

Crystal Structures of Trifluoromethanesulfonato Complexes of Nickel(II) and Palladium(II), $[\text{Ni}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2]$ and $[\text{Pd}(\text{triphosphine})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)\cdot\text{C}_6\text{H}_6$, and Characterization of the Coordination Ability of CF_3SO_3^-

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The bis(trifluoromethanesulfonato)nickel(II) complex with two 2,2'-bipyridine (bpy), $[\text{Ni}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2]$ (**1**), and the mono(trifluoromethanesulfonato)palladium(II) complex with bis(2-diphenylphosphinoethyl)phenylphosphine (p_3), $[\text{Pd}(\text{p}_3)(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)\cdot\text{C}_6\text{H}_6$ (**2**), were isolated. The crystal structures for **1** and **2** have been determined by an X-ray crystal structure analysis. Complex **1** crystallizes in monoclinic space group Aa with $a=18.55(1)$, $b=14.48(1)$, $c=9.941(7)$ Å, $\beta=101.98(3)^\circ$, and $Z=4$. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a=17.211(5)$, $b=27.175(7)$, $c=9.962(2)$ Å, $\beta=105.66(2)^\circ$, and $Z=4$. The crystal of **1** contains a distorted octahedral nickel(II) complex with a *cis* arrangement, and the crystal of **2** contains a distorted square-planar palladium(II) complex. The metal–oxygen bond distances for triflate (CF_3SO_3^-), (2.135(5) and 2.148(4) Å for **1** and 2.126(7) Å for **2**), are comparable to those for the other oxygen donors. Three S–O bond distances in the coordinated triflate are close to one another. The stability of the metal–oxygen bond is discussed in terms of the electronic property of triflate.

Keywords Trifluoromethanesulfonato complex, oxygen donor, coordination ability

Recently, trifluoromethanesulfonate (triflate) instead of perchlorate has often been used as a counter anion of the metal complexes from the point of view of safety in order to avoid any potential explosion of perchlorate compounds. Though the triflate anion is a quite weak donor as a Lewis base, it would be coordinated to transition-metal ions in the absence of other donors. In fact, there has been a report of a cobalt(II) complex, $[\text{Co}(\text{terpy})(3,4,7,8\text{-tetramethyl-1,10-phenanthroline})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$ (terpy=2,2':6',2''-terpyridine), in which the Co–O bond distance is 2.165 Å.¹ However, the coordination ability of triflate is vague. On the other hand, the first-row transition-metal ions are moderately solvated in such oxygen-donor solvents as water, *N,N*-dimethylformamide (DMF), and 1,1,3,3-tetramethylurea (TMU).^{2–4} In order to deal with solvated metal ions together with triflate in an inert diluent, it is quite important to clarify the relative coordination ability of both triflate and the donor solvents.

The oxygen donors can bring about a π -donating interaction with metal ions having unoccupied d orbitals with appropriate symmetry. In a first-row transition-metal ion with octahedral geometry, it is well known that the metal–oxygen bond is strengthened by π -donation to unoccupied t_{2g} orbitals for Mn^{2+} and Fe^{3+} ($t_{2g}^3e_g^2$), Cr^{3+} and Mn^{4+} (t_{2g}^3), V^{3+} (t_{2g}^2), and Ti^{3+} and V^{4+} (t_{2g}^1). Since the oxygen of triflate is generally a poorer σ - and π -donor than the other oxygen donors, it is obvious that the metal–oxygen bond for the early transition-metal series is

weakened in the case of triflate. To the contrary, those first-row transition-metal ions with occupied t_{2g} orbitals can have a repulsive interaction with occupied p orbitals of a coordinated oxygen which do not participate in σ -bonding. It is therefore significant to compare the metal–oxygen bonds between triflate and the other stronger donors for the late transition-metal series.

