isomers. This chemistry is exploited in the Pd-catalyzed copolymerizaton of SO_2 and various alkanes.[4,5] SO_2 will readily insert into a variety of M−alkyl bonds.[1,2,6] However, comparatively fewer studies have been carried out on the insertion of SO_2 into M−Si, M−Ge, or M−Sn bonds.[7−12]

The diversity of bonding modes of SO_2−metal complexes[2,13] is mirrored in a diversity of possible SO_2 insertion isomers. Insertion of SO_2 into M−R bonds has been shown to give three different isomeric structures (Figure 1). The *S*-sulfinate (I) predominates in mid to late transition metal complexes, while the *O*-sulfinate (II) and the *O,O′*-sulfinate (III) isomers are observed with nontransition metals and early transition metals.[1,2] A fourth isomer, the *O*-alkyl-*S*-sulfoxylate (IV), is also chemically possible and has been proposed in reviews and textbooks; however, this isomer has not been observed from SO_2 insertion reactions.[1−3,14,15]

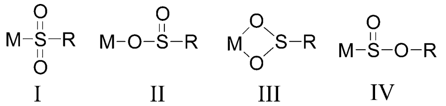

Figure 1. SO_2 insertion isomers.

The insertion of SO_2 into M−R bonds is typically irreversible,[1,16−18] although a few reports exist of partial desulfination of *S*-sulfinates to restore the original M−R complex with the extrusion of SO_2.[19−21] The entire *S*-sulfinate fragment has also been removed from some Pt and Rh complexes by addition of strong acids such as HCl to eliminate the *S*-sulfinate fragments as sulfinic acids and leave a metal halide complex.[22,23] Oxidative demetalation[21] with H_2O_2 to give free sulfinates and sulfonates as well as

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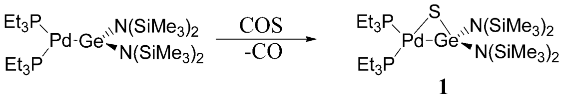
decomposition, including disproportionation of insertion products,[19,24] has also been observed in some complexes.

We have been studying the reactivity of Pt and Pd germylene complexes toward insertions of small organic and inorganic molecules. We have observed that numerous forms of unsaturation will add across the M−Ge bond, and subsequent insertions can be affected to further modify the germyl substrate.[25−28] However, attempts to isolate products from the reaction of SO_2 with $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ failed despite the successes forming four-membered rings using CO_2, $H_2C{=}O$, O_2, and PhNO.[25,26,29,30] With the notable exception of O_2, the analogous Pd complex failed to reproduce any of the addition chemistry noted for Pt,[27] and direct reaction with SO_2 was also unsuccessful. However, we recently demonstrated the reactivity of $(Et_3P)_2PdGe[N(SiMe_3)_2]_2$ with COS to extrude S atoms and form the sulfide bridged species $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ (**1**)[28] (eq 1).



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(1)

Herein we report the further insertion chemistry of the palladium germylene system. Interestingly, the presence of the sulfide bridge dramatically improved our ability to isolate a clean addition product of SO_2 across the Pd−Ge bond. The formation of a stable *O*-germyl-*S*-sulfoxylate insertion isomer, the Ge analogue to the *O*-alkyl-*S*-sulfoxylate, is demonstrated in the insertion of SO_2 into the Pd−germyl bond of complex **1**. The product of this reaction, $(Et_3P)_2Pd(\mu\text{-}S)S(O)OGe[N(SiMe_3)_2]_2$, is observed to undergo two subsequent modes of reactivity upon heating. The first is the reductive elimination of the modified fragment to regenerate the original Pd(0) metal center. This complex is also observed to undergo a subsequent insertion of a germylsulfide moiety into the Pd−S bond, generating an unusal tridentate, dianionic S donor ligand containing a unique digermoxysulfane connectivity.

Experimental Section

All manipulations were performed using air-free techniques. Benzene, toluene, THF, hexanes, pentane, and benzene-d_6 were dried over sodium benzophenone ketyl and degassed. Acetonitrile was dried over 4 Å molecular sieves and degassed. ^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).[31] IR spectra were acquired on a Perkin-Elmer Spectrum BX. Sulfur dioxide and 2-methyl-1,3-pentadiene were purchased from Aldrich and used as received. $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ [28] and $Ge[N(SiMe_3)_2]_2$ [32] were made according to literature procedures. $\{[(Me_3Si)_2N]_2GeS\}_2$ was made by the method of Wegner,[33] using benzene as the solvent and omitting the refluxing step.

