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Oxidative Addition of a Hypervalent Transannular Sulfur–Sulfur Bond to a Pd(0) Complex: Synthesis and Crystal Structures of 1,5-Dithiacyclooctanepalladium(II) Bis(trifluoromethanesulfonate) Having Phosphine Ligands

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A hypervalent compound 1,5-bis(trifluoromethylsulfonyloxy)-1λ^4,5λ^4-dithiabicyclo[3.3.0]octane (**1**) oxidatively reacted with $Pd_2(dba)_3$ (dba = dibenzylidene acetone) in acetonitrile to give a dicationic complex $[Pd(dtco)(CH_3CN)_2](OTf)_2$ (**2**) (DTCO = 1,5-dithiacyclooctane), in which the DTCO ligand coordinated in *cis*-chelation to the palladium metal. Acetonitrile in **2** was labile enough to be readily replaced by phosphine ligands to give dicationic DTCO-phosphine palladium complexes of the formula $[Pd(dtco)(L)_2](OTf)_2$ (**3**: L = PMe_2Ph; **4**: L = PPh_3; **5**: L_2 = 1,2-bis(diphenylphosphino)ethane; **6**: L_2 = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl). Molecular structures of **5** and **6** have been characterized by X-ray analysis, indicating that each of these two complexes consists of a discrete dicationic palladium(II) species $[Pd(dtco)L_2]^{2+}$ and two trifluoromethanesulfonate ions without any cation–anion bonding interaction, and revealing that the DTCO is coordinated to the palladium center as a bidentate ligand and that two phosphorus atoms ultimately coordinated to the metal in *cis*-fashion.

Oxidative addition of an E–E bond such as B–B,[1—5] Si–Si,[6—18] Sn–Sn,[19—23] S–S,[24] and Se–Se[24] to a low valent late transition metal complex giving the corresponding complex with *cis* E–M–E bonds has been extensively investigated. A hypervalent transannular E–E bond in medium-sized heterocyclic compounds is of considerable interest as another σ-bond for the oxidative addition, which has attracted less attention;[25] the transannular σ-bond was formed as a result of a dication formation by oxidation of a neutral heterocyclic compound containing two heteroatoms and has an oxidizing ability toward organic compounds.[26—28] A thionia dication, 1,5-bis(trifluoromethylsulfonyloxy)-1λ^4,5λ^4-dithiabicyclo[3.3.0]octane (**1**) is the most attractive compound (Chart 1), because **1** is the only crystallographically characterized compound that contains a transannular S–S bond.[29] We report here a new aspect to the chemistry of a hypervalent transannular compound **1**; oxidative addition of the hypervalent transannular S–S σ-bond of **1** to a Pd(0) complex $Pd_2(dba)_3$ (dba = dibenzylidene acetone, 1,5-diphenyl-1,4-pentadien-3-on) in the presence of donating ligands such as acetonitrile and tertiary phosphine yielded bis(triflate) complexes of general formula $[Pd(dtco)(L)_2](OTf)_2$ (L = acetonitrile or tertiary phosphine; DTCO = 1,5-dithiacyclooctane).

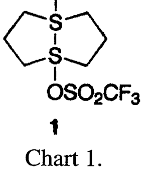
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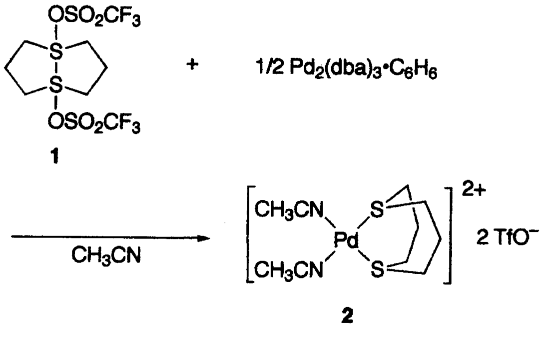
Chart 1.

