Inorg. Chem. **1997,** *36,* 5959−5961 **5959**

Synthesis and Crystal Structure of the First Cluster Displaying Pd^{I}−Ag^{I} Interactions: $[Ag_2Pd_2(SC_6F_5)_2(SO_3CF_3)(dppm)_3]SO_3CF_3\cdot CH_2Cl_2$

Rafael Usón,* Miguel A. Usón, and Santiago Herrero

Departamento de Química Inorgánica, Instituto de Ciencia de
Materiales de Aragón, Universidad de Zaragoza-CSIC,
E-50009 Zaragoza, Spain

Received April 24, 1997

Introduction

Only a few compounds containing a Pd−Ag bonding interaction have been structurally characterized,[1] all of them palladium(II) complexes.

It is a common belief that bis(diphenylphosphino)methane (and related ligands) locks together two metal atoms in close proximity, thus favoring the formation of metal−metal bonds and stabilizing unusual oxidation states,[2] as has been found for many species containing the $M_2(dppm)_2$ moiety. However, dppm is a very flexible ligand and can also act as a chelate or span wide distances. For instance, the metal to metal separation is 4.361 Å in $[(CH_3)_2Pt(\mu\text{-dppm})_2Pt(CH_3)_2]$,[3] 4.421 Å in $[(^tBu_2C_6H_2O_2)Pd(\mu\text{-dppm})_2Pd(^tBu_2C_6H_2O_2)]$[4] or even 4.907 Å in $[(CH_3)_2Pt(\mu\text{-dppm})_2Pt(o\text{-}C_6H_4CH_3)_2]$,[6] all of them binuclear compounds doubly bridged by dppm.

Experimental Section

The compound $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_4\cdot 2O(C_2H_5)_2$ was prepared as previously reported.[7]

C, H, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded (over the range 4000−250 cm^{-1}) on a Perkin-Elmer 833 spectrophotometer, using Nujol mulls between polyethylene sheets.[8] The ^{19}F and ^{31}P spectra of $CDCl_3$ solutions of compound **1** were run on a Varian UNITY 300 spectrometer; chemical shifts are relative to $CFCl_3$ or external 85% H_3PO_4, respectively. The conductivity of a 5×10^{-4} M acetone solution was measured with a Philips PW9509 apparatus, using a PW9550/60 cell. Mass spectrometric data were obtained using FAB$^+$ techniques on a VG Autospec apparatus; the matrix used was 3-nitrobenzyl alcohol, and the sample was dissolved in CH_2Cl_2.

Table 1. Crystal and Structure Refinement Data for **1**

empirical formula	$C_{90}H_{68}Ag_2Cl_2F_{16}O_6P_6Pd_2S_4$
fw	2362.94
T, K	293(2)
$\lambda_{\text{Mo K}\alpha}$, Å	0.710 73
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	15.462(5)
b, Å	17.297(6)
c, Å	19.933(6)
α, deg	79.03(3)
β, deg	87.14(2)
γ, deg	76.44(2)
V, Å^3	5088(3)
Z	2
D, Mg/m^{-3}	1.542
$\mu_{\text{Mo K}\alpha}$, mm^{-1}	1.033
θ range, deg	1.61−22.97
R1[a] $[I > 2\sigma(I)]$	0.0536
wR2[b] (all data)	0.1454
goodness-of-fit on F^2 [c]	1.030
largest diff peak and hole, e·Å^{-3}	0.965 and −0.667

[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 $w = [\sigma^2(F_o^2) + (0.0926P)^2 + 0.0000P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$. [c] Goodness of fit $= [\sum[w(F_o^2 - F_c^2)^2/(N_{\text{observns}} - N_{\text{params}})]^{0.5}$.