$(Et_3P)_2Pd(\mu\text{-}S)S(O)OGe[N(SiMe_3)_2]_2$ (2). Complex **1** (344 mg, 0.48 mmol) was placed into a 100 mL round-bottom flask connected to a gas addition bulb. Toluene (40 mL) was vacuum distilled into the flask, and 2 equiv of SO_2 was then added. The brown solution rapidly became orange-red and was allowed to stir for 24 h. The volatiles were evaporated leaving a red oil. Recrystallization of the oil from cold pentane gave 238 mg (64%) of **2** as an orange solid. ^1H NMR (C_6D_6) δ 0.63 (s, 18H, $SiCH_3$), 0.74 (s, 18H, $SiCH_3$), 0.84 (m, 18H, CH_2CH_3) 1.43 (m, 12H, CH_2CH_3). Note: The ethyl groups of the phosphine ligands display accidental overlap in their ^1H NMR resonances. ^{31}P NMR and ^{13}C NMR spectra indicate that the two phosphine ligands are chemically inequivalent. $^{31}P\{^1H\}$ NMR (C_6D_6) exhibits strong second-order splitting giving the appearance of a pseudoquartet δ 12.84 (d, $^2J_{P-P}$ 102 Hz) 13.47 (d, $^2J_{P-P}$ 102 Hz). $^{13}C\{^1H\}$ NMR δ 6.43 (s, $SiCH_3$), 6.56 (s, $SiCH_3$), 8.17 (s, CH_2CH_3), 8.39 (s, CH_2CH_3), 15.20 (d, J_{P-C} 21 Hz, CH_2CH_3), 17.29 (d, J_{P-C} 13 Hz, CH_2CH_3). IR KBr pellet 1059 cm^{-1} ν(S=O), 674 cm^{-1} ν(S−O). Calculated for $C_{24}H_{66}GeN_2O_2P_2PdS_2Si_4$: C 34.64, H 7.99, N 3.37. Found: C 34.73, H 7.84, N 2.99.

$(Et_3P)Pd(SGe[N(SiMe_3)_2]_2OSOGe[N(SiMe_3)_2]_2S)$ (3). A 100 mL flask was charged with **2** (150 mg, 0.18 mmol) and ~40 mL of benzene. The orange solution was heated at reflux for 70 h under an atmosphere of Ar. The solution darkened to a deep wine red color after a few hours of heating. The volatiles were stripped leaving a dark red oily solid. This solid was dissolved in hexanes, and the red solution was filtered away from a small amount of brown precipitate. The filtrate was stripped to give a dark red solid that was recrystallized from THF/acetonitrile to give yellow microcrystalline **3** (32 mg, 31% yield). ^1H NMR (C_6D_6) δ 0.56 (s, 36H, $SiCH_3$), 0.60 (s, 36H, $SiCH_3$), 0.88 (m, 9H, CH_2CH_3) 1.52 (m, 6H, CH_2CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 21.5 (s). $^{13}C\{^1H\}$ NMR δ 6.38 (s, $SiCH_3$), 6.41 (s, $SiCH_3$), 7.95 (s, CH_2CH_3), 16.55 (d, J_{P-C} 25 Hz, CH_2CH_3). IR KBr pellet 674 cm^{-1}, 681 cm^{-1} ν(O−S−O). Calculated for $C_{30}H_{87}Ge_2N_4O_2PPdS_3Si_8$: C 31.62, H 7.70, N 4.92. Found: C 31.87, H 7.32, N 4.76.