Results and Discussion

Syntheses and Characterization of Palladium(II) Complexes (2—5). Oxidative addition of **1** to a Pd(0) complex, $Pd_2(dba)_3$ in acetonitrile proceeded readily at room temperature to give $[Pd(dtco)(CH_3CN)_2](OTf)_2$ (**2**). The formulation of **2** was suggested by ^1H NMR and IR spectroscopies. The ^1H NMR spectrum of **2** in CD_3CN displayed multiplet signals due to the DTCO ligand bound to the palladium metal. The coordination of acetonitrile to the palladium atom was supported by its IR spectrum; an absorption band at 2328 cm^{-1}. The SO_3 moiety of the triflates of **2** exhibited strong bands at 1261, 1157, and 637 cm^{-1} in the IR spectrum. Complex **2** gradually turned into a viscous oil from brown powder even in argon, and decomposed on exposure to air and moisture; such chemical properties are quite similar to those of a dicationic acetonitrile complex $[Pd(NCCH_3)_4](BF_4)_2$.[30]



(1)

The lability of acetonitrile of **2** hampered its characterization, and hence we prepared and characterized dicationic DTCO–phosphine palladium complexes by treating **2** with monodentate and bidentate phosphine ligands. Addition of two molar amounts of PMe_2Ph and PPh_3 to **2** in acetonitrile gave $[Pd(dtco)(PMe_2Ph)_2](OTf)_2$ (**3**) and $[Pd(dtco)(PPh_3)_2](OTf)_2$ (**4**) respectively in almost quantitative yields. Similarly, dicationic palladium complexes **5** and **6** can be prepared by the reaction of **2** with DPPE [1,2-bis(diphenylphosphino)ethane] and (*R*)-BINAP [(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], respectively (Chart 2). These palladium complexes are quite air-stable.

The ^1H NMR spectrum of **3** in $CDCl_3$ at 35 °C displayed a set of broad peaks at $\delta = 2.30$—2.50, 2.70—2.90, and 3.02—3.30 in a 4 : 4 : 4 integral ratio for the coordinated DTCO methylene protons, the former two signals being assignable to the magnetically nonequivalent α-methylene protons and the last one to the β-methylene protons, as revealed by its ^1H–^1H COSY spectrum. The ^1H NMR spectrum of **4** was essentially the same as that of **3**, β-protons ($\delta = 2.20$—2.35 and 2.35—2.45) of the DTCO and the α protons ($\delta =$ 2.50—2.65 and 2.80—2.95) being observed. Two phosphine ligands of **3** and **4** were arranged to be *cis* because of the chelation of the DTCO ligand. The ^{31}P NMR signal of **4** ($\delta = 29.8$) appeared at a lower field than that of **3** ($\delta = 4.6$), presumably due to the deshielding by the phenyl group of the triphenylphosphine. The UV-vis spectra of **3** and **4** showed characteristic intense bands at 318 and 351 nm respectively due to LMCT from a filled S(pπ) orbital to an empty Pd-(dπ^*) orbital.[31] Complexes **5** and **6** have also been identified by IR and NMR spectroscopies together with their X-ray analysis (vide infra). The ^1H NMR resonances assignable to the DTCO ligand of **5** was observed as three multiplets at $\delta = 2.25$—2.50, 2.65—2.82, and 3.00—3.10, while those of **6** appeared as broad multiplets at $\delta = 2.30$—2.80 due to the DTCO ligand. Absorption spectra of **5** (318 nm) and **6** (357 nm) were comparable with those found for **3** and **4**. The presence of trifluoromethylsulfonyloxy groups as separated anions for these four complexes was confirmed by IR and ^{19}F NMR spectroscopies. Thus, the well-defined hypervalent transannular S–S bond of **1** added in *cis* fashion to the Pd(0) metal.