Synthesis of $[Ag_2Pd_2(SC_6F_5)_2(SO_3CF_3)(dppm)_3]SO_3CF_3$ (1). To a mixture of 0.2056 g (0.8 mmol) of $Ag(SO_3CF_3)$ and 0.3075 g (0.8 mmol) of dppm in dichloromethane/acetone (20/5 mL) was added 0.4130 g (0.1 mmol) of $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_4\cdot 2Et_2O$ and a further 25 mL of dichloromethane. After 24 h of stirring, the solution was filtered and evaporated to *ca.* 5 mL under reduced pressure, and 40 mL of diethyl ether was added. The red solid so obtained was filtered off, washed with diethyl ether (3 × 5 mL), and dried *in vacuo*.

Yield: 92%. Anal. Calcd (found): C, 46.92 (46.45); H, 2.92 (2.89); S, 5.63 (5.57). Conductivity (acetone, 5×10^{-4} M): $\Lambda_M = 162.2$ S m^2 mol^{-1}. IR (Nujol, cm^{-1}): 1638 w, 1589 w, 1577 w, 1512 s, 1440 vs, 1279 vs, br, 1156 s, br, 1099 m, 1087 m, 1031 s, 1000 w, 974 m, 852 m, 783 m, 637 vs, 519 s, 507 w, 481 m, 351 w. ^{19}F NMR (282 MHz, saturated $CDCl_3$ solution, 20 °C, reference $CFCl_3$; δ): −128.5 (br, F_o), −132.4 (d, $J_{om} = 26$ Hz, $F_{o'}$), −160.5 (br, F_m), −162.7 (m, $F_{m'}$), −150.3 (t, $J_{mp} = 20$ Hz, F_p), −159.5 (t, $J_{m'p'} = 21$ Hz, $F_{p'}$). ^{31}P NMR (121 MHz, external 85% H_3PO_4 reference; δ): −2.0 (dm, $J_{P_aAg} = 635$ Hz, P_a), 11.4 (m, P_b), −0.4 (d, $J_{bc} = 26$ Hz, P_c). MS (FAB$^+$, 3-nitrobenzyl alcohol matrix; *m/e*): 2129 (M^{2+}+ SO_3CF_3 5%), 1289 (M^{2+} − Pd − SC_6F_5 − dppm, 22%), 1181 (M^{2+} − 2Ag − SC_6F_5 − dppm, 23%), 1105 (M^{2+} − 2Pd − 2dppm + Ag, 38%), 981 (M^{2+} − 2Ag − $2SC_6F_5$ − dppm, 100%).

X-ray Structural Characterization. Data were purchased from Crystalytics Co. A red-orange parallelepiped (0.82 × 0.58 × 0.34 mm) was sealed with epoxy in a thin-walled capillary and placed in a four-circle Nicolet (Siemens) autodiffractometer. Cell parameters were obtained from 15 reflections with $2\theta > 15°$. Cell dimensions and structure refinement data are available in Table 1. Of the 14 370 reflections measured (ω-scan, ±16,±18,+21), 13 857 ($R_{\text{int}} = 0.019$) were unique and were used for all calculations. Data were corrected for Lorentz, polarization, and absorption effects (seven Ψ-scans with $\mu = 1.03$ mm^{-1}, transmission factors 0.836−1.000). The structure was solved by the heavy atom method. Full-matrix least-squares analyses[9] were performed with all non-hydrogen atoms, with the exception of solvent, anisotropic; the hydrogen atoms were included in fixed calculated positions with assigned isotropic temperature factors. The disordered solvent molecules were restrained. Refinement of 1268 parameters on all data on F^2 gave wR2 = 0.1454 (R1 = 0.0536, for 9939 data with $F_o > 4\sigma(F_o)$), goof = 1.030, and residual electron density 0.97 to −0.67 e Å^{-3}.

Selected bond lengths and angles are given in Table 2. Additional crystallographic data are available as Supporting Information.

Results and Discussion

When the recently described[7] octanuclear palladium(I) compound $\{[Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd](\mu\text{-}SC_6F_5)\}_4$ is reacted with additional bis(diphenylphosphino)methane (dppm) and silver triflate (1:8:8, eq 1), a heterometallic tetranuclear species is

---

(1) Ebihara, M.; Tokoro, K.; Maeda, M.; Ogami, M.; Imaeda, K.; Sakurai, K.; Masuda, H.; Kawamura, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3621. Ebihara, M.; Tsuchiya, M.; Yamada, M.; Tokoro, K.; Kawamura, T. *Inorg. Chim. Acta* **1995**, *231*, 35. Kickham, J. E.; Loeb, S. J. *Organometallics* **1995**, *14*, 3584.