Structure Determination of 2. Irregular, orange crystals of **2** were grown from a toluene solution at 25 °C. A crystal of dimensions 0.18 × 0.12 × 0.12 mm^3 was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K; the detector was placed at a distance 4.959 cm from the crystal. A total of 2338 frames were collected with a scan width of 0.3° in ω and φ with an exposure time of 30 s/frame. The frames were integrated with the Bruker SAINT software package[34] with a narrow frame algorithm. The integration of the data yielded a total of 76431 reflections to a

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Table 1. Summary of Crystallographic Data for **2** and **3**

	2	**3**
empirical formula	$C_{24}H_{66}GeN_2$-$O_2P_2PdS_2Si_4$	$C_{30}H_{87}Ge_2N_4$-$O_2PPdS_3Si_8$
fw	832.20	1139.49
T	158(2) K	158(2) K
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
unit cell dimensions	$a = 9.8961(13)$ Å	$a = 11.6210(14)$ Å
	$b = 38.098(5)$ Å	$b = 13.5478(16)$ Å
	$c = 21.789(3)$ Å	$c = 20.595(3)$ Å
	$\alpha = 90°$	$\alpha = 76.298(2)°$
	$\beta = 98.026(2)°$	$\beta = 78.385(2)°$
	$\gamma = 90°$	$\gamma = 64.863(2)°$
V	8134.5(19) Å^3	2833.1(6) Å^3
Z, calcd density	8, 1.359 Mg/m^3	2, 1.336 Mg/m^3
abs coeff	1.503 mm^{-1}	1.705 mm^{-1}
	0.71073 Å	0.71073 Å
final R indices [$I > 2\sigma(I)$]	R1 = 0.0547,	R1 = 0.0221,
	wR^2 = 0.1004	wR^2 = 0.0546
R indices (all data)	R1 = 0.0968,	R1 = 0.0258,
	wR^2 = 0.1129	wR^2 = 0.0565

maximum 2θ value of 52.85° of which 16928 were independent and 11279 were greater that 2σ(I). The final cell constants (Table 1) were based on the *xyz* centroids of 5866 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[35] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package,[36] using the space group $P2_1/n$ with $Z = 8$ for the formula $C_{24}H_{66}N_2O_2S_2Si_4P_2GePd$ with two crystallographically independent molecules in the asymmetric unit. All non-hydrogen atoms were refined anisotropically with the hydrogens placed in idealized positions. Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0547 and wR2 = 0.1004 [based on $I > 2\sigma(I)$], R1 = 0.0968 and wR2 = 0.1129 for all data. Additional details are presented in Table 1 and are given as Supporting Information as a CIF file.

Structure Determination of 3. Yellow irregular crystals of **3** were grown from a benzene solution at 22 °C. A crystal of dimensions 0.60 × 0.44 × 0.46 mm^3 was mounted as for **2**. A total of 3030 frames were collected with a scan width of 0.3° in ω and φ with an exposure time of 20 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 36064 reflections to a maximum 2θ value of 56.6° of which 13818 were independent and 12595 were greater than 2σ(I). The final cell constants (Table 1) were based on the *xyz* centroids of 6803 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[35] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package,[36] using the space group $P\bar{1}$ with $Z = 2$ for the formula $C_{30}H_{87}N_4O_2Si_8PS_3Ge_2Pd$. 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 = 0.0221 and wR2 = 0.0546 [based on $I > 2\sigma(I)$], R1 = 0.0258 and wR2 = 0.0565 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

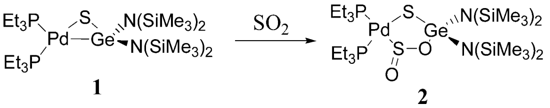
Formation of 3 in the Presence of PPh$_3$. An NMR tube fitted with a Teflon valve was filled with a benzene-d_6 solution containing 15 mg (0.02 mmol) of **2** and 10 mg (0.04 mmol) of PPh$_3$. The solution was frozen and then degassed. The mixture was allowed to thaw and placed in an oil bath maintained at 70 ± 5 °C. Through the course of the heating, the orange solution darkened to a deep red color. NMR spectra were acquired periodically over several days. After 3 days the volatiles were stripped from the solution leaving a yellow-brown solid, which was kept under dynamic vacuum for 1 h. The solid was then redissolved in benzene-d_6, and NMR spectra of the red orange solution were taken. Subsequently, $Ge[N(SiMe_3)_2]_2$ (3.5 mg, 0.01 mmol) was added, and the solution immediately lightened to a bright orange color.