Molecular Structures of 5 and 6. Crystals of complexes **5** and **6** suitable for X-ray structure determination were obtained by recrystallization from a mixture of acetonitrile and diethyl ether. The molecular structures of these complexes **5** and **6** are presented in Figs. 1 and 2, respectively, and the selected bond distances and bond angles are collected in Table 1. It is obvious that each crystal structure of **5** and **6** consists of a discrete dicationic palladium(II) species $[Pd(dtco)L_2]^{2+}$ and two trifluoromethanesulfonate ions without any cation–anion bonding interaction. Complex **5** has a *cis*-bisphosphine ligand (Fig. 1); the acute P(1)–Pd–P(2) angle (85.0(1)°) is comparable with that observed for $[PdCl_2(dppe)]$ (85.82(7)°)[32] and [Pd(NCS)-(SCN)(dppe)] (85.1(1)°).[33] The S(1)–Pd–S(2) (89.6(1)°) and S(2)–Pd–P(2) (90.9(1)°) angles are approximately 90°. The palladium atom deviates 0.156 Å from the S(1)–S(2)–P(1)–P(2) least squares plane. The DTCO is coordinated to the palladium center as a bidentate ligand and the two phosphorus atoms are ultimately coordinated to the metal in *cis*-fashion. The bond distances, Pd–S(1) (2.372(3) Å) and Pd–S(2) (2.374(3) Å), are comparable to those of the reported dicationic Pd(II) cyclic sulfide complexes; the Pd–S bond distances for $[PdL_2][PF_6]_2$ (L = 1,4,7,10,13,16-hexathiacyclooctadecane) lie in the range of 2.3114(14)—2.3067(15) Å[34] and those for $[PdL_2][PF_6]_2$ (L = 1,4,7-trithiacyclononane) in the range of 2.309(1)—2.333(2) Å.[35] Both of the sulfur atoms

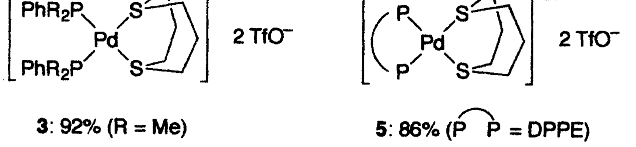


Chart 2.

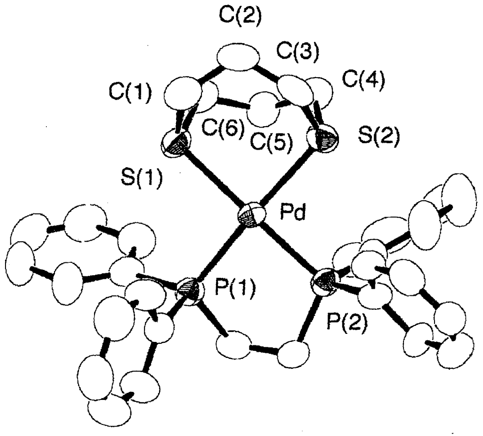


Fig. 1. ORTEP drawing of the cation of complex **5** with the numbering scheme. Hydrogen atoms are omitted for clarity.

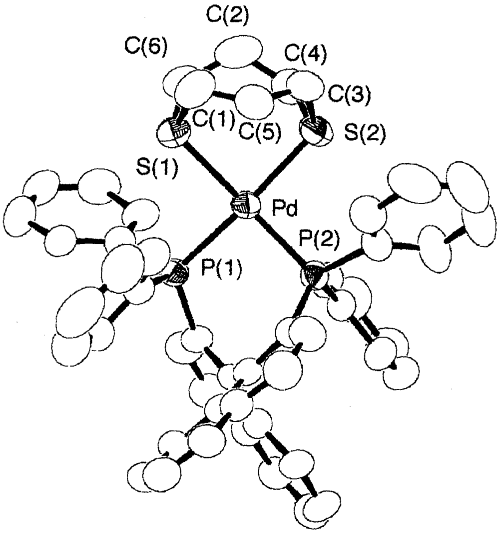


Fig. 2. ORTEP drawing of the cation of complex **6** with the numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (degree) for Palladium Complexes **5** and **6**

