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Single-Thiolato-Bridged Pd_2 or PdPt Binuclear Compounds: Crystal Structure of $[\{Pd(C_6F_5)phen\}(\mu\text{-}SC_6F_5)\{Pt(C_6F_5)dppe\}]SO_3CF_3\cdot CH_2Cl_2$

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Introduction

The ability of thiolate groups to act as bridging ligands is well-known, "enormous numbers of complexes containing (μ-SR)$_2$ bridges" having been reported.[1] However, excluding compounds with a neat metal−metal bond or Au_2 species with metal−metal interactions, few compounds containing just a single thiolato bridge between two transition metal centers have been synthesized so far, and only nine of them have been structurally characterized.[2]

We here report the synthesis of cationic binuclear Pd_2 or PdPt compounds with a sole bridging pentafluorobenzenethiolato ligand.

Experimental Section

Instrumentation and general experimental techniques were as described earlier.[3] All reactions were carried out at room temperature in purified solvents. $Tl(SC_6F_5)$,[4] $[MCl(C_6F_5)L_2]$ (M = Pd, Pt),[5,6] and $[MX(C_6F_5)L_2]$ (M = Pd, Pt; X = $OClO_3$, OSO_2CF_3)[7] were prepared as previously published.

Synthesis of the Complexes. General Procedure for the Synthesis of Compounds of the Type $[M(SC_6F_5)(C_6F_5)L_2]$ (M = Pd, L = $PPhEt_2$, PPh_2Me, PPh_3, L_2 = bipy, phen, dppe; M = Pt, L = $PPhEt_2$, L_2 = bipy, phen, dppe). The corresponding $[MCl(C_6F_5)L_2]$ complex was reacted (1:1) with $Tl(SC_6F_5)$, and the formed TlCl was removed. The solution was evaporated to dryness and the residue was washed with diethyl ether. A typical preparation was as follows: To a suspension of 0.6166 g (1.53 mmol) of $Tl(SC_6F_5)$ in 30 mL of dichloromethane was added 1.2164 g (1.53 mmol) of $[PtCl(C_6F_5)dppe]$. After 19 h of stirring, the formed TlCl was filtered off and the solvent was removed under reduced pressure. The residue was treated with diethyl ether (8 mL), filtered off, washed with ether (2 × 2 mL), and dried in vacuo.

General Procedure for the Synthesis of Compounds of the Type $[\{M(C_6F_5)L_2\}(\mu\text{-}SC_6F_5)\{M'(C_6F_5)L_2'\}]CF_3SO_3$ (M, M′ = Pd, Pt; L_2, L_2' = bipy, phen, dppe). The necessary $[M(SC_6F_5)(C_6F_5)L_2]$ complex was treated (1:1) with the corresponding $[M'(OSO_2CF_3)(C_6F_5)L_2']$ species. The solvent was removed and the residue washed with hexane or diethyl ether. A standard preparation is described here: To a suspension of 0.0894 g (0.15 mmol) of $[Pd(OSO_2CF_3)(C_6F_5)phen]$ in 30 mL of dichloromethane was added 0.1423 g (0.15 mmol) of white $[Pt(SC_6F_5)(C_6F_5)dppe]$; the green color intensified. After 50 h of stirring, the solvent was evaporated and the residue was treated with hexane (10 mL), filtered off, washed with ether (3 × 2 mL), and dried in vacuo.

Synthesis of $[\{Pd(C_6F_5)dppe\}_2(\mu\text{-}SC_6F_5)]ClO_4$. Caution!: *Perchlorate salts of metal complexes with organic ligands are potentially explosive.* Although isolation of the intermediate covalent perchlorato complex leads to higher yields, this is unnecessary and is not recommended.

A solution of 0.0232 g (0.11 mmol) of $AgClO_4$ in 30 mL of benzene was reacted with 0.0792 g (0.11 mmol) of $[PdCl(C_6F_5)dppe]$, under exclusion of light. After 1 h stirring, the formed AgCl was filtered off and washed with benzene (4 × 15 mL).

To the collected filtrate and washings was added 0.0975 g (0.11 mmol) of $[Pd(SC_6F_5)(C_6F_5)dppe]$. After 3 days of stirring, the solvent was removed under reduced pressure. The residue was treated with hexane (6 mL), filtered off, washed with ether (4 × 6 mL) and dried in vacuo.