(2) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99. Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(3) Manojlovic-Muir, L.; Muir, K. W.; Frew, A. A.; Ling, S. S. M.; Thomson, M. A.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 1637.

(4) Abakumov, G. A.; Cherkasov, V. K.; Nevodchikov, V. I.; Teplova, I. A.; Zakharov, L. N.; Fukin, G. K.; Struchkov, Yu. T. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1996**, 464; retrieved from ref 5, *refcode NACLUY.*

(5) *Cambridge Structural Database*; Cambridge Crystallographic Data Centre, University Chemical Laboratory: Cambridge, U.K.; April 1997 release.

(6) Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1677.

(7) Usón, R.; Forniés, J.; Falvello, L. R.; Usón, M. A.; Usón, I.; Herrero, S. *Inorg. Chem.* **1993**, *32*, 1066.

(8) Usón, M. A. *J. Chem. Educ.* **1990**, *66*, 412.

(9) Sheldrick, G. M. SHELXL-93, Universität Göttingen, FRG, 1993.

S0020-1669(97)00457-6 CCC: $14.00

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pd1−P1C	2.283(2)	Ag1−P1A	2.368(2)
Pd1−S3	2.351(2)	Ag1−S4	2.416(2)
Pd1−P1B	2.359(2)	Ag1−O1D	2.64(3)
Pd1−Pd2	2.6526(11)	Ag1−O1A	2.825(14)
Pd1−Ag1	3.0903(12)	Ag1−Ag2	3.2549(14)
Pd2−P2C	2.303(2)	Ag2−P2A	2.409(2)
Pd2−S3	2.316(2)	Ag2−O1F	2.49(3)
Pd2−P2B	2.350(2)	Ag2−S4	2.508(2)
Pd2−Ag2	3.2454(12)	Ag2−O1A	2.605(12)

P1C−Pd1−S3	148.61(7)	O1A−Ag1−Pd1	127.6(3)
P1C−Pd1−P1B	99.73(7)	P1A−Ag1−Ag2	141.84(6)
S3−Pd1−P1B	110.69(7)	S4−Ag1−Ag2	49.85(5)
P1C−Pd1−Pd2	94.94(6)	O1D−Ag1−Ag2	71.9(8)
S3−Pd1−Pd2	54.75(5)	O1A−Ag1−Ag2	50.1(3)
P1B−Pd1−Pd2	165.32(5)	P2A−Ag2−O1F	102.5(8)
P2C−Pd2−S3	149.35(7)	P2A−Ag2−S4	154.28(7)
P2C−Pd2−P2B	103.97(7)	O1F−Ag2−S4	99.0(7)
S3−Pd2−P2B	106.36(7)	P2A−Ag2−O1A	118.2(3)
P2C−Pd2−Pd1	93.38(6)	S4−Ag2−O1A	87.4(3)
S3−Pd2−Pd1	55.98(5)	P2A−Ag2−Ag1	148.26(6)
P2B−Pd2−Pd1	159.87(6)	O1F−Ag2−Ag1	85.0(10)
P1A−Ag1−S4	167.17(7)	S4−Ag2−Ag1	47.43(5)
P1A−Ag1−O1D	89.7(6)	O1A−Ag2−Ag1	56.3(3)
S4−Ag1−O1D	91.1(6)	Ag1−S4−Ag2	82.72(7)
P1A−Ag1−O1A	101.4(3)	Ag2−O1A−Ag1	73.5(3)
S4−Ag1−O1A	84.4(3)		

obtained in high yield (92%). No precipitate of the scarcely soluble $Ag(SC_6F_5)$ is formed in this reaction.