	5	**6**
	Bond distances (Å)	
Pd–S(1)	2.372(3)	2.371(3)
Pd–S(2)	2.374(3)	2.374(3)
Pd–P(1)	2.287(3)	2.303(2)
Pd–P(2)	2.277(3)	2.317(3)
S(1)–C(1)	1.83(1)	1.87(2)
C(1)–C(2)	1.49(2)	1.52(2)
C(2)–C(3)	1.52(2)	1.53(2)
C(3)–S(2)	1.82(1)	1.79(2)
S(2)–C(4)	1.83(1)	1.82(2)
C(4)–C(5)	1.50(2)	1.47(3)
C(5)–C(6)	1.55(2)	1.47(3)
C(6)–S(1)	1.82(1)	1.86(2)
S(1)–S(2)	3.343(4)	3.31(4)
	Bond angles (deg)	
S(1)–Pd–S(2)	89.6(1)	88.61(12)
S(2)–Pd–P(2)	90.9(1)	92.44(11)
P(2)–Pd–P(1)	85.0(1)	92.08(8)
P(1)–Pd–S(1)	93.7(1)	88.87(10)
S(1)–Pd–P(2)	169.1(1)	168.13(12)
S(2)–Pd–P(1)	174.1(1)	169.65(11)
Pd(1)–S(1)–C(1)	107.5(4)	104.4(5)
Pd(1)–S(1)–C(6)	103.2(4)	108.5(6)
C(6)–S(1)–C(1)	103.1(6)	104.3(9)
Pd(1)–S(2)–C(3)	107.6(4)	106.5(5)
Pd(1)–S(2)–C(4)	102.5(5)	102.9(5)
C(3)–S(2)–C(4)	105.1(6)	104.2(8)
S(1)–C(1)–C(2)	119.0(9)	115.6(9)
C(1)–C(2)–C(3)	116(1)	116(2)
S(2)–C(4)–C(5)	117.0(9)	118.6(13)
C(4)–C(5)–C(6)	116(1)	118(2)
C(5)–C(6)–S(1)	115.9(7)	115.2(13)

bound to the palladium adopt a slightly distorted tetrahedral geometry.

The molecular structure of **6** is essentially the same as that of **5**, and reveals the expected square planar geometry around the palladium atom; the sum of the four angles around Pd is 361.93°. The dissymmetry of (*R*)-BINAP fixes the λ-conformation of the seven-membered chelate ring of **6** (Fig. 2). Bond lengths Pd–P(1) (2.303(2) Å) and Pd–P(2) (2.317(3) Å) are normal and nonequivalent to each other. The P(1)–Pd–P(2) bite angle (92.08(8)°) is comparable with that found for $PdCl_2$((*R*)-BINAP) (92.69(8)°).[36] One of the most interesting features is the dihedral angle (θ) between the two naphthyl planes. The value of 83.8° for complex **6** is larger than that (73.0°) of [$PdCl_2${(*R*)-BINAP}] as well as those (71.0(3)—75.5(6)°) for cationic rhodium(I) complexes which are also d^8 species and thus adopt square planar geometry.[37] These facts show that the BINAP ligand is flexible enough to accommodate metal ions under various environments.

The structure of the DTCO ligand is notable because there is considerable interest in a conformation of a medium sized heterocyclic ring and an intramolecular interaction between two heteroatoms.[26,38—40] Although the crystal structure determination of the free DTCO ligand has not been carried out, X-ray crystallographic studies of some DTCO metal complexes have been reported. The DTCO ligands of **4** and **5** take a boat-chair conformation similar to that for monodentate DTCO complexes such as *trans*-[$SnCl_4(dtco)_2$][41] and [$NiCl_2$(dtco)].[42] Complexes **5** and **6** have also the boat-chair conformation. Thus, our results are the first examples of crystallographically characterized DTCO ligand bound to the metal center in bidentate fashion. Nonbonding S(1)···S(2) distances (3.343(4) and 3.31(4) Å), which are significantly shorter than the van der Waals contact (3.70 Å), are comparable to those found for *trans*-[$SnCl_4(dtco)_2$] (3.272(3) Å)[41] and [$NiCl_2$(dtco)] (3.335(3) Å).[42]

Conclusion

We have demonstrated that the organosulfur compound **1** having a hypervalent S–S bond oxidatively added to a Pd(0), $Pd_2(dba)_3$, giving the dicationic palladium trifluoromethanesulfonate **2**. The Pd(II) complexes **3**—**6** are isolated in high yield when a tertiary phosphine was used as an auxiliary ligand. X-Ray crystallographic analysis of **5** and **6** confirmed that the cationic part of these complexes adopts a square planar structure comprised of two sulfur atoms of a bidentate DTCO ligand and two phosphorus atoms in *cis*-fashion.