Structure Determination of $[\{Pd(C_6F_5)phen\}(\mu\text{-}C_6F_5)\{Pt(C_6F_5)dppe\}]SO_3CF_3\cdot CH_2Cl_2$. Single crystals were grown by slow diffusion of pentane into a diluted dichlorometane solution of compound **20** at room temperature. A fragment was mounted on top of a glass fiber in a drop of HMP lithium grease and rapidly cooled to 200 K.

Direct methods[8] were used to locate the palladium, sulfur, and phosphorus atoms, while subsequent cycles of full-matrix least-squares refinement[9] and difference Fourier maps were used to locate the remaining non-hydrogen atoms; all non-H atoms are anisotropic. Hydrogen atoms were placed at calculated positions, and their coordinates were constrained to ride on those of the corresponding carbon atoms, with dependent isotropic displacement parameters.

Results and Discussion

Addition (1:1) of $Tl(SC_6F_5)$ to an acetone solution of $[MCl(C_6F_5)L_2]$ leads to the formation of the corresponding pentafluorothiophenolato complex.

$$[MCl(C_6F_5)L_2] + Tl(SC_6F_5) \rightarrow [M(SC_6F_5)(C_6F_5)L_2] + TlCl\downarrow \quad (1)$$

$$\begin{gathered} M = Pd,\ L = PPhEt_2\ (\mathbf{1}),\ PPh_2Me\ (\mathbf{2}),\ PPh_3\ (\mathbf{3})\ \text{or} \\ L_2 = \text{bipy}\ (\mathbf{4}),\ \text{phen}\ (\mathbf{5}),\ \text{dppe}\ (\mathbf{6}) \\ M = Pt,\ L = PPhEt_2\ (\mathbf{7})\ \text{or}\ L_2 = \text{bipy}\ (\mathbf{8}), \\ \text{phen}\ (\mathbf{9}),\ \text{dppe}\ (\mathbf{10}) \end{gathered}$$

The IR spectra of the solids show a strong, slightly broad band at 855−860 cm^{-1} assignable[10] to the ν(C−S) vibrations of the thiolato groups, along with other typical absorptions of the pentafluorophenyl ring[10,11] and those due to the neutral ligands. Complex **3** shows three absorptions in the 550−490 cm^{-1} region, which demonstrate[12] that the trans geometry of the PPh_3 ligands is maintained.

The ^{31}P NMR spectra (Table 1) of complexes **1**−**3** and **7** show a single signal (along with platinum satellites in the case of **7**), which implies a trans configuration. The chelate ligands

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Table 1: NMR Data for Complexes **1**−**20**

	C_6F_5			SC_6F_5							
complex	δ_o	J_{o-m}	J_{Pt-Fo}	δ_o	J_{o-m}	δ_m	δ_p	J_{m-p}	δ_P	J_{P-P}	J_{Pt-P}
1	−115.2	27.0	−	−135.3	21.3	−161.9	−160.0	20.5	16.8		
						−165.5[a]					
2	−116.4	28.9	−	−134.8	23.4	−162.6	−161.7	20.0	9.6		
						−165.3[a]					
3	−116.5	32.7	−	−132.7	25.6	−162.8	−162.5	20.0	22.6		
						−165.9	−165.1	20.8			
4	−118.4	30.5	−	−131.7	27.3	−162.6	−160.0	20.0			
						−165.4	−160.0	20.8			
5	−118.2	34.4	−	−131.5	26.2	−162.6	−159.7	19.6			
						−165.3	−160.0	20.5			
6	−115.7	*b*	−	−131.7	28.0	−163.0	−161.3	19.8	47.8[c]	20.4	
						−166.4	−162.5	20.9	54.6[d]		
7	−118.0	28.3	374	−134.6	27.6	−163.1	−161.7	20.0	10.5		2561
						−165.4	−164.6	20.7			
8	−118.3	28.3	379	−130.8	26.2	−165.1	−161.5	20.7			
						−166.5	−163.4	19.3			
9[e]	−118.1	28.5	382	−130.7	26.7	−165.0	−161.4	20.4			
						−166.4	−163.3	19.3			
10	−117.5	31.4	273	−131.3	26.2	−164.2	−161.3	20.5	43.0[c]	8.3	2320
						−166.3	−162.3	19.6	42.9[d]		2936
11	−120.5	25.0		−128.6	19.5	−160.1[f]	−155.9	19.6			
						−161.1[g]	−151.0	21.3			
12[e]	−123.3[a]			−132.1	*h*	−165.0[f]	−162.7				
						−167.4[g]	−157.5	*h*			
13	−116.5	*b*		*i*		−161.0	−154.0	20.4	50.9[c]	12.5	
	−121.5	*h*				−161.7	−157.3	20.4	61.2[d]		
						−163.3	−158.1	19.6			
14[e]	−119.0	23.1		−127.8	22.9	−161.7[f]	−158.5	18.0			
						−163.1[g]	−153.3	21.3			
15	−116.1	*b*		*i*		−161.1	−154.2	21.3	51.3[c]	12.0	
	−121.4	*h*				−161.7	−157.1	19.7	62.0[d]		
						−163.5	−158.3	19.7			
16[e]	−116.8	*b*		−128.5	*b*	−161.7[f]	−159.2	20.0	43.5[c]	10.2	
						−163.2[g]	−156.5	20.9	59.8[d]		
17[e]	−119.4[a]	*b*	300	−128.2		−161.7	−152.8	21.3			
						−163.1[a]	−158.3	19.6			
							−159.8	18.0			
18	−117.5	*b*	235	*i*		−161.5[a]	−153.2	20.5	45.0[c]	*b*	2227
	i					−163.0[h]	−156.8	20.5	46.3[d]		3243
							−159.1	19.6			
19[e]	−119.7	19.6	311	−128.4	19.6	−161.7	−152.8	19.6			
	−119.5	22.9				−163.1[a]	−158.4	19.6			
							−159.9	19.6			
20[e]	−117.6	*b*	252	*i*		−162.5[a]	−154.9	19.7	45.6[c]	*b*	2241
	i					−164.1[h]	−159.0	19.6	47.5[d]		3270
							−160.2	18.0			