$$[Pd_8(SC_6F_5)_8(dppm)_4]\cdot 2Et_2O + 8dppm + 8Ag(SO_3CF_3) \rightarrow 4\underset{\mathbf{1}}{[Ag_2Pd_2(SC_6F_5)_2(SO_3CF_3)(dppm)_3]SO_3CF_3} + 2Et_2O \quad (1)$$

The infrared spectrum of the red solid features a broad band with its maximum at 1157 cm^{-1}, an intermediate position for that expected for ionic or covalent SO_3CF_3. The ^{19}F NMR spectrum of a $CDCl_3$ solution at room temperature shows the presence of two different thiolato groups (one of them undergoing a dynamic process; at −45 °C the exchange is frozen and all the five fluorine nuclei of one of these ligands appear as inequivalent). On the other hand, the room-temperature ^{31}P spectrum of compound **1** consists of three groups of signals (a doublet, a multiplet, and a doublet of multiplets), which can easily be assigned in view of their increased coupling to $^{107,109}Ag$. These data would be consistent with a formulation where both palladium, and both silver centers, would be symmetrically related, at least on the NMR time scale. However, at temperatures below −90 °C (CD_2Cl_2 solution) the signals broaden and the former doublet, assigned to the phosphorus nuclei of the dppm ligand that bridges the palladium−palladium bond, appears as two distinct broad signals.

An X-ray crystal structure determination was undertaken: the tetranuclear cation is highly distorted to accommodate a handful of interactions, as shown in Figure 1. It comprises the "$Pd(\mu\text{-}SC_6F_5)(\mu\text{-dppm})Pd$" unit linked through two dppm ligands to two silver centers, which are themselves bridged by a pentafluorothiophenolato group, forming an 11-membered cycle. The palladium−palladium distance (2.6526(11) Å) is longer than that in the starting compound. The five-membered ring formed by Pd1, Pd2, P1C, P2C, and C1C is strongly puckered[10] (92% twist and 8% envelope), in contrast to the statistically preferred envelope conformation found by Orpen *et al.*[11] for such systems; the donor atoms *trans* to the metal−metal bond are not collinear with it: The P1B−Pd1−Pd2−P2B torsion angle (−23.5(3)°) is far from zero.

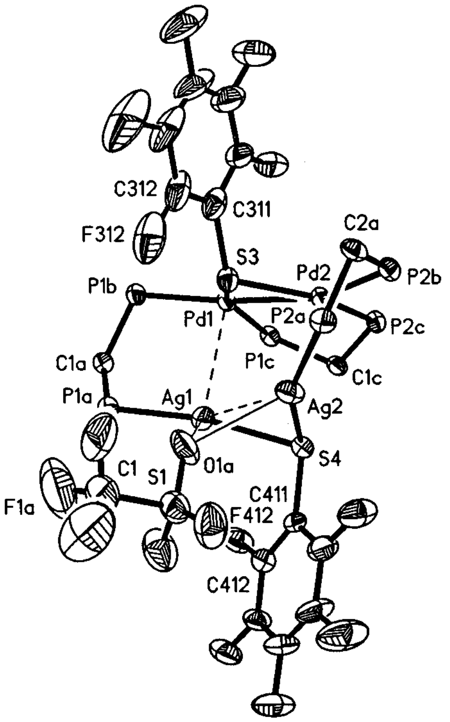

Figure 1. View of compound **1** (ellipsoids at 30% electron probability level, H atoms and phenyl groups omitted). Only one of the triflato anions (in its major orientation) is shown, for the sake of clarity.

The Ag1−Pd1 distance (3.0903(12) Å), although greater than the sum of covalent radii, is shorter than the sum of van der Waals radii, pointing to a weak bonding interaction between these atoms. Similar distances (2.8−3.1 Å) have been found[1] for other palladium(II)−silver(I) bonds and for the platinum(II) compounds $[Pt_3(S_2CNR_2)_6Ag_2]X_2$ (R = ^iPr, ^nBu; X = ClO_4, BF_4), which show[1] a $^1J(^{195}Pt-^{107,109}Ag)$ coupling of about 200 Hz, pointing to a significant interaction.