Experimental

General. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. THF, toluene, and hexane were dried over sodium benzophenone ketyl and then distilled before use. Compounds **1**[29] and $Pd_2(dba)_3 \cdot C_6H_6$[43] were prepared according to the literature procedures. Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, and (*R*)-BINAP were purchased from Kanto Chem. Co.

IR spectra were measured on a JASCO FT/IR-120 spectrometer. Other spectra were recorded by the use of the following instruments. UV/vis spectra were measured on a JASCO V-570. Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer. All melting points were measured in sealed tubes and were not corrected.

Oxidative Addition of 1 to $Pd_2(dba)_3 \cdot C_6H_6$. $Pd_2(dba)_3 \cdot C_6H_6$ (29.1 mg, 5.85×10^{-2} mmol) was added to an acetonitrile (1.0 mL) solution of **1** (26.1 mg, 5.85×10^{-2} mmol) and the mixture was stirred at room temperature for 10 min. The reaction mixture was filtered through a pad of Celite and the filtrate was concentrated to 0.5 mL. Addition of diethyl ether (10 mL) resulted in the formation of [Pd(dtco)$(NCCH_3)_2$]$(OTf)_2$ (**2**) (35.2 mg, 95% yield) as a pale brown powder, and then **2** gradually turned into a viscous oil. ^1H NMR (CD_3CN) $\delta = 2.20$—3.00 (br m, methylene protons due to the DTCO ligand). IR (Nujol/KBr) 2328, 1261, 1157, 1028, 638 cm^{-1}.

Preparation of [Pd(dtco)$(PR_3)_2$]$(OTf)_2$. A typical procedure is described for the preparation of [Pd(dtco)$(PMe_2Ph)_2$]-$(OTf)_2$ (**3**). A mixture of compound **1** (92.7 mg, 0.208 mmol) and $Pd_2(dba)_3 \cdot C_6H_6$ (103.4 mg, 0.104 mmol) in acetonitrile (10 mL) was stirred at room temperature for 10 min. To this was added dimethylphenylphosphine (59 μL, 0.415 mmol) at room temperature and the resulting yellow reaction mixture was stirred at that temperature for 20 min. The yellow solution containing a small amount of precipitates was filtered through a bed of Celite and the filtrate was concentrated to 1 mL. Addition of diethyl ether (10 mL) resulted in the formation of **3** (158.8 mg, 92% yield) as a pale yellow powder. An analytically pure sample was obtained by recrystallization from a mixture of acetonitrile and diethyl ether at room temperature, mp 125—128 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 1.80$ (d, $^2J_{HP} = 10.5$ Hz, 12 H), 2.30—2.50 (m, 4 H), 2.70—2.90 (m, 4 H), 3.02—3.30 (m, 4 H), 7.20—7.80 (m, 10 H); ^{31}P NMR ($CDCl_3$) $\delta = 4.6$ (s); ^{19}F NMR ($CDCl_3$) $\delta = -79.3$ (s). IR (Nujol/KBr) 1378, 1260, 1220, 1161, 1093, 1030, 744, 697, 634 cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} 318 nm ($\varepsilon = 11000$ M^{-1} cm–1)(1 M = 1 mol dm^{-3}). Anal. Calcd for $C_{24}H_{34}F_6O_6P_2PdS_4$: C, 34.77; H, 4.13%. Found: C, 34.58; H, 4.33%.