[a] Overlapping signals. [b] Unresolved coupling. [c] Trans to C_6F_5. [d] Trans to SC_6F_5. [e] Hexadeuterioacetone. [f] C_6F_5. [g] SC_6F_5. [h] Broad. [i] Coalescence at room temperature.

in complexes **4**−**6** and **8**−**10** impose a cis geometry, as shown by the presence of two signals in the spectra of compounds **6** and **10** (for this last one, with platinum satellites). A residual $^4J_{F-P}$ coupling results in a complex multiplet for the phosphorus nuclei trans to the pentafluorophenyl ligand.

The ^{19}F NMR spectra of complexes **1**−**10** show (in the region assigned[13] to the *ortho*-fluorine nuclei of pentafluorothiophenolato groups, −125 to −135 ppm) a doublet. No coupling to ^{31}P or ^{195}Pt is observed. On the other hand, in the range assigned to the *ortho*-fluorine nuclei of the pentafluorophenyl ligand (−110 to −122 ppm) a doublet is observed for all complexes, except **6** and **10**, where the weak $^4J_{F-P}$ coupling to the trans phosphorus gives rise to a doublet of doublets. The platinum compounds **7**−**10** show the expected satellites.

All these data support a mononuclear nature for complexes **1**−**10** what, together with the ability of thiolato groups to act as bridging ligands,[1] makes them especially adequate for the synthesis of binuclear compounds. Thence, reactions between the complexes $[M(SC_6F_5)(C_6F_5)L_2]$, which provide the bridging ligand, and species with one readily displaceable ligand were studied.

Nevertheless, if the ancillary neutral ligands are monodentate ($L = PEt_3$, $PPhEt_2$, PPh_2Me, PPh_3), redistribution takes place leading to mixtures containing the binuclear *cis*- and *trans*-$[Pd(\mu\text{-}SC_6F_5)(C_6F_5)PPh_3]_2$. Shorter reaction times do not lead to the desired single bridged compounds, but to the presence of unreacted starting materials.

Using a chelate (bipy) on one of the metal centers leads to no better results. Therefore, the synthesis of binuclear compounds with a single pentafluorobenzenethiolato bridge was attempted by reacting a complex holding a SC_6F_5 group with another compound with a readily displaceable ligand, both containing chelating bidentate ancillary ligands, to keep them anchored to their respective metal center.

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(13) Usón, R.; Forniés, J.; Usón, M. A.; Apaolaza, J. A. *Inorg. Chim. Acta* **1991**, *187*, 175.