We selected nickel(II) ion as an instance of octahedral first-row transition-metal ions with occupied t_{2g} orbitals ($t_{2g}^6e_g^2$). In order to prepare a stable complex, 2,2'-bipyridine (bpy) was used as a bound ligand which is a π acceptor. Furthermore, we investigated the palladium(II) complex with bis(2-diphenylphosphinoethyl)phenylphosphine (p_3), which forms stable square-planar palladium(II) complexes.⁵ It is thus possible to compare the first- and second-row transition-metal ions. Here, we report on the syntheses and crystal structures for $[\text{Ni}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2]$ and $[\text{Pd}(\text{p}_3)(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)\cdot\text{C}_6\text{H}_6$, and characterize the metal–oxygen bond for triflate.

Experimental

Materials

Solvents 1,1,3,3-tetramethylurea (TMU) and *N,N*-dimethylformamide (DMF) were purified by distillation under reduced pressure after dehydration using activated 4A molecular sieves. The other solvents and ligands,

2,2'-bipyridine (bpy, Wako, Sp. Gr.) and bis(2-diphenylphosphinoethyl)phenylphosphine (p_3 , Strem), were used without further purification.

Preparation of $[Ni(bpy)_2(CF_3SO_3)_2]$ (**1**)

Hexaaquanickel(II) trifluoromethanesulfonate, $[Ni(H_2O)_6](CF_3SO_3)_2$, was prepared by the concentration of an aqueous solution of trifluoromethanesulfonic acid (triflic acid, Wako, 98%) containing $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (Wako, Pr. Gr.). After the aquanickel(II) complex was dissolved in TMU, the water in the solution was removed under reflux in a modified Soxhlet extractor⁶ with activated 4A molecular sieves at 40°C under reduced pressure. The reflux was repeated twice with freshly activated molecular sieves. Two equivalent amounts of bpy were added to a TMU solution of the nickel(II) ion, which was stirred for ca. 2 h at 50°C. A purple powder was obtained upon adding diethylether to the TMU solution, and recrystallized from nitromethane (Wako, Sp. Gr.) to obtain single crystals suitable for an X-ray diffraction measurement.

Preparation of $[Pd(p_3)(CF_3SO_3)](CF_3SO_3) \cdot C_6H_6$ (**2**)

The chloropalladium(II) complex with p_3 , $[Pd(p_3)Cl]Cl$, was prepared by a reaction of $K_2[PdCl_4]$ with an equivalent amount of p_3 in an acetonitrile-water-dichloromethane (7:1:8) solution. Under a nitrogen atmosphere a small excess of $AgCF_3SO_3$ was added to a solution of $[Pd(p_3)Cl]Cl$ in DMF; the resultant precipitate of $AgCl$ was filtered off. The filtrate was evaporated to dryness, and the residue was crystallized from dichloromethane by the addition of hexane. *Anal.* Calcd for $[Pd(p_3)(CF_3SO_3)](CF_3SO_3)$: C, 46.04; H, 3.54; N, 0.00%. Found: C, 46.06; H, 3.57; N, 0.00%. Single crystals suitable for X-ray diffraction measurements were obtained by recrystallization from a dichloromethane-benzene solution.

X-Ray structure analysis

Single crystals were sealed in 0.5-mm o.d. capillary tubes. X-Ray diffraction measurements were performed on a MAC Science Rapid X-Ray Diffraction Image Processor (DIP 320N) with graphite-monochromated Mo K_α radiation ($\lambda=0.71073 \text{ \AA}$) at ambient temperature. Reflections were collected by using continuous 30 Weissenberg photographs with a ϕ range of 6° (total ϕ range, 0–180°). The intensity data were corrected for the standard Lorentz and polarization effects. An empirical absorption correction was not applied. The structures were solved by a direct method, and refined by a full-matrix least-squares technique.⁷ All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were placed in the observed positions with fixed thermal parameters. The atomic scattering factors were taken from ref. 8. The crystal and experimental data are summarized in Table 1. The anisotropic thermal parameters and U values, bond distances and angles for non-hydrogen atoms, positional parameters for all atoms containing hydrogen atoms observed, and structural factors are deposited in Tables S1–S4, respectively.