Formation of 3 in the Presence of 2-Methyl-1,3-pentadiene. An NMR tube fitted with a Teflon valve was filled with a benzene-d_6 solution containing 15 mg (0.02 mmol) of **2**, and 2-methyl-1,3-pentadiene (41 μL, 0.4 mmol) was added. The solution was frozen and then degassed. The mixture was allowed to thaw and placed in an oil bath maintained at 70 ± 5 °C. NMR spectra were acquired periodically over 2 days.

Formation of 3 in the Presence of $\{[(Me_3Si)_2N]_2GeS\}_2$. An NMR tube fitted with a Teflon valve was filled with a benzene-d_6 solution containing 30 mg (0.04 mmol) of **2**, and $\{[(Me_3Si)_2N]_2GeS\}_2$ (15 mg, 0.02 mmol) was added. The solution was frozen and then degassed. The mixture was allowed to thaw and placed in an oil bath maintained at 70 ± 5 °C. NMR spectra were acquired periodically over 2 days.

Results and Discussion

Addition of a small excess (2 equiv) of SO$_2$ to toluene solutions of $(Et_3P)_2\overline{Pd(\mu\text{-}S)Ge}[N(SiMe_3)_2]_2$ (**1**) results in the insertion of SO$_2$ into the Pd−Ge bond generating the five-membered metallocycle $(Et_3P)_2Pd(\mu\text{-}S)S(O)OGe[N(SiMe_3)_2]_2$ (**2**) (eq 2). The ^{31}P NMR spectrum of this complex contains inequivalent phosphine resonances. However, the pair of doublets displays a strong second-order coupling giving the appearance of a pseudoquartet.[38] This suggests that the two trans sulfide ligands provide a similar electronic ligand environment about the Pd metal center. In the ^{1}H NMR spectrum, the resonances for the trimethylsilyl groups are shifted downfield from the starting complex and now appear as two singlets instead of one, indicating greater steric constraints of the product. IR bands show ν(S=O) at 1059 cm^{-1}, and ν(S−O) at 674 cm^{-1}, and are consistent with similar structures.[39,40]



1 **2** (2)

The crystal structure of complex **2** is shown in Figure 2. Bond lengths confirm the *O*-germyl-*S*-sulfoxylate structure with the S1−O2 single bond of 1.601(4) Å and the S1−O1 double bond of 1.435(6) Å (see Table 2). The Pd−S bond

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

Complex 2							
Pd−S1	2.3571(14)	Pd−S2	2.3438(14)	P1−Pd−P2	99.47(5)	Pd−S1−O2	107.93(14)
Pd1−P1	2.3190(14)	S1−O1	1.435(6)	P1−Pd−S1	82.12(5)	O2−Ge−S2	103.82(11)
Ge1−N1	1.837(4)	S1−O2	1.601(4)	S1−Pd−S2	92.52(5)	N1−Ge−N2	115.23(18)
Ge−S2	2.1589(13)	Ge−O2	1.815(3)	Pd−S1−O1	107.3(2)	Ge−S2−Pd	104.27(5)
				P2−Pd−S2	85.98(5)	O2−Ge−N2	106.52(17)
Complex 3							
Pd1−P1	2.3072(5)	S1−O2	1.5889(12)	O2−S1−O1	99.21(6)	S1−Pd1−S3	90.356(17)
Pd1−S1	2.2937(5)	S1−O1	1.6041(12)	O2−S1−Pd	106.98(5)	S1−Pd1−P1	174.211(16)
Pd1−S2	2.3321(4)	Ge1−S2	2.1781(5)	O1−S1−Pd1	108.47(5)	P1−Pd1−S2	91.587(17)
Pd1−S3	2.3420(4)	Ge2−S3	2.1794(5)	P1−Pd−S3	85.971(17)	S1−Pd1−S2	92.494(17)
Ge2−N4	1.8305(14)						

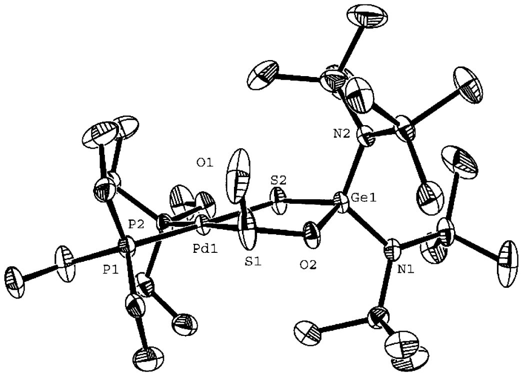


Figure 2. ORTEP representation of $(PEt_3)_2Pd(\mu S)S(O)OGe[N(SiMe_3)_2]_2$ (**2**) (50% probability).