Table 2. Crystallographic Data for **20**

chemical formula	$C_{58}H_{34}Cl_2F_{18}N_2O_3P_2PdPtS_2$
fw	1647.32
space group	$P\bar{1}$ (No. 2)
a, Å	11.949(4)
b, Å	14.380(6)
c, Å	17.372(7)
α, deg	88.24(6)
β, deg	77.04(5)
γ, deg	88.46(4)
V, Å^3	2907(2)
Z	2
T, K	200(2)
λ, Å	0.71073
ρ_{calc}, g/cm^3	1.882
μ, cm^{-1}	30.37
$R1(F_o)$[a]	0.0282
w$R2$ (F_o^2)[b]	0.0617

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]]^{0.5}$, where $w = [\sigma^2(F_o^2) + (0.0366P)^2 + 2.2870P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

So, the reactions

$$[MX(C_6F_5)L_2] + [M'(SC_6F_5)(C_6F_5)L_2'] \rightarrow [\{M(C_6F_5)L_2\}(\mu\text{-}SC_6F_5)\{M'(C_6F_5)L_2'\}]X \quad (2)$$

$M = M' = Pd$; L_2 = bipy; L_2' = bipy (**11**), phen (**12**), dppe (**13**)
$M = M' = Pd$; L_2 = phen; L_2' = phen (**14**), dppe (**15**)
$M = M' = Pd$; $L_2 = L_2'$ = dppe (**16**)
$M = Pd$; L_2 = bipy; $M' = Pt$; L_2' = bipy (**17**), dppe (**18**)
$M = Pd$; L_2 = phen; $M' = Pt$; L_2' = phen (**19**), dppe (**20**)

lead to the desired binuclear species ($X = SO_3CF_3$, except for **16** where $X = ClO_4$). The same products and similar yields are obtained for the alternative reactions between $[MX(C_6F_5)L_2']$ and $[M'(SC_6F_5)(C_6F_5)L_2]$.

The molar conductivity of acetone solutions of compounds **11**−**20** is adequate for 1:1 electrolytes.[14]

The IR spectra of the solids show a strong, slightly broad band at 855−860 cm^{-1} assignable[10] to the ν(C−S) vibrations of the thiolato groups, along with other typical absorptions of the pentafluorophenyl ring[10,11] and those due to the neutral ligands; the X-sensitive mode[11] of the C_6F_5 ligand, appears as a single absorption for the symmetrical complexes, or as two bands (or, in the case of complexes **12** and **18**, as a single, slightly broad absorption).

The ^{19}F NMR spectra of complexes **11**−**20** confirm the proposed stoichiometry. In all cases, dynamic processes take place in solution, as seen in the *ortho*-fluorine region where the inequivalence of F*o* and F*o*′ is observed both for the pentafluorophenyl and the pentafluorobenzenethiolato rings. Although this is seen for some complexes already at room temperature, the case is the same for all of them if the solution is cooled.

The ^{31}P NMR spectra of the compounds containing dppe show the inequivalence of the phosphorus nuclei of the diphosphine, which give rise to two equally integrating signals: a doublet and a multiplet (as a consequence of the weak $^4J_{F-P}$ coupling to the *ortho*-fluorine nuclei of the trans C_6F_5 ligand).

The structure of the heteronuclear compound **20** (Tables 2 and 3) has been established by single-crystal X-ray diffraction.

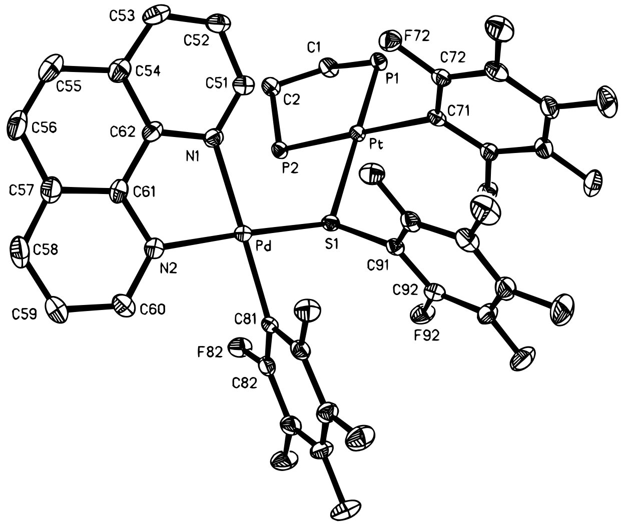

Figure 1. View of the cation in compound **20**, $[\{PdR(phen)\}(\mu\text{-}SR)\{PtR(dppe)\}]^+$ (ellipsoids at 30% electron probability level, H atoms and phenyl groups omitted for the sake of clarity).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **20**