Results and Discussion

Crystal structure of **1**

The crystal of **1** comprises a complex molecule of $[Ni(bpy)_2(CF_3SO_3)_2]$. A perspective view of the molecule is given in Fig. 1 with the atomic labeling scheme. The final atomic coordinates as well as selected bond distances and angles are listed in Tables 2 and 3, respectively. Nitrogen atoms of two bpy ligands and oxygen atoms of two triflate ions are coordinated to the nickel(II) ion, which is in a distorted octahedral geometry with a *cis* arrangement. The chelate bite angles of bidentate bpy (78.8(2) and 80.4(2)°) are appreciably smaller than those of ethylenediamine chelate (82.1–

Table 1 Crystal and experimental data

Complex	1	2
Formula	$NiS_2F_6O_6N_4C_{22}H_{16}$	$PdS_2P_3F_6O_6C_{42}H_{39}$
Formula weight	669.2	1017.2
Crystal system	monoclinic	monoclinic
Space group	Aa	$P2_1/n$
$a/\text{\AA}$	18.55(1)	17.211(5)
$b/\text{\AA}$	14.48(1)	27.175(7)
$c/\text{\AA}$	9.941(7)	9.962(2)
$\beta/^\circ$	101.98(3)	105.66(2)
$V/\text{\AA}^3$	2612(3)	4486(2)
Z	4	4
$D_c/g \text{ cm}^{-3}$	1.70	1.51
R	0.047	0.109
R_w	0.057	0.133
No. of reflections used	3069	6835
Diffractionmeter	MAC Science DIP320N	
Computer program	MULTAN76	

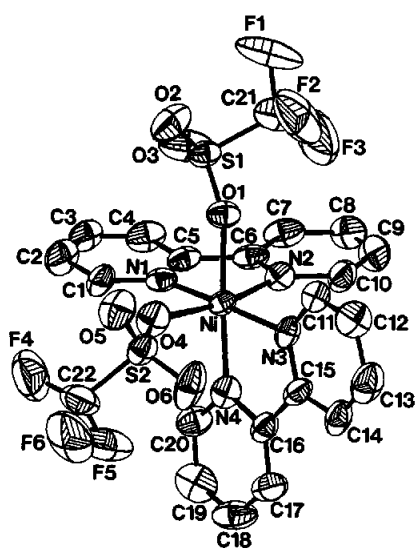


Fig. 1 ORTEP diagram of 1.

83.6°) for tris and bis(ethylenediamine)nickel(II) complexes^{9,10}, which is attributed to the smaller chelate ring size of bpy compared with that of ethylenediamine. The Ni–N bond distances (2.03 – 2.08 Å) for bpy are slightly shorter than those for ethylenediamine (2.08 – 2.12 Å)^{9,10} in accord with the general trend. Additionally, this is due to the π -accepting ability of the bpy ligand, which can interact with the occupied nonbonding t_{2g} orbitals of the nickel(II) center. No difference in the mean bond distances between the Ni–N bonds *trans* to oxygen and those *trans* to nitrogen was observed (2.05 Å for both).

The two Ni–O bond distances for coordinated triflates are comparable (2.135(5) and 2.148(4) Å), and the two triflate ions have no steric interaction with each other. The Ni–O distances for the oxygen donors are variable, reflecting the geometry of the complexes, the other bound ligands, and/or packing in the crystal. For example, the Ni–O distance for water in *trans*-[Ni(stren)₂(H₂O)₂](Cl₂CHCO₂)₂·2H₂O (stren=1,2-diphenylethylenediamine) is 2.12 Å¹¹, while that in *cis*-[Ni(en)₂(H₂O)(BF₄)](BF₄) is considerably longer (2.19 Å).¹⁰ Distinct Ni–O bond distances were observed for dichloroacetate in the same crystal of *trans*-[Ni(stren)₂(Cl₂CHCO₂)₂]-2/3C₂H₅OH·4/3H₂O (2.16 and 2.08 Å).¹¹ The Ni–O bond distances for triflate in the present work are in the middle range of the Ni–O bond distances reported.