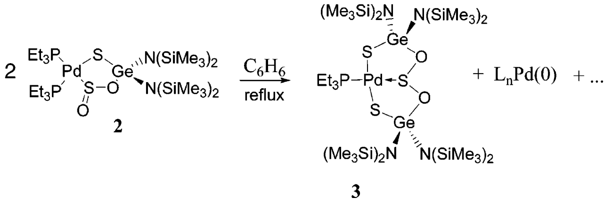
lengths are similar with Pd−S1 2.357(4) Å and Pd−S2 2.3438(4) Å. The Ge−S bond length at 2.1589(13) Å is slightly shorter than the 2.21−2.29 Å range typically reported for Ge−S single bonds.[41] The palladium metal center is square planar, and a tetrahedral geometry is observed about the Ge center. The pyramidal geometry at the S1 atom causes the O2 atom to pucker down in the metallocyclic ring. Thus, the S1−O1 bond vector is almost perpendicular to the square plane of the Pd center with a Pd1−S2−S1−O1 dihedral angle of 97.57(21)°.

In principle, SO_2 insertion could have occurred at many locations with the three most likely being the Pd−Ge, Pd−S, and Ge−S bonds. Insertion into the Pd−Ge bond does give the thermodynamically most favored product. Insertion into the Pd−S or Ge−S bonds must generate either a S−S bond or an even more unfavorable O−S bond. In addition, the Pd−Ge bond is likely weaker than the Pd−S or Ge−S bonds. The two leading formal mechanisms for insertion forming a five-membered ring, SO_2 binding to Pd followed by migratory insertion or a 2 + 2 reaction, also both favor the Pd−Ge bond. The Ge should be preferred over S for migration to the SO_2 oxygen, and the O−Ge interaction should be favored over an O−S interaction in a 2 + 2 type reaction.

Complex **2** represents to our knowledge the first SO_2 insertion into M−R (R = C, Si, Ge) bonds to give an *O*-alkyl-, *O*-silyl-, or *O*-germyl-*S*-sulfoxylate structural isomer. A search of the Cambridge Crystallographic Database did not give any examples of the MS(O)OR connectivity. *O*-Alkyl-*S*-sulfoxylate complexes of Ir and Ni have been prepared from the oxidative addition of alkyl chlorosulfinates.[39,42] Additionally, the insertion of SO_2 into M−H bonds (M = Mo, W) has been reported to give $(C_5R_5)M(CO)_3(S(O)OH)$ (R = H or Me).[40,43] Insertions into Pd−C bonds typically give *S*-sulfinate complexes,[5,17−19] as does the insertion of SO_2 into the Fe−Ge bond of $CpFe(CO)_2GeMe_3$.[11] However, SO_2 insertions into the Ge−C bond indicate the preference for the O binding to the Ge center generating Ge−OS(O)C moieties.[44]

The stability of complex **2** under various conditions was investigated. The $(C_5R_5)M(CO)_3(S(O)OH)$ complexes described above were found to extrude SO_2 and revert to the parent $(C_5R_5)M(CO)_3H$ upon dissolving in organic solvents.[40] Complex **2** is stable in the solid state at room temperature and does not lose SO_2 after being kept under dynamic vacuum for 1 h. In benzene-d_6 solution, **2** does not revert back to **1**; however, very slow conversion to **3** is observed, with 6% **3** present in NMR spectra after 6 days (vida infra). In the presence of excess SO_2, benzene solutions of **2** change color from orange to red-orange, and NMR spectra show a concentration dependent shift in resonances in the ^1H NMR, ^{31}P NMR, and ^{13}C NMR spectra. Upon removal of volatiles, solid **2** is regenerated. These color and spectral changes are consistent with reversible SO_2 binding to complex **2**, possibly at the sulfide bridge site.[45] Such SO_2 coordination may also be occurring at the sulfide bridge in complex **1** during the formation of **2**.