Pt−C(71)	2.091(4)	Pd−N(2)	2.057(4)
Pt−P(1)	2.265(2)	Pd−N(1)	2.094(4)
Pt−P(2)	2.301(2)	Pd−S(1)	2.316(2)
Pt−S(1)	2.385(2)	Pd−F(86)	3.055(3)
Pt−Pd	4.164(2)	S(1)−C(91)	1.769(4)
Pd−C(81)	2.002(4)		
C(71)−Pt−P(1)	93.23(13)	N(2)−Pd−S(1)	172.78(11)
C(71)−Pt−P(2)	176.79(12)	N(1)−Pd−S(1)	101.74(11)
P(1)−Pt−P(2)	85.26(7)	C(81)−Pd−F(86)	50.82(14)
C(71)−Pt−S(1)	92.49(13)	N(2)−Pd−F(86)	86.67(12)
P(1)−Pt−S(1)	171.70(4)	N(1)−Pd−F(86)	120.87(11)
P(2)−Pt−S(1)	88.73(7)	S(1)−Pd−F(86)	97.84(7)
C(71)−Pt−Pd	101.53(12)	C(81)−Pd−Pt	112.22(12)
P(1)−Pt−Pd	155.34(4)	N(2)−Pd−Pt	151.89(11)
P(2)−Pt−Pd	80.86(5)	N(1)−Pd−Pt	74.13(11)
S(1)−Pt−Pd	27.22(3)	S(1)−Pd−Pt	28.11(4)
C(81)−Pd−N(2)	94.4(2)	F(86)−Pd−Pt	116.71(6)
C(81)−Pd−N(1)	170.9(2)	C(91)−S(1)−Pd	104.29(14)
N(2)−Pd−N(1)	80.5(2)	C(91)−S(1)−Pt	108.4(2)
C(81)−Pd−S(1)	84.18(13)	Pd−S(1)−Pt	124.67(6)

The counteranion is disordered in two alternative orientations; similarity restraints on bond distances and angles were applied to them.

The cation contains a palladium and a platinum center, separated by 4.164(2) Å (Figure 1). Coordination around platinum is aproximately square planar, with a mean deviation of 0.045 Å for the best plane defined by the Pt, S1, P1, P2, and C71 atoms. The bonding angles around platinum vary between 85.26(7) (for the chelate P1−Pt−P2 bite) and 93.23(13)°.

The geometry around the palladium center is slightly more distorted, with a mean deviation of 0.117 Å for the Pd, S1, N1, N2, and C81 atoms, the furthest atom being N2 (−0.144(2) Å). The dihedral angle between the PdN1N2 and the PdS1C81 planes is 10.86(19)°. On the other hand, coordination of the 1,10-phenanthroline ligand to palladium implies higher distortions of the angles around this center (which range from 101.74(11) to 80.54(15)°) than those caused by the more flexible 1,2-bis(diphenylphosphino)ethane, bonded to platinum. The dihedral angle between the two coordination planes of the metal centers is 73.82(8)°.

The aromatic ring of the bridging thiolate ligand forms dihedral angles of 27.66(10) and 13.19(9)° with the planes of the neighboring pentafluorophenyl groups. The shortest distance

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(14) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

between any *ortho*-fluorine and one of the metal centers is 3.055(3) Å (for F86−Pd).

The principal feature in this structure is the single thiolato bridge between the metal centers. Compound **20** is the first structurally characterized compound having a sole pentafluorobenzenethiolate link between two transition metals.[2] Despite the many structures of transition metal thiolato compounds reported so far, only nine contain a single thiolato bridge, and only three of these are heteronuclear complexes.

The Pd−S1−Pt angle, 124.67(6)°, is far from pseudotetrahedral geometry, though this is not exceptional: other complexes with a single μ^2-thiolato bridge show M−S−M angles between 115.9 and 131.5°. Compounds with an additional metal−metal bond, or some Au_2 species (with metal−metal interactions as the consequence of relativistic effects) show[2] smaller angles ranging from 87.9 to 79.4°. Although the Pd−S1−Pt angle is close to 120°, this is not the consequence of an sp^2 hibridization (which would yield an approximately trigonal planar coordination around the sulfur atom) since the other bond angles are 104.29(14) and 108.40(15)°.

A view of the crystal packing shows a stacking of the phenantroline ligands, between which the C31−C36 phenyl ring is layered. The dihedral angle between these aromatic systems is 7.5° and the distance from the phenyl centroid to the phenantroline plane is 3.46 Å.

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Supporting Information Available: Elemental analyses, molar conductivities, yields and characteristic IR absorptions for complexes **1**−**20** (3 pages). An X-ray crystallographic file, in CIF format, for the structure determination of **20** is available on the Internet only. Ordering and access information is given on any current masthead page.

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