No significant difference in the three S–O bond distances for the coordinated triflate in this work was observed, while two distinct C–O bond distances with a difference of 0.1–0.05 Å are usually observed in the coordinated carboxylato group^{12,13}, in which the C–O bond for the coordinated oxygen has a single-bond character because of the metal–oxygen σ -bonding, and the other C–O bond has a double-bond character. Therefore, the electron localization of the sulfonato group in the coordinated triflate is clearly different from that of a carboxylato group, though both free groups

Table 2 Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms for 1

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
Ni	0.31480	0.16454(2)	0.20052	2.78(1)
S1	0.20539(8)	0.0090(1)	0.0011(2)	3.54(3)
S2	0.42316(8)	0.0097(1)	0.4024(2)	3.74(4)
F1	0.1462(5)	-0.0142(6)	0.2638(8)	10.1(2)
F2	0.2588(5)	-0.0118(9)	0.2176(8)	10.9(3)
F3	0.2101(8)	0.1131(7)	0.2159(8)	12.8(4)
F4	0.3734(5)	-0.0132(7)	0.6300(8)	9.4(3)
F5	0.4392(6)	0.1158(8)	0.6115(8)	10.7(3)
F6	0.4903(5)	-0.0059(9)	0.6546(9)	11.0(3)
O1	0.2740(2)	0.0552(3)	0.0591(4)	3.8(1)
O2	0.2928(4)	-0.0903(4)	0.0064(8)	6.3(2)
O3	0.1400(3)	0.0567(5)	0.0202(8)	6.4(2)
O4	0.3556(2)	0.0550(4)	0.3393(6)	4.6(1)
O5	0.3120(4)	-0.0883(3)	0.3799(7)	5.6(1)
O6	0.4883(3)	0.0494(5)	0.3765(8)	6.5(2)
N1	0.2195(3)	0.1701(3)	0.2704(6)	3.1(1)
N2	0.2577(3)	0.2615(3)	0.0648(5)	3.1(1)
N3	0.4132(3)	0.1713(4)	0.1331(6)	3.4(1)
N4	0.3713(3)	0.2590(4)	0.3323(6)	3.8(1)
C1	0.2020(4)	0.1201(5)	0.3730(8)	4.3(1)
C2	0.1307(4)	0.1236(6)	0.4038(9)	5.4(2)
C3	0.0809(4)	0.1774(5)	0.3328(9)	4.4(2)
C4	0.0955(4)	0.2325(6)	0.2342(8)	4.5(2)
C5	0.1678(3)	0.2268(4)	0.2023(6)	3.4(1)
C6	0.1905(3)	0.2769(4)	0.0851(6)	3.5(1)
C7	0.1415(4)	0.3384(4)	0.005(1)	4.4(2)
C8	0.1677(5)	0.3822(5)	0.1143(8)	4.8(2)
C9	0.2373(5)	0.3622(5)	0.1281(8)	5.1(2)
C10	0.2847(4)	0.3026(6)	0.0404(8)	4.7(2)
C11	0.4294(4)	0.1192(5)	0.0292(7)	4.4(2)
C12	0.4970(4)	0.1192(6)	0.0016(9)	5.1(2)
C13	0.5523(5)	0.1815(6)	0.073(1)	5.9(2)
C14	0.5314(4)	0.2363(5)	0.1773(8)	4.3(2)
C15	0.4636(3)	0.2271(4)	0.2073(6)	3.4(1)
C16	0.4423(3)	0.2788(4)	0.3201(6)	3.4(1)
C17	0.4862(5)	0.3368(4)	0.4020(9)	4.6(2)
C18	0.4612(5)	0.3758(5)	0.506(1)	5.4(2)
C19	0.3898(5)	0.3632(6)	0.5235(9)	5.5(2)
C20	0.3500(4)	0.3001(4)	0.4330(8)	4.1(1)
C21	0.2028(6)	0.0317(8)	0.183(1)	6.4(2)
C22	0.4281(6)	0.0204(6)	0.5837(8)	5.6(2)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j).$$

