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Practical Synthesis of Palladium Bis(trifluoromethanesulfonate) and Its Application to the Synthesis of Palladium Complexes

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Synopsis. Palladium bis(trifluoromethanesulfonate) is usually prepared from the reaction of palladium dinitrate or diacetate and trifluoromethanesulfonic acid. Reactions of palladium bis(trifluoromethanesulfonate) with various ligands (L and/or X^-) give corresponding palladium(II) complexes, such as $[Pd(CF_3SO_3)_2L_2]$ and $[PdX_2L_2]$.

Metal trifluoromethanesulfonates and complexes coordinated by trifluoromethanesulfonate are attracting great attention in fields of inorganic and organic chemistry.[1] Because trifluoromethanesulfonate is the most stable and nonexplosive anion, it has been widely employed in inorganic chemistry, instead of perchlorate, to produce highly electron-deficient metal complexes. Many organometallic compounds coordinated by trifluoromethanesulfonate have been synthesized and employed for important transformations in organic syntheses.[2—9] Palladium salts and complexes have been known to be important reagents and catalysts in both organic and industrial chemistry.[10] Since the reactivity of palladium(II) compounds mainly depends on the electrophilicity of the palladium atom, palladium(II) complexes coordinated by trifluoromethanesulfonate might be the most powerful palladium(II) reagents and catalysts. However, only one method has been reported regarding the preparation of palladium bis(trifluoromethanesulfonate) (**1**); the procedure is not practical due to the waste of fluorosulfonic acid and the fact that it requires a long reaction period.[11] A few kinds of palladium complexes with trifluoromethanesulfonate have been synthesized from the corresponding chloropalladium complexes by using $Cl^-/CF_3SO_3^-$ substitution reactions, which are carried out using strongly acidic trifluoromethanesulfonic acid[1c,12] or silver trifluoromethanesulfonate.[13] These procedures are not flexible and are hardly employable in the syntheses of complexes which are sensitive in acidic conditions. Described herein are a practical procedure of **1** and its applications to the syntheses of the Pd(II) complexes.

The reaction of palladium dinitrate prepared *in situ* from palladium metal and nitric acid with trifluoromethanesulfonic acid proceeded at 20 °C to give palladium bis(trifluoromethanesulfonate) dihydrate ($\mathbf{1}\cdot 2H_2O$) in 96% yield. Although the product was thermally stable up to 300 °C, it was strongly hygroscopic upon contact to air.[14] Commercial palladium diacetate was also employable for the preparation of $\mathbf{1}\cdot 2H_2O$ (86% yield), but the reaction of palladium dichloride with trifluoromethanesulfonic acid did not occur, even at 100 °C.[15]

$$\begin{array}{lcl} PdX_2 + 2CF_3SO_3H & \rightarrow & Pd(CF_3SO_3)_2 + 2HX \\ X = NO_3 \text{ and } CH_3COO & & \qquad \mathbf{1} \end{array} \tag{1}$$

When **1** was dissolved in acetonitrile, the obtained yellow solution was stable up to 25 °C under an Ar atmosphere.[16] On the other hand, a suspension of **1** in diethyl ether was stable at −78 °C, but was unstable at over −50 °C. The reaction of **1** with 2 equivalents of triphenylphosphine proceeded in acetonitrile at 20 °C or in diethyl ether at −78 °C to give *trans*-$[Pd(CF_3SO_3)_2(PPh_3)_2]$ (**2a**) in high yields. The reactions of **1** with 1,2-bis(diphenylphosphino)ethane (dppe), 1,5-cyclooctadiene (cod), and diphenyl sulfide in acetonitrile (20 °C) or diethyl ether (−78 °C) gave **2b—2d**.[17] The stereochemical structures of the products were confirmed by the ^{31}P NMR spectra.[18] The results are summarized in Table 1.

$$\begin{array}{lcl} Pd(CF_3SO_3)_2 + L & \rightarrow & [Pd(CF_3SO_3)_2L_2] \\ \qquad \mathbf{1} & & \qquad \mathbf{2a—d} \end{array} \tag{2}$$

The ^{31}P NMR chemical shifts of several palladium(II) phosphine complexes, $[PdX_2(PR_3)_2]$, are given in Table 2. Here, the chemical shifts of *cis*-$[PdX_2(PR_3)_2]$ were 10—15 ppm lower than *trans*-$[PdX_2(PR_3)_2]$, probably because of the trans influences.[18,19] About a 12 ppm low-field shift was recognized when chloride was replaced by trifluoromethanesulfonate in $[PdX_2(dppe)]$. Thus, the chemical shift of **2a**, 37.8 ppm and 14 ppm lower than *trans*-$[PdCl_2(PPh_3)_2]$ (**3a**), could be assigned to the trans geometry.