Refluxing orange solutions of **2** in benzene result in a color change to dark red with the formation of a grayish black precipitate. Filtration and subsequent recrystallization gives $(Et_3P)Pd(SGe[N(SiMe_3)_2]_2OSOGe[N(SiMe_3)_2]_2S)$ (**3**) as a bright yellow powder (eq 3). This complex formally consists



(3)

of all the atoms of complex **2** with the addition of a germyl

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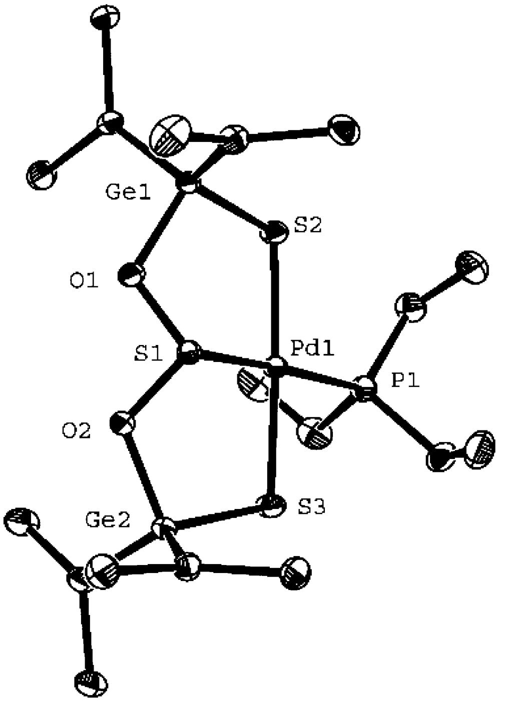


Figure 3. ORTEP representation of $(Et_3P)Pd(SGe[N(SiMe_3)_2]_2OSOGe[N(SiMe_3)_2]_2S)$ (**3**) (50% probability), methyl groups have been excluded for clarity.

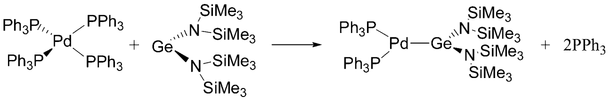
sulfide moiety and rearrangement of the connectivity of the SO_2 bridge. The ^1H NMR spectrum shows the two large singlets in the trimethyl silyl region, slightly upfield from the trimethylsilyl resonances of **2**. The ^{31}P NMR contains only one large singlet at 21.5 ppm, consistent with a single phosphine ligand.

The crystal structure of **3** (Figure 3) shows the unique tridentate S ligand formed by the reaction. The Pd metal center takes on a distorted square planar structure with the S1 atom puckering down below the square plane formed by the other three ligands. The two adjacent oxygen atoms in the ligand are both puckering above the plane (see Table 2 for bond lengths and angles). The Ge−S bond lengths are 0.02 Å longer than in complex **2**.

From the stoichiometry of the reaction, the formation of complex **3** can consume at most 50% of the Pd from complex **2**. Thus, we wanted to investigate the fate of the remaining $^1/_2$ equiv of Pd in this reaction. The metallic precipitate formed during reflux (vide supra) suggests that a Pd(0)(s) is being generated. To trap Pd(0), a benzene-d_6 solution of **2** with 2 equiv of PPh_3 was heated to 70 °C in a sealed tube and monitored by ^1H NMR and ^{31}P NMR spectroscopies over a period of several days. After 3 days of heating, the trimethylsilyl region of the ^1H NMR spectrum and the ^{31}P NMR spectrum indicate ~80% conversion to **3**. However, the presence of free PEt_3 and possibly also free SO_2 complicated determination of the other Pd species in solution. The volatiles were evacuated to remove PEt_3 and any free SO_2 that was present. Upon redissolving in benzene-d_6, the ^1H NMR spectrum contained the partially overlapping multiplets for both free PPh_3 and $(Ph_3P)_4Pd$. The ^{31}P NMR spectrum indicated a broad resonance at 1.6 ppm consistent with rapidly exchanging PPh_3 on the Pd(0) center (eq 4).

$$\mathbf{2} + 2\mathrm{PPh_3} \xrightarrow[\text{2. removal of volatiles}]{\text{1. 70 }^{\circ}\text{C, 3 days}} \mathbf{3} + (\mathrm{Ph_3P})_n\mathrm{Pd} \qquad (4)$$