have a conjugated structure. The equivalent S–O bond distances in the coordinated triflate indicate the very weak σ -bonding ability with the metal ion. The π -donation for the coordinated oxygen in triflate is also relatively weaker than that for the other oxygen-donor ligands, because of the low electron density of the lone pairs due to the electronegativity of the fluorine atoms. Considering that the π -donating oxygen atoms have a repulsive interaction with the occupied t_{2g} orbitals of the transition metals, it is expected that the weaker π -donation for triflate can compensate for the weaker σ -donation compared with the other oxygen donors.

Crystal structure of 2

The crystal of 2 contains a complex cation [Pd(p₃)-

Table 3 Selected bond distances (Å) and angles (°) for 1

Bond distances			
Ni-N1	2.031(6)	Ni-N2	2.079(4)
Ni-N3	2.074(6)	Ni-N4	2.029(5)
Ni-O1	2.148(4)	Ni-O4	2.135(5)
S1-O1	1.452(4)	S1-O2	1.441(6)
S1-O3	1.450(6)	S1-C21	1.83(1)
S2-O4	1.438(5)	S2-O5	1.437(5)
S2-O6	1.410(7)	S2-C22	1.792(8)
N1-C5	1.335(7)	N2-C6	1.323(8)
N3-C15	1.336(7)	N4-C16	1.379(8)
C5-C6	1.505(9)	C15-C16	1.469(9)
Bond angles			
N1-Ni-N2	80.4(2)	N1-Ni-N3	174.9(2)
N1-Ni-N4	97.0(2)	N1-Ni-O1	92.2(2)
N1-Ni-O4	91.4(2)	N2-Ni-N3	97.0(2)
N2-Ni-N4	95.1(2)	N2-Ni-O1	90.6(2)
N2-Ni-O4	170.3(2)	N3-Ni-N4	78.8(2)
N3-Ni-O1	92.2(2)	N3-Ni-O4	91.5(2)
N4-Ni-O1	169.8(2)	N4-Ni-O4	91.0(2)
Ni-N1-C5	115.8(4)	Ni-N2-C6	112.6(4)
N1-C5-C6	113.7(5)	N2-C6-C5	117.4(5)
Ni-N3-C15	114.3(5)	Ni-N4-C16	117.3(4)
N3-C15-C16	117.5(5)	N4-C16-C15	112.0(5)
Ni-O1-S1	140.2(3)	Ni-O4-S2	141.3(3)
O1-S1-O2	115.4(3)	O1-S1-O3	114.2(3)
O2-S1-O3	118.6(4)	O4-S2-O5	111.5(3)
O4-S2-O6	115.9(4)	O5-S2-O6	113.4(4)

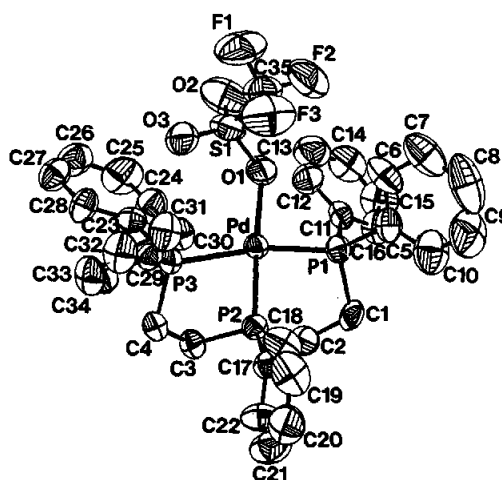


Fig. 2 ORTEP diagram of 2. Triflate counter anion and crystallizing benzene have been omitted for clarity.