Since trifluoromethanesulfonate is a good leaving group and is easily substituted by an appropriate nucleophile under mild conditions, **1** and the complexes (**2**) seem to be useful starting materials for the preparation of various Pd(II) derivatives. Indeed, **1** was con-

Table 1. Reaction of **1** with Ligands

Ligand (L)	Complex (number)	Yield/% (solvent)
PPh_3	*trans*-$[Pd(CF_3SO_3)_2(PPh_3)_2]$ (**2a**)	80(CH_3CN) 92 (Diethyl eter)
dppe	$[Pd(CF_3SO_3)_2(dppe)]$ (**2b**)	92(CH_3CN) 90(Diethyl ether)
cod	$[Pd(CF_3SO_3)_2(cod)]$ (**2c**)	88 (Diethyl ether)
SPh_2	$[Pd(CF_3SO_3)_2(SPh_2)_2]$ (**2d**)	81(Diethyl ether)[a]

a) Stereochemical structure has been unknown.

Table 2. ^{31}P NMR Spectra of Phosphine Pd(II) Complexes

Complex (number)	Geometry	δ/ppm[a)]	Reference
$[PdCl_2(PMe_3)_2]$	trans	−11.9	18a)
$[PdCl_2(PMe_3)_2]$	cis	−1.9	18a)
$[PdBr_2(PMe_3)_2]$	trans	−16.9	18a)
$[PdBr_2(PMe_3)_2]$	cis	−1.7	18a)
$[PdCl_2(PEtPh_2)_2]$	trans	19.3	18c)
$[PdCl_2(PEtPh_2)_2]$	cis	30.2	18c)
$[PdCl_2(PPh_3)_2]$ **(3a)**	trans	23.9	18c)
$[PdCl_2(dppe)]$ **(3b)**	cis	63.7	18c)
		64.2	18b)
		64.4	This work
$[Pd(CF_3SO_3)_2(PPh_3)_2]$ **(2a)**	trans	37.8	This work
$[Pd(CF_3SO_3)_2(dppe)]$ **(2b)**	cis	76.4	This work

a) Observed in $CDCl_3$. Chemical shifts were reported relative to 85% H_3PO_4(δ=0).

verted to $PdCl_2$ in quantitative yield by a treatment with aq NaCl. The reaction of **1** with 2,4-pentanedione in accetonitrile proceeded at 0 °C, giving palladium bis(2,4-pentanedionato) (**4**) in 81% yield. Phosphine complexes **2a** and **2b**, obtained *in situ* from **1** in acetonitrile, gave **3a** (91% yield) and **3b** (95%) by the treating aq NaCl, respectively.

$$\underset{\mathbf{1}}{Pd(CF_3SO_3)_2} + 2Cl^- \longrightarrow PdCl_2 \tag{3}$$

$$\underset{\mathbf{2a,2b}}{[Pd(CH_3SO_3)_2L_2]} + 2Cl^- \longrightarrow \underset{\mathbf{3a,3b}}{[PdCl_2L_2]} \tag{4}$$

$$\underset{\mathbf{1}}{Pd(CF_3SO_3)_2} + 2CH_3COCH_2COCH_3 \longrightarrow \underset{\mathbf{4}}{[Pd(acac)_2]} \tag{5}$$

Experimental

General Methods. The melting points were uncorrected. Samples which did not melt nor change at 300 °C were reported as mp>300°C. The IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were observed on a JEOL Ex-270, and the chemical shifts were reported relative to internal tetramethylsilane (δ=0 ppm, ^{1}H and ^{13}C) and external 85% phosphoric acid (δ=0 ppm, ^{31}P). Micro elemental analyses were carried out at the Analytical Center of Department of Agriculture of Nagoya University and the Central Research Center of Mitsui Mining & Smelting Co., Ltd. Trifluoromethanesulfonic acid (obtained from Central Grass Co., Ltd.) and palladium sponge and palladium diacetate (obtained from NE Chem Cat Co., Ltd.) were used without purification. Dry diethyl ether was obtained from Sanraku Co. Acetonitrile was distilled over CaH_2.

Palladium(II) Bis(trifluoromethanesulfonate) Dihydrate (1). A solution of $Pd(NO_3)_2$, obtained by dissolving Pd sponge (0.62 g, 5.7 mmol) in concd HNO_3 (1.5 ml), was added to CF_3SO_3H(20 ml) at 0 °C. The solution was stirred under bubbling argon for 2 h, and the precipitates were separated by centrifuge. Drying the precipitates under reduced pressure (30—70 Pa) at 70 °C for 18 h gave dihydrate of **1** (2.0 g, 86%) as light-purple powder. **1**·$2H_2O$: Mp>300°C; IR(Nujol) ν/cm^{-1} 1211, 1184, 1055, 646, 592, 523, 490, 476, 461, 444, 428, 418. Found: C, 5.36; Pd, 24.4%. Calcd for $C_2F_6H_4O_8PdS_2$: C, 5.45; Pd, 24.2%.

