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Molecular Structure and Carbonylation of Ethyl(benzenethiolato)palladium(II) Complex, *trans*-PdEt(SPh)(PMe$_3$)$_2$

Kohtaro Osakada,* Youichi Ozawa, and Akio Yamamoto*,†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

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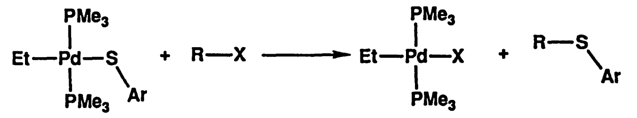
Synopsis. X-Ray crystallography of ethylpalladium thiolato complex, *trans*-PdEt(SPh)(PMe$_3$)$_2$, shows the detailed features of the Pd–C and Pd–S bonding. Reaction of the complex with CO at 5 atm gives *S*-phenyl thiopropionate. The NMR spectrum of the reaction mixture under 1 atm of CO shows the presence of *trans*-Pd(COEt)(SPh)(PMe$_3$)$_2$ formed through CO insertion into the Pd–C bond.

Recently attention has been paid to organotransition metal thiolato complexes which are regarded as key intermediates in the metal complex-catalyzed synthetic organic reactions such as desulfurization of organosulfur compounds[1–4] and coupling reaction of organic halides with thiolate anion to give dialkyl sulfides.[5–7] In the course of our study on chemical properties of organonickel and -palladium thiolato complexes[8] we found that the palladium complexes, *trans*-PdEt(SAr)(PMe$_3$)$_2$ (Ar=Ph, *p*-MeC$_6$H$_4$, and *p*-MeOC$_6$H$_4$), reacted with various organic halides to give sulfides through selective coupling of the thiolato ligand with the alkyl or acyl group of the substrates.[9]



(R–X = MeCOCl, MeI, CH$_2$=CHCH$_2$Cl, PhCH$_2$Br)

Although various interesting properties of thiolato complexes of transition metals were already revealed, there have been few reports on the alkylpalladium thiolato complexes. We carried out further investigation on the structure and reactivities of *trans*-PdEt(SPh)(PMe$_3$)$_2$. Here we report the results of the X-ray crystallography and of the study on the reaction with CO.

Results and Discussion

Table 1. Bond Distances and Bond Angles for Non-H Atoms with esd's in Parentheses

	Bond distance/Å		
Pd1–S2	2.384(2)	Pd1–P3	2.307(3)
Pd1–P4	2.309(3)	Pd1–C5	2.098(9)
C5–C6	1.491(15)	S2–C13	1.737(9)
C13–C14	1.408(11)	C14–C15	1.380(15)
C15–C16	1.357(15)	C16–C17	1.376(13)
C17–C18	1.440(14)	C18–C13	1.412(12)
P3–C7	1.799(14)	P3–C8	1.811(14)
P3–C9	1.845(11)	P4–C10	1.794(12)
P4–C11	1.800(11)	P4–C12	1.819(13)
	Bond angle/°		
S2–Pd1–P3	87.04(9)	S2–Pd1–P4	91.83(9)
S2–Pd1–C5	172.7(3)	P3–Pd1–P4	174.4(1)
P3–Pd1–C5	92.0(3)	P4–Pd1–C5	89.8(3)
Pd1–C5–C6	107.6(6)	Pd1–S2–C13	109.2(3)
S2–C13–C14	119.8(7)	C13–C14–C15	121.9(9)
C14–C15–C16	120.3(8)	C15–C16–C17	120.8(1.0)
C16–C17–C18	120.5(9)	C17–C18–C13	118.3(7)
Pd1–P3–C7	113.7(5)	Pd1–P3–C8	113.3(4)
Pd1–P3–C9	120.7(5)	C7–P3–C8	104.3(7)
C8–P3–C9	101.8(6)	C7–P3–C9	101.0(6)
Pd1–P4–C10	117.6(5)	Pd1–P4–C11	120.3(4)
Pd1–P4–C12	110.5(5)	C10–P4–C11	99.9(6)
C11–P4–P12	103.0(6)	C10–P4–C12	103.3(6)