(CF₃SO₃)⁻, triflate counter anion, and crystallizing benzene. The *R* value is considerable large due to a disorder of the benzene molecules. The relatively high thermal factors for fluorine atoms in triflate also prevented any improvement of the *R* factor by a refinement. However, by a Fourier synthesis, all non-

Table 4 Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms for 2

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
Pd	-0.07388(3)	0.16942(2)	-0.33142(6)	3.83(2)	C13	0.1937(8)	0.2118(4)	-0.046(2)	7.7(5)
S1	0.0004(2)	0.24366(9)	-0.5339(2)	5.98(8)	C14	0.2234(7)	0.2117(4)	0.096(2)	7.6(4)
S2	0.1427(2)	0.03948(8)	-0.0756(3)	5.80(8)	C15	0.1715(8)	0.2113(5)	0.174(1)	7.4(4)
P1	-0.0478(1)	0.20464(7)	-0.1085(2)	4.10(6)	C16	0.0880(6)	0.2085(4)	0.115(1)	6.0(4)
P2	-0.1190(1)	0.10739(7)	-0.2335(2)	3.84(5)	C17	-0.2268(5)	0.1103(3)	-0.2750(8)	4.3(2)
P3	-0.0930(1)	0.11409(7)	-0.5175(2)	3.99(6)	C18	-0.2714(7)	0.1502(4)	-0.337(1)	6.8(4)
F1	-0.0035(6)	0.3249(7)	-0.669(1)	12.0(4)	C19	-0.3521(8)	0.1515(6)	-0.370(1)	8.1(5)
F2	-0.0063(7)	0.3346(3)	-0.463(1)	12.7(4)	C20	-0.3929(8)	0.1146(7)	-0.334(2)	8.7(5)
F3	-0.112(6)	0.3090(4)	-0.618(1)	12.8(4)	C21	-0.3516(8)	0.0729(6)	-0.269(1)	8.1(5)
F4	0.2616(6)	0.0951(3)	-0.094(1)	13.8(4)	C22	-0.2687(6)	0.0714(4)	-0.240(1)	6.5(4)
F5	0.2972(5)	0.0252(4)	0.002(1)	13.5(4)	C23	0.0017(5)	0.1034(2)	-0.5597(9)	4.2(2)
F6	0.2542(6)	0.0832(4)	0.111(1)	13.9(4)	C24	0.0722(6)	0.1072(4)	-0.452(1)	6.6(4)
O1	-0.0375(5)	0.2326(2)	-0.4250(7)	8.2(3)	C25	0.1455(7)	0.0984(5)	-0.480(1)	8.1(5)
O2	0.0859(5)	0.2464(3)	-0.490(1)	9.8(3)	C26	0.1475(7)	0.0868(4)	-0.613(1)	7.0(4)
O3	-0.0340(4)	0.2174(3)	-0.6588(7)	7.4(2)	C27	0.0783(6)	0.0811(3)	-0.718(1)	5.9(3)
O4	0.0941(4)	0.0822(2)	-0.0842(8)	7.2(2)	C28	0.0060(6)	0.0891(4)	-0.688(1)	5.4(3)
O5	0.1412(6)	0.0188(3)	-0.2069(9)	9.8(3)	C29	-0.1708(4)	0.1288(3)	-0.6731(8)	4.2(2)
O6	0.1380(5)	0.0036(3)	0.024(1)	9.6(3)	C30	-0.2023(6)	0.1759(3)	-0.693(1)	5.2(3)
C1	-0.0904(6)	0.1634(3)	-0.003(1)	4.7(3)	C31	-0.2644(7)	0.1869(5)	-0.812(1)	7.0(4)
C2	-0.0809(6)	0.1116(3)	-0.0470(9)	4.8(3)	C32	-0.2942(6)	0.1515(5)	-0.908(1)	7.0(4)
C3	-0.0930(6)	0.0502(3)	-0.3026(8)	4.4(2)	C33	-0.2640(6)	0.1048(5)	-0.888(1)	6.6(4)
C4	-0.1228(6)	0.0542(3)	-0.4608(9)	4.8(3)	C34	-0.2027(6)	0.0924(3)	-0.773(1)	5.4(3)
C5	-0.0837(5)	0.2659(3)	-0.0885(9)	5.1(3)	C35	-0.0343(9)	0.3064(5)	-0.476(1)	8.0(5)
C6	-0.0576(8)	0.3025(4)	-0.164(1)	8.0(4)	C36	0.2421(8)	0.0613(5)	-0.015(2)	8.8(5)
C7	-0.0850(9)	0.3517(5)	-0.153(2)	9.8(5)	C37	-0.650(3)	0.012(1)	-0.367(5)	20(2)
C8	-0.132(1)	0.3610(8)	-0.066(3)	11.8(7)	C38	-0.638(2)	-0.026(2)	-0.355(4)	21(2)
C9	-0.160(1)	0.3234(6)	0.000(2)	10.9(7)	C39	-0.578(3)	-0.054(1)	-0.278(4)	19(2)
C10	-0.1308(9)	0.2769(5)	-0.004(1)	8.6(5)	C40	-0.518(2)	-0.019(2)	-0.32(1)	51(7)
C11	0.0600(5)	0.2070(2)	-0.0384(8)	4.2(2)	C41	-0.579(4)	0.040(1)	-0.242(6)	27(3)
C12	0.1111(6)	0.2079(3)	-0.109(1)	5.7(3)	C42	-0.527(2)	-0.014(4)	-0.161(5)	31(4)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j)$$