***trans*-Bis(trifluoromethanesulfonato)bis(triphenylphosphine)palladium Trihydrate (2a):** Under an Ar atmosphere, to a solution of **1** (0.17 g, 0.42 mmol) in dry acetonitrile (2 ml) was added triphenylphosphine (0.35 g, 1.3 mmol) at 18 °C. After 5 min, diethyl ether (20 ml) was added, and the resulting precipitates were separated and washed with diethyl ether. Complex **2a** (0.31 g, 80%) was obtained as a yellow powder. **2a**: Mp 175—176 °C (decomp); IR (KBr disk) ν/cm^{-1} 1481, 1437, 1306, 1235, 1165, 1096, 1028, 999, 748, 691, 639, 579, 517; ^{1}H NMR ($CDCl_3$) δ=7.39—7.32 (2H, m, Ph), 7.56—7.47 (3H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=124.79 (d, J_{C-P}=59.8 Hz), 129.39 (d, J_{C-P}=10.9 Hz), 132.81 (d, J_{C-P}=2.4 Hz), 134.38 (d, J_{C-P}=11.0 Hz); ^{31}P NMR ($CDCl_3$) δ=37.8. Found: C, 46.4; H, 3.3%. Calcd for $C_{38}F_6H_{36}O_9P_2PdS_2$: C, 46.4; H, 3.7%.

[1,2-(Diphenylphosphino)ethane]bis(trifluoromethanesulfonato)palladium (2b): Colorless powder; mp> 300°C; IR (KBr disk) ν/cm^{-1} 2924, 1439, 1259, 1169, 1105, 1030, 750, 690, 639, 530; ^{1}H NMR ($CDCl_3$) δ=2.43 (4H, d, J_{P-H}=23.1 Hz), 7.64—7.43 (12H, m, Ph), 7.92—7.83 (8H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=15.43 (CH_2); ^{31}P NMR ($CDCl_3$) δ=76.4. Found: C, 41.9; H, 3.1%. Calcd for $C_{28}F_6H_{24}O_6P_2PdS_2$: C, 41.9; H, 3.0%.

1,5-Cyclooctadienebis(trifluoromethanesulfonato)palladium(II) (2c): Pale yellow crystals; mp 188—193 °C (decomp); IR (KBr disk) ν/cm^{-1} 2932, 1638, 1487, 1448, 1270, 1155, 1043, 1032, 637; ^{1}H NMR ($CDCl_3$) δ=2.8—1.8 (8H, m, CH_2), 6.3—5.5 (4H, m, =CH); ^{13}C NMR ($CDCl_3$) δ=26.25, 27.24, 28.83, 38.49, 92.36, 111.25. Found: C, 23.3; H, 2.4%. Calcd for $C_{10}F_6H_{12}O_6PdS_2 \cdot H_2O$: C, 22.6; H, 2.7%.

Bis(diphenyl sulfide)bis(trifluoromethaneslufonato)palladium (2d): Deep red powder; mp 108—109 °C (decomp); IR (KBr disk) ν/cm^{-1} 1638, 1476, 1443, 1256, 1152, 1030, 745, 685, 637; ^{1}H NMR ($CDCl_3$) δ= 7.6—7.3 (20H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=126.41, 130.36, 132.02, 132.25. Found: C, 40.8; H, 3.0%. Calcd for $C_{26}F_6H_{20}O_6PdS_4 \cdot H_2O$: C, 40.2; H, 2.6%.

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11) Compound **1** has been synthesized as follows:
$Pd+2BrOSO_2F \rightarrow Pd(OSO_2F)_2$
$Pd(OSO_2F)_2+2CF_3SO_3H \rightarrow Pd(CF_3SO_3)_2+2FSO_3H$
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14) The characters of $\mathbf{1}\cdot 2H_2O$ were completely identical with those reported in the Ref. 11. The dihydrate formula was confirmed by ICP analysis.

15) Treatment of $H_2[PdCl_4]$ by trifluoromethanesulfonic acid gave dark brown solid together with HCl gas. The product had two absorption at 1250—1150 cm^{-1} assignable to $\nu(SO_2)$, but was converted to $PdCl_2$ and **3a** by heating (150 °C/10 Pa) and a treatment with PPh_3, respectively. Presumably, the structure of the product might be $H_2[Pd(CF_3SO_3)_2Cl_2]$.

16) In acetonitrile, **1** formed acetonitrile complexes, like $[Pd(CF_3SO_3)_2(CH_3CN)_2]$ and $[Pd(CH_3CN)_4](CF_3SO_3)_2$. Attempts for isolation and characterization of the complex were unsuccessful.

17) Complexes **2b** and **2d** were identical with authentic samples obtained by the Cl/CF_3SO_3 exchanging reaction cited in the Ref. 12a. Complex **2a** was also prepared from **3a** by the similar manner. However, the reaction is not applicable to the preparation of **2c** from $[PdCl_2(cod)]$.

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