[Pd(dtco)(PPh$_3$)$_2$](OTf)$_2$ (4): 95% yield, mp 246—248 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 2.20$—2.35 (m, 2 H), 2.35—2.45 (m, 2 H), 2.50—2.65 (m, 4 H), 2.80—2.95 (m, 4 H), 7.35—7.60 (m, 30 H); ^{31}P NMR ($CDCl_3$) $\delta = 29.8$ (s); ^{19}F NMR ($CDCl_3$) $\delta = -79.3$ (s). IR (Nujol/KBr) 1378, 1256, 1221, 1161, 1093, 1028, 744, 697, 636 cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} 351 nm ($\varepsilon = 2000$ M^{-1} cm^{-1}). Anal. Calcd for $C_{44}H_{42}F_6O_6P_2PdS_4$: C, 49.05; H, 3.93%. Found: C, 48.72; H, 3.84%.

[Pd(dtco)(dppe)](OTf)$_2$ (5): 86% yield, mp 217—218 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 1.55$—1.70 (m, 2 H), 2.25—2.50 (m, 4 H), 2.65—2.82 (m, 4 H), 3.00—3.10 (m, 4 H), 3.10—3.18 (m, 2 H), 7.60—7.80 (m, 20 H); ^{31}P NMR ($CDCl_3$) $\delta = 66.5$ (s); ^{19}F NMR ($CDCl_3$) $\delta = -79.3$ (s). IR (Nujol/KBr): 1377, 1262, 1156, 1100, 1028, 753, 695, 637 cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} 318 nm ($\varepsilon = 3000$ M^{-1} cm^{-1}). Anal. Calcd for $C_{34}H_{36}F_6O_6PdS_4$: C, 42.93; H, 3.81%. Found: C, 42.76; H, 3.63%.

[Pd(dtco){(*R*)-binap}](OTf)$_2$ (6): 97% yield, mp > 300°C. ^{1}H NMR ($CDCl_3$) $\delta = 2.30$—2.80 (m, 12 H), 6.90—8.00 (m, 32 H); ^{31}P NMR ($CDCl_3$) $\delta = 34.0$; ^{19}F NMR ($CDCl_3$) $\delta = -79.3$. IR (Nujol/KBr): 1378, 1256, 1221, 1161, 1093, 1028, 744, 697, 636 cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} 357 nm ($\varepsilon = 26000$ M^{-1} cm^{-1}). Anal. Calcd for $C_{52}H_{44}F_6O_6P_2PdS_4$: C, 53.13; H, 3.77%. Found: C, 52.85; H, 3.67%.

Crystallographic Data Collections and Structure Determination of 5 and 6. Data Collection: Each suitable crystal was sealed and mounted in a glass capillary under argon atmosphere. Data for the three complexes were collected by a Rigaku AFC-7R diffractometer with a graphite monochromated Mo *Kα* radiation and a 10 kW rotating anode generator. The incident beam collimator was 1.0 mm and the crystal to detector distance was 235 mm. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections, corresponded to the cells with dimensions listed in Table 2, where details of the data collection were summarized. The weak reflections ($I < 10\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. Three standard reflections were chosen and monitored every 150 reflections.

Data Reduction: An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. Each variation of intensities of three representative reflections was +0.11% for **5** or