Table 5 Selected bond distances (Å) and angles (°) for 2

Bond distances			
Pd-O1	2.126(7)	Pd-P1	2.347(2)
Pd-P2	2.192(2)	Pd-P3	2.340(2)
P1-C1	1.82(1)	P1-C5	1.806(9)
P1-C11	1.813(8)	P2-C2	1.799(8)
P2-C3	1.804(8)	P2-C17	1.790(8)
P3-C4	1.842(9)	P3-C23	1.814(9)
P3-C29	1.798(7)	S1-O1	1.441(9)
S1-O2	1.420(9)	S1-O3	1.418(7)
S1-C35	1.82(1)	S2-O4	1.421(7)
S2-O5	1.417(9)	S2-O6	1.41(1)
S2-C36	1.76(1)		
Bond angles			
O1-Pd-P1	94.7(2)	O1-Pd-P2	175.8(2)
O1-Pd-P3	99.6(2)	P1-Pd-P2	83.84(7)
P1-Pd-P3	164.03(7)	P2-Pd-P3	82.37(8)
Pd-P1-C1	106.9(3)	Pd-P1-C5	119.8(3)
Pd-P1-C11	110.0(3)	C1-P1-C5	107.5(5)
C1-P1-C11	107.0(4)	C5-P1-C11	105.0(3)
Pd-P2-C2	109.7(3)	Pd-P2-C3	109.8(3)
Pd-P2-C17	109.4(3)	C2-P2-C3	113.0(4)
C2-P2-C17	107.6(4)	C3-Pd2-C17	107.3(4)
Pd-P3-C4	108.5(3)	Pd-P3-C23	110.0(2)
Pd-P3-C29	116.9(3)	C4-P3-C23	105.8(4)
C4-P3-C29	104.9(4)	P1-C1-C2	108.5(7)
P2-C2-C1	108.8(6)	P2-C3-C4	106.6(5)
P3-C4-C3	109.6(5)	Pd-O1-S1	138.2(4)
O1-S1-O2	114.9(5)	O1-S1-O3	112.9(4)
O2-S1-O3	116.6(5)	O4-S2-O5	113.8(5)
O4-S2-O6	117.6(6)	O5-S2-O6	112.7(5)