As a final test for the presence of $(Ph_3P)_4Pd$ in this reaction mixture, 1 equiv of the germylene $Ge[N(SiMe_3)_2]_2$ was added to the solution. We have previously reported the rapid, quantitative generation of $(Ph_3P)_2PdGe[N(SiMe_3)_2]_2$ and 2 equiv of PPh_3 from the reaction of $(Ph_3P)_4Pd$ with $Ge[N(SiMe_3)_2]_2$ (eq 5).[27] Upon addition of the germylene ligand,



(5)

the red-brown solution immediately turned bright orange, consistent with the formation of the orange palladium germylene complex. NMR spectra confirmed the formation of $(Ph_3P)_2PdGe[N(SiMe_3)_2]_2$ and the liberation of free PPh_3.

The formation of **3** from **2** illustrates two different modes of reactivity of the *O*-germyl-*S*-sulfoxylate insertion isomer. The first is the ability of this isomer to eliminate the sulfinated fragment with reduction of the metal to form $(Et_3P)_nPd(0)$. It is possible that the entire metallocyclic fragment is reductively eliminated. Subsequent fragmentation would then occur to liberate the SO_2 moiety as only a germylsulfide fragment is incorporated into complex **3**. However, we cannot exclude the possibility that SO_2 is extruded first and that the resulting germyl sulfide fragment is reductively eliminated in the form of a germylsulfanone (eq 6) (vida infra). The SO_2 could be liberated or remain weakly bound to the metal giving a $(Et_3P)_nPd(SO_2)$ complex.

In light of the high affinity of Pd for sulfur, it is interesting that complex **2** with its two Pd−S bonds will readily undergo reductive elimination. Formation of complex **3** can even be observed at room temperature, albeit slowly, with 6% conversion to **3** occurring in benzene-d_6 solutions of **2** after 6 days. Sulfur compounds have been known to poison noble metal catalysts,[46] and Pd catalysts have been shown to be poisoned by direct interactions with SO_2.[47] Complex **2** does not appear to be deactivated in this regard.

A second mode of reactivity demonstrated by the formation of **3** is the net insertion of other atoms into the M−S bond. Complex **3** can be viewed as the net insertion of a germyl sulfide moiety into the Pd−S bond. The original S atom remains bound to the Pd center; however, it is no longer a formerly anionic ligand and is instead datively coordinating the metal through the lone pairs on the digermoxysulfane moiety. Subsequent insertions into the various sulfinate isomers are rare in the literature. Most reported reactivities of SO_2 inserted species involve desulfonation, decomposition, and the removal of the inserted moiety described above. A noteworthy exception is the report that cationic Pd complexes are effective catalysts for the copolymerization of ethane,

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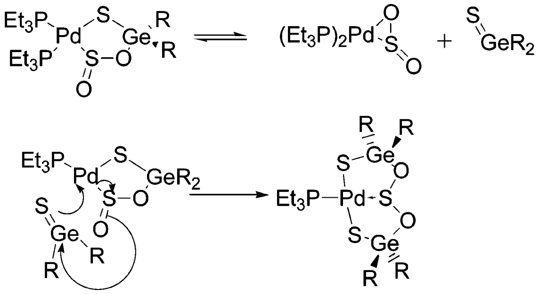
propene, and cyclopentene with sulfur dioxide to make alternating copolymers.[4]

The tridentate S-donor ligand of complex **3** is rather unusual. Tridentate S ligands are most commonly thio crown ether derivatives such as 1,4,7-trithiacyclononane and 1,4,7-trithacyclodecane.[48] However, these are neutral ligands with all three S atoms participating in dative coordination of the metal center. A class of radiopharmaceutically significant complexes of Re, Tc, and Ru with the tridentate 3-thiapentane-1,5-dithiolate ligand, $S(CH_2CH_2S)_2$, have also been synthesized.[49−51] This ligand contains two anionic sulfides as well as a neutral sulfur moiety with a binding mode similar to the ligand in complex **3**. However, like the thio crowns, it contains hydrocarbon chains as the linker between sulfur atoms. In complex **3**, these carbon linkers are replaced with a unique digermoxysulfane moiety. In addition, the bis(bistrimetlysilylamido) functionalization on the Ge centers introduces a substantial steric component not typically observed in other examples of tridentate sulfide ligands.