Table 2. Crystal and Refinement Data of Palladium Complexes **5** and **6**

Complex	5	Complex	6
Formula	$C_{34}H_{36}F_6O_6P_2PdS_4$		$C_{52}H_{44}F_6O_6P_2PdS_4$
Formula weight	951.23		1175.45
Cryst. system	Monoclinic		Trigonal
Space group	$P2_1/c$ (#14)		$P3_2$ (#145)
a/Å	15.481(3)		12.1591(12)
b/Å	14.174(2)		—
c/Å	18.191(1)		30.325(6)
β/deg	99.042(9)		
Z	4		3
V/Å^3	3942.1(8)		3882.7(8)
D_{calcd}/g cm^{-3}	1.603		1.508
Radiation	Mo *Kα* (λ = 0.71069 Å)		Mo *Kα* (λ = 0.71069 Å)
Crystal size/mm	0.2×0.2×0.4		0.5×0.5×0.5
Abs. coeff/cm^{-1}	8.35		6.52
Scan mode	ω–2θ		ω–2θ
Temp/°C	20		26
$2\theta_{max}$/deg	55.0		55.0
Data collected	9764		6543
Unique data	9423 (R_{int} = 0.042)		6130 (R_{int} = 0.0684)
No. of observation ($I > 3\sigma(I)$)	4181	No. of observation ($I > 2\sigma(I)$)	5449
No. of variables	414	No. of variables	514
R ($I > 3\sigma(I)$)	0.073	$R1$ ($I > 2\sigma(I)$)	0.0843
R_w ($I > 3\sigma(I)$)	0.097	$wR2$ ($I > 2\sigma(I)$)	0.2262
GOF	1.76	$R1$ (all data)	0.0943
$\Delta\rho$/e Å^{-3}	1.61 (max.)	$wR2$ ($I > 2\sigma(I)$)	0.2402
	−1.06 (min.)	GOF on F^2	1.054
		$\Delta\rho$/e Å^{-3}	1.436 (max.)
			−1.217 (min.)

-1.56% for **6** and thus linear correction factors were applied to the decay of these observed data.

Structure Determination and Refinement. Calculation for **5** was performed using a TEXSAN crystallographic software package, and illustrations were drawn with ORTEP. Crystallographic calculations were performed on an IRIS Indigo workstation. The systematic absence (h 0 l) with $l =$ odd and (0 k 0) with $k =$ odd indicated the space group of **5** to be $P2_1/c$ (#14). The location of the Pd atom of **5** were determined by a direct method (SHELXS-86).[44] A series of standard full matrix least-squares refinement and Fourier syntheses revealed the remaining atoms. All hydrogen atoms were placed at the calculated positions (C–H = 0.95 Å). In the subsequent refinement, the function $\sum w(|F_o|-|F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. All non-hydrogen atoms as anisotropic and hydrogen atoms as isotropic temperature factor were refined to reach $R = 0.073$ and $R_w = 0.097$ for **5**. The agreement indices are defined as $R = \sum||F_o|-|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o|-|F_c|)^2/\sum w(|F_o|)^2]^{1/2}$ where $w^{-1} = \sigma^2(F_o) = \sigma^2({F_o}^2)/(4{F_o}^2)$.

For complex **6**, calculations were carried out on a Silicon Graphics SGI Power Challenge workstation at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. The data were reduced to ${F_o}^2$ value for the refinements. The structure was solved by a direct method (SHELXS-86)[44] and weighted Fourier techniques[45] and refined on F^2 by full-matrix least-squares methods, using SHELXL-93.[46] Non-hydrogen atoms of the cationic part were anisotropically refined. The atoms of one trifluoromethanesulfonate anion were fixed in the refinements. The atoms of CF_3S of the other anions were refined with the riding motion. Non-hydrogen atoms were anisotropically refined. Hydrogen atom parameters of aromatic and aliphatic groups were constrained to the parent sites (riding model, $\text{C–H}_{(sp^2)} = 0.93$ Å, $\text{C–H}_{(sp^3)} = 0.97$ Å, $U_{iso}(\text{H}) = 1.2\times U_{eq}(\text{C})$ e Å^{-2}). The function minimized was $[\Sigma w(F_o^2-F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2)+(0.1888P)^2+2.3856P]$), where $P = (\text{Max}({F_o}^2,0)+2{F_c}^2)/3$ with $\sigma^2({F_o}^2)$ from counting statistics and an extinction parameter was introduced in the refinement as $F_c^* = kF_c[1+0.001\times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, extinction coefficient: 0.0078(15). The function $R1$ and $wR2$ were $(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ and $[\Sigma w({F_o}^2-{F_c}^2)^2/\Sigma(w{F_o}^4)]^{1/2}$, respectively. Final R factors, $R1$ and $wR2$ are 0.0943 and 0.2402 for 6130 reflections (all data), respectively.

The complete F_o-F_c data are deposited as Document No. 71063 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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