hydrogen atoms of the complex cation and triflate anion were found, and their structures were adequately refined. A perspective view of the complex cation is displayed in Fig. 2 along with the atomic labeling scheme. The final atomic coordinates and selected bond distances and angles are listed in Tables 4 and 5, respectively. The palladium(II) is in a distorted square-planar environment consisting of three phosphorus atoms of the p_3 ligand and one oxygen atom of triflate. The distortion is mainly due to the small chelate ring size of two five-membered rings in p_3 , which is represented by the nonlinearity of P1-Pd-P3 (164.03(7)°). A similar distortion has been observed for the diethylenetriamine (dien) complex, [Pd(dien)(CH₃CN)](CF₃SO₃)₂, in which the corresponding N-Pd-N angles are 167.8(5) and 168.0(5)°. The Pd-P2 distance (2.192(2) Å) is comparable to the Pd-P bond distances for monodentate dimethylphenylphosphine *trans* to the oxygen atom in the μ -acetato dimer, [Pd(CH₃CO₂)Cl(PMe₂Ph)]₂ (2.200(3) and 2.212(4) Å). The significantly longer Pd-P distances for the terminal phosphorus atoms (Pd-P1=2.347(2) Å and Pd-P3=2.340(2) Å) are obviously due to the *trans* influence of the phosphorus to each other; such an elongation of the Pd-P bond is observed in the dinuclear palladium(I) complex with p_3 , [Pd(p_3)]₂²⁺ (2.30–2.33 Å). The Pd-O bond distance (2.126(7) Å) for the coordinated triflate is comparable to those for the acetato ligand *trans* to

phosphine in [Pd(CH₃CO₂)Cl(PMe₂Ph)]₂ (2.110(9) and 2.130(9) Å)¹⁵, though the donation ability of oxygen atoms in triflate should be weaker than that in acetate. As observed in the crystal of 1, the coordinated triflate does not show a clear difference in the three S-O bond distances, and its structure is essentially the same as that of the counter anion. This fact indicates that the σ -donation of the coordinated triflate to palladium(II) is weak, and that the weak π -donation can reduce the repulsive interaction with the occupied d_{xy} , d_{xz} , and d_{yz} orbitals of the palladium(II) center, as in the case of nickel(II).

Syntheses of trifluoromethanesulfonato complexes of Ni(II) and Pd(II)

In the TMU solution containing the nickel(II) ion and two equivalent amounts of bpy during an early stage in preparation of [Ni(bpy)₂(CF₃SO₃)₂] exists the solvated complex [Ni(bpy)₂(TMU)₂]²⁺.¹⁷ During the recrystallization procedure using an inert solvent, such as nitromethane, the coordinated TMU molecules were completely substituted by two triflate ions, even though TMU is a considerably strong donor solvent (DN=31).¹⁸ Analogously, the coordinated DMF (DN=26.6)¹⁸ was removed by the purification procedure of the palladium(II) complex with p_3 . This is consistent with the fact that the Ni-O and Pd-O bonds for triflate are relatively strong, which is represented by bond distances comparable to those for the other oxygen donors. We can compare the present results with those for the tetrafluoroborate (BF₄⁻) ion. Only one of two coordinated water molecules in [Ni(en)₂(H₂O)₂](BF₄)₂ was replaced with the BF₄⁻ ion in a large excess of isopropyl alcohol to give *cis*-[Ni(en)₂(H₂O)(BF₄)](BF₄).¹⁰ Furthermore, the coordinated acetonitrile molecule in [Pd(p_3)(CH₃CN)](BF₄)₂ was not replaced with the BF₄⁻ ion upon removing the solvent in vacuo at 50°C and by recrystallization of the residue in a large excess of dichloromethane and ethanol.¹⁶ These facts draw a distinction in the coordination ability between triflate and tetrafluoroborate. A consideration of the coordination ability of the triflate ion is essential in the case of the reactions of metal complexes in the presence of triflate ion in inert solvents as well as in the syntheses of metal complexes with the triflate ion.

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 06640779, 07454199, and 07504003) from the Ministry of Education, Science, and Culture of Japan. S.A. gratefully acknowledges financial support by a grant from the Kurata Foundation.

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(Received April 10, 1995)

(Accepted June 19, 1995)