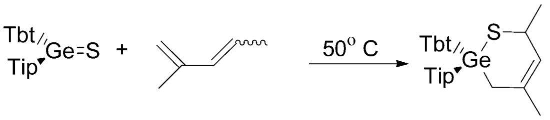
As discussed above, one of the simplest mechanisms for the formation of **3** begins with the reductive elimination of a germylsulfanone. This species could then undergo insertion into another molecule of **2** to give complex **3**, possibly after initial displacement of one phosphine ligand (see eq 6). To investigate this mechanism, we attempted to observe the germylsulfanone moiety directly.



(6)

In the absence of extremely bulky groups on the Ge center, germylsulfanone species are not kinetically stable but can be generated in situ.[52,53] If a substantial concentration of a $R_2Ge{=}S$ were to build up in solution, it should dimerize.[54,55] The dimeric form of $[(Me_3Si)_2N]_2Ge{=}S$, $\{[(Me_3Si)_2N]_2GeS\}_2$, is a known compound and has been made directly from the reaction of germylene with elemental sulfur.[33] ^1H NMR spectra of the reactions making **3** do not show any traces of $\{[(Me_3Si)_2N]_2GeS\}_2$. Heating solutions of **2** in the presence of $\{[(Me_3Si)_2N]_2GeS\}_2$ generated **3**; however, it appears that this was due to the direct reaction of **2**, as the overall amount of $[(Me_3Si)_2N]_2GeS\}_2$, in solution, did not change over time. Thus, if such a dimer were to form, it does not appear likely to break apart and react further under the experimental conditions. The absence of the dimer in the NMR spectra of these reactions suggests that a substantial concentration of the germylsulfanone is not building up in solution.

We also attempted to trap the $[(Me_3Si)_2N]_2Ge{=}S$ fragment directly. The stable germylsulfanone, Tbt(Tip)Ge=S (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl), can be trapped by 2-methyl-1,3-pentadiene.[52] The germylsulfanone will undergo a [2 + 4] cycloaddition at 50 °C to give a six membered ring (eq 7). For the trapping reaction, 20 equiv of 2-methyl-1,3-pentadiene was added to a benzene-d_6 solution of **2** that was heated to 70 °C in a sealed tube. After 2 days of heating, NMR spectra indicated the formation of **3**; however, no resonances consistent with the formation of a cycloaddition product were observed, even after stripping the volatiles to remove excess pentadiene. These experiments are inconsistent with the presence of a free germylsulfanone fragment being formed in situ.



(7)

The absence of a free germylsulfanone fragment suggests that a more complex process is occurring in the formation of **3**. Another possible mechanism involves the elimination of SO_2 from one molecule of **2** leaving an acyclic Pd−S−Ge moiety and/or regenerating **1**. This would be consistent with reversible and partially reversible SO_2 insertions described above.[19−21,40] The acyclic Pd−S−Ge moiety or **1** could then react with another molecule of **2** to give **3** following the concomitant extrusion of a $L_nPd(0)$ species. This mechanistic hypothesis was tested by mixing **1** and **2** in a 1:1 ratio along with an equivalent of $Ge[N(SiMe_3)_2]_2$ to stabilize any $(Et_3P)_2Pd(0)$ formed. Complex **3** and $(Et_3P)_2PdGe[N(SiMe_3)_2]_2$ were formed over a 4 day period; however, there was no change in the concentration of **1**, and there was no enhancement of the rate as compared to the direct conversion of **2** to **3** in the absence of added **1**. This observation rules out **1** as being an intermediate in the process. Loss of SO_2 from **2** to generate an acyclic Pd−S−Ge moiety followed by reaction of this intermediate with a second equivalent of **2** and extrusion of $(Et_3P)_2Pd(0)$ remains a plausible mechanistic hypothesis for the formation of **3**.

Conclusions

We have demonstrated the insertion of SO_2 into the Pd−germyl bond to give an *O*-germyl-*S*-sulfoxylate insertion isomer. The palladium metal center continues to undergo insertion chemistry and exhibits redox activity despite the presence of potentially deactivating sulfur ligands. The

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insertion product demonstrates two different simultaneous modes of reactivity, undergoing both reductive elimination and further insertion to give a new Pd complex with a unique tridentate sulfide ligand.

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

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