

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

Shizuaki MURATA* and Yoshiyuki IDO

Graduate School of Human Informatics, Nagoya University, Chikusa, Nagoya 464-01

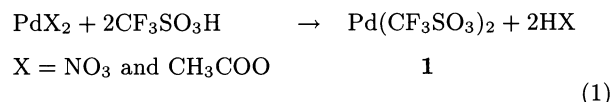
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Synopsis. Palladium bis(trifluoromethanesulfonate) is usually prepared from the reaction of palladium dinitrate or diacetate and trifluoromethanesulfonic acid. Reactions of palladium bis(trifluoromethanesulfonate) with various ligands (L and/or X[−]) give corresponding palladium(II) complexes, such as [Pd(CF₃SO₃)₂L₂] and [PdX₂L₂].

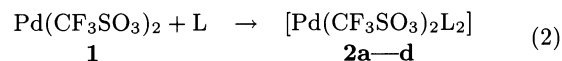
Metal trifluoromethanesulfonates and complexes coordinated by trifluoromethanesulfonate are attracting great attention in fields of inorganic and organic chemistry.¹⁾ Because trifluoromethanesulfonate is the most stable and nonexplosive anion, it has been widely employed in inorganic chemistry, instead 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[−]/CF₃SO₃[−] 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 (**1**·2H₂O) 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 **1**·2H₂O (86% yield), but the reaction of palladium dichloride with trifluoromethanesulfonic acid did not oc-

cur, even at 100 °C.¹⁵⁾



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(CF₃SO₃)₂(PPh₃)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 ³¹P NMR spectra.¹⁸⁾ The results are summarized in Table 1.



The ³¹P NMR chemical shifts of several palladium(II) phosphine complexes, [PdX₂(PR₃)₂], are given in Table 2. Here, the chemical shifts of *cis*-[PdX₂(PR₃)₂] were 10–15 ppm lower than *trans*-[PdX₂(PR₃)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 [PdX₂(dppe)]. Thus, the chemical shift of **2a**, 37.8 ppm and 14 ppm lower than *trans*-[PdCl₂(PPh₃)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	<i>trans</i> -[Pd(CF ₃ SO ₃) ₂ (PPh ₃) ₂] (2a)	80(CH ₃ CN)
dppe	[Pd(CF ₃ SO ₃) ₂ (dppe)] (2b)	92 (Diethyl eter)
		90(CH ₃ CN)
cod	[Pd(CF ₃ SO ₃) ₂ (cod)] (2c)	90(Diethyl ether)
		88 (Diethyl ether)
SPh ₂	[Pd(CF ₃ SO ₃) ₂ (SPh ₂) ₂] (2d)	81(Diethyl ether) ^{a)}

a) Stereochemical structure has been unknown.

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- 11) Compound **1** has been synthesized as follows:
$$\text{Pd} + 2\text{BrOSO}_2\text{F} \rightarrow \text{Pd}(\text{OSO}_2\text{F})_2$$
$$\text{Pd}(\text{OSO}_2\text{F})_2 + 2\text{CF}_3\text{SO}_3\text{H} \rightarrow \text{Pd}(\text{CF}_3\text{SO}_3)_2 + 2\text{FSO}_3\text{H}$$
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- 14) The characters of **1**·2H₂O were completely identical with those reported in the Ref. 11. The dihydrate formula was confirmed by ICP analysis.
- 15) Treatment of H₂[PdCl₄] by trifluoromethanesulfonic acid gave dark brown solid together with HCl gas. The product had two absorption at 1250–1150 cm⁻¹ assignable to ν(SO₂), but was converted to PdCl₂ and **3a** by heating (150 °C/10 Pa) and a treatment with PPh₃, respectively. Presumably, the structure of the product might be H₂[Pd-(CF₃SO₃)₂Cl₂].
- 16) In acetonitrile, **1** formed acetonitrile complexes, like [Pd(CF₃SO₃)₂(CH₃CN)₂] and [Pd(CH₃CN)₄](CF₃SO₃)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/CF₃SO₃ 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 [PdCl₂(cod)].
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