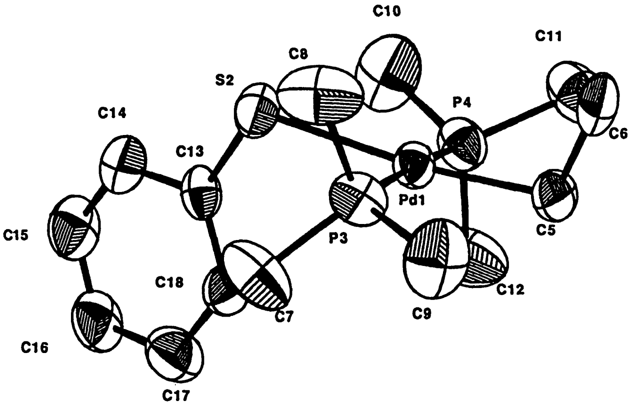


Fig. 1. The molecular structure of *trans*-PdEt(SPh)(PMe$_3$)$_2$ (**1**) with the atomic numbering scheme. Non-hydrogen atoms are shown by thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for simplicity.

Structure. Figure 1 shows the molecular structure of *trans*-PdEt(SPh)(PMe$_3$)$_2$ (**1**) determined by X-ray crystallography. The bond distances and angles of the non-hydrogen atoms are summarized in Table 1. The molecule has a square-planar coordination around the palladium center. The phenyl plane of the thiolato ligand is almost perpendicular to the coordination plane similarly to the phenoxide ligand of the already reported methylpalladium phenoxide complexes with PMe$_3$ ligands.[10] The methyl carbon atoms of the two PMe$_3$ ligands are staggered with respect to the P–Pd–P axis. The molecule of the already reported *trans*-PdEt(Br)(PMe$_3$)$_2$ has an eclipsed conformation regarding with the carbon atoms in the PMe$_3$ ligands, and has a pseudo-mirror plane that includes Pd, Br, and the car-

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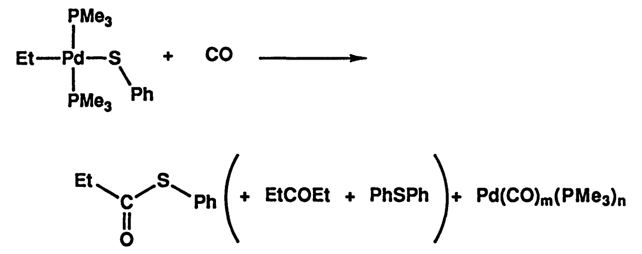
† Present address: Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1, Ohkubo, Shinjuku-ku, Tokyo 169.

bon atoms in the ethyl ligand.[9] The Pd–C bond distance [2.098(9) Å] in the present ethylpalladium thiolato complex is longer than that in *trans*-PdEt(Br)$(PMe_3)_2$ [2.063(5) Å], suggesting a larger trans influence of the thiolato ligand than the bromo ligand. The Pd–S bond distance [2.384(2) Å] is somewhat longer than the Pd–S bond of the terminal thiolato ligand in $[Pd(SC_6F_5)(PPh_3)(\mu\text{-}SC_6F_5)]_2$.[11]

A recent review on the structures of transition metal thiolato complexes indicated that the M–S–C bond angles of the benzenethiolato complexes are in the range 103—118°.[12] The Pd–S–C angle in the title compound (109.2(3)°) is within the range.

Reaction of 1 with CO. Reaction of complex **1** with CO at 5 atm for 3 h gives *S*-phenyl thiopropionate in 62% yield accompanied by formation of small amounts of diethyl ketone and diphenyl sulfide. The resulting palladium complexes consisted of a mixture of several palladium(0) carbonyl complexes $Pd(CO)_m(PMe_3)_n$[13] as deduced on the basis of the IR spectrum. The NMR study of the reaction mixture was carried out in CD_2Cl_2 under 1 atm of CO. NMR spectra (^1H, ^{13}C, and ^{31}P) indicated the presence of *trans*-Pd(COEt)(SPh)$(PMe_3)_2$ as the major palladium complex. Signals due to unreacted **1** are also observed, while the signals due to the *S*-thioester are not observed under the conditions. The above carbonylation of **1** under 5 atm of CO seems to proceed through formation of a propionyl palladium complex through CO insertion into the Pd–C bond in **1** followed by reductive elimination of the propionyl and thiolate ligands.[14]



Previously we have reported carbonylation of similar organonickel and -palladium alkoxide complexes. PdMe(OCH$(CF_3)_2$)(dppe) (dppe=1,2-[bis(diphenylphosphino)ethane]) reacts with CO easily to give PdMe(COOCH$(CF_3)_2$)(dppe) through selective CO insertion into the Pd–O bond.[15] On the other hand, *trans*-PdMe(OAr)L_2 (L=PEt_3) undergoes CO insertion into the Pd–C bond to give Pd(COMe)(OAr)L_2.[16] In the present case it is noted that CO insertion occurs into the Pd–C bond rather than into the Pd–S bond.

Experimental

trans-PdEt(SPh)$(PMe_3)_2$ (**1**) was prepared by the method reported previously.[9] GC-MS measurement was preformed on a Hitachi M-80 mass spectrometer. GC was measured on a Shimadzu 3BT gas-chromatograph using a 1-m column packed with Silicone OV-1. NMR spectra were recorded at −40 °C on a JEOL FX-100 spectrometer.

Crystallography. The single crystals suitable for crystallography were grown in acetone at −20 °C.

Crystald Data: $C_{14}H_{28}P_2SPd$, M=396.55, triclinic, $P\bar{1}$, a=9.613(7), b=12.204(6), c=8.419(4) Å, α=91.10(4), β=101.85(5), γ=94.82(5)°, U=962.5(9) Å^3, Z=2, D_c=1.369 g cm^{-3}, μ(Mo$K\alpha$)=12.1 cm^{-1}, F(000)=408.

Data Collection and Structure Refinement: A crystal with approximate dimensions of 0.45×0.50×0.50 mm sealed in a glass capillary under argon was mounted on a Rigaku AFC-5 automated four-cycle diffractometer. Unit cell parameters were determined by the least-squares calculation of 2θ values of 25 reflections with $19° < 2\theta < 22°$. Intensity data collection was carried out using Mo$K\alpha$ radiation (λ=0.71069 Å) by the ω–2θ mode. The scan speed and range were 4° min^{-1} in 2θ and $\Delta(2\theta)=(1.40+0.7\tan\theta)°$, respectively. Among 2516 unique reflections ($3° < 2\theta < 45°$ and $-10 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 8$), 2407 reflections with $F_o \geqslant 3\,\sigma(F_o)$ were used in the structure calculation. No absorption correction was applied.

Calculations were carried out on a FACOM A-70 computer. The position of palladium was determined by a direct method (SAPI85).[17] The other non-hydrogen atoms were found in the subsequent Fourier procedure. A full-matrix least-squares refinement was carried out applying anisotropic thermal factors for the non-hydrogen atoms. Hydrogen atoms were located in the difference Fourier map or at the idealized positions, and included in least-squares calculations without refinement of their parameters. Atomic coordinates are listed in Table 2. The weighting scheme, $w=1/\{\sigma^2(F_o)+[0.009(F_o)]^2\}$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R_w values were 0.059 and 0.064, respectively.**

Reaction of 1 with CO. To a tetrahydrofuran (3 cm^3) solution of **1** (36 mg, 0.091 mmol) in a glassware autoclave was introduced CO at 5 atm at room temperature. The orange yellow solution soon changed into deep red. After stirring for 3 h GC and GC-MS analyses of the solution indicated formation of *S*-phenyl thiopropionate (9.4 mg, 62%); MS (70 eV) m/z (rel intensity) 166 (M$^+$; 29), 110 (81), 109 (36), 57 (100), and 29 (87). Formation of small amounts (<10%) of diethyl ketone and diphenyl sulfide was also observed in the reaction mixture. IR spectrum of the reaction mixture after removal of the solvent showed strong broad peaks near 1700

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-H Atoms with esd's in Parentheses

Atom	x	y	z	$B_{eq}/Å^2$
Pd1	0.63172(6)	0.72191(5)	0.04074(6)	3.39
S2	0.4785(3)	0.6863(2)	−0.2203(3)	4.35
P3	0.8095(3)	0.7767(2)	−0.0953(3)	4.70
P4	0.4453(3)	0.6838(2)	0.1716(3)	4.46
C5	0.7757(10)	0.7333(8)	0.2666(11)	4.7
C6	0.8270(12)	0.6217(9)	0.2942(11)	6.5
C7	0.7626(13)	0.8828(11)	−0.2375(17)	7.7
C8	0.8565(14)	0.6667(10)	−0.2169(18)	8.0
C9	0.9864(12)	0.8344(12)	0.0179(16)	7.7
C10	0.2846(13)	0.6126(11)	0.0557(15)	7.8
C11	0.4702(12)	0.6036(9)	0.3514(13)	6.3
C12	0.3848(13)	0.8106(10)	0.2402(17)	7.8
C13	0.3611(8)	0.7885(7)	−0.2579(10)	3.6
C14	0.2307(10)	0.7676(8)	−0.3709(11)	4.6
C15	0.1358(10)	0.8471(9)	−0.4084(12)	5.3
C16	0.1686(10)	0.9501(9)	−0.3400(12)	5.3
C17	0.2927(11)	0.9755(8)	−0.2259(13)	5.5
C18	0.3940(9)	0.8946(8)	−0.1828(11)	4.4

** The complete F_o—F_c data, temperature factors of the non-hydrogen atoms, and bond distances and angles of the hydrogen atoms are deposited as Document No. 9117 at the Office of the Editor of Bull. Chem. Soc. Jpn.

cm^{-1} which are assigned to the CO stretching vibrations of palladium carbonyl complexes with the phosphine ligands.

A CD_2Cl_2 (ca. 0.3 cm^3) solution of **1** (32 mg, 0.081 mmol) was introduced to an NMR tube (5 mmϕ) which was then capped with a rubber septum under argon atmosphere. After removal of the argon in the system with a needle connected with a vacuum line, CO (1 atm) was charged with a syringe. After setting the solution at room temperature for 6 h the NMR spectra indicated formation of *trans*-Pd(COEt)(SPh)(PMe_3)$_2$ in ca. 80% yield. Signals due to unreacted **1** were also observed. ^{1}H NMR (CD_2Cl_2) δ=0.99 (t, CH_3, J(HH)=7 Hz), 1.21 (t, P(CH_3)$_3$, J=4Hz),[18] 2.55 (q, CH_2, J(HH)=7 Hz), and 6.8—7.5 (m, C_6H_5); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ=149.7 (s, C_6H_5), 132.0 (s, C_6H_5), 127.3 (s, C_6H_5), 120.3 (s, C_6H_5), 49.6 (t, CH_2, J(PC)=16 Hz), 13.9 (t, P(CH_3)$_3$, J=15 Hz),[18] 8.4 (s, CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, chemical shift referred to external H_3PO_4) −20.4 ppm.

Reaction of **1** with ^{13}CO in an NMR tube was carried out similarly. ^{13}C{^{1}H} NMR spectrum of the reaction mixture showed a singlet at 250.1 ppm due to the carbonyl carbon atom of *trans*-Pd(COEt)(SPh)(PMe_3)$_2$. The signals of the ethyl ligand in the ^{1}H and ^{13}C{^{1}H} NMR spectra showed splitting due to the C–C and C–H coupling. The obtained coupling constants ^1J(CC), ^2J(CH), and ^3J(CH) are 33, 5, and 7 Hz, respectively.

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