This close contact cannot exclusively be ascribed to the presence of the bridging diphosphine, since the Ag2−Pd2 distance is longer (3.2454(12) Å). This can be compared with the 3.205 Å separation between the metal centers in the doubly dppm bridged palladium−silver compound $[(NC)_2Pd(\mu\text{-dppm})_2Ag(O_2N)]$.[12]

One of the triflate anions maintains short contacts to the silver centers (Figure 2), especially to Ag2. It is rotationally disordered around the C−S bond in two orientations: In one of them, one oxygen atom bridges[13] both silver atoms, while in the other one, the metal centers interact each with one donor oxygen. As a result of this, and of the short Ag−Ag distance (3.2549(14) Å), the coordination around the silver atoms is not

---

(10) Gould, R. O.; Taylor, P.; Thorpe, M. C. PUCKER, University of Edinburgh, U.K., 1995.

(11) Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1992**, 641. Orpen, A. G. *Chem. Soc. Rev.* **1993**, 191.

(12) Shi-Jie, Lu; Fronczek, F. R.; Selbin, J. *Jiegou Huaxue (J. Struct. Chem.)* **1990**, *9*, 154, retrieved from ref 5, *refcode KESKEY*.

(13) Richmond, T. G.; Kelson, E. P.; Arif, A. M.; Carpenter, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2334. Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartman, J. A. R.; Wolf, R. E., Jr.; Yagbasan, R.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040. Arif, A. M.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1990**, 871. Burrows, A. D.; Jeffrey, J. G.; Machell, J. C.; Mingos, D. M. P. *J. Organomet. Chem.* **1991**, *406*, 399. Irotsu, K.; Miyahara, I.; Higuchi, T.; Toda, M.; Tsukube, H.; Matsumoto, K. *Chem. Lett.* **1992**, 699. Edema, J. J. H.; Buter, J.; van Bolhuis, F.; Meetsma, A.; Kellogg, R. M.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1993**, *207*, 263.

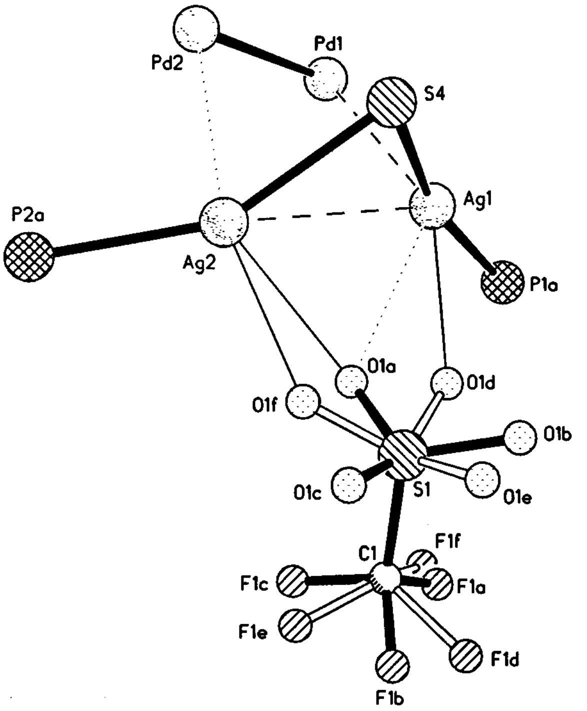

Figure 2. Coordination around the silver centers. The major orientation (67%) of the bridging triflate is shown as solid bonds.

digonal at all. The Ag2 center takes part in shorter distances to its sourrounding atoms other than Pd2, as compared to the Ag1 centre.

A close view of the packing shows that two SC_6F_5 rings of contiguous cations are parallel (dihedral angle = 0°, symmetry imposed). However, both rings are apart (2.82 Å) and strongly set off (5.10 Å), so that only the C314−F314 bonds overlap; these bonds deviate from the aromatic rings, leaning to each other (the *para* fluorines lie 0.04 Å away from the best C_6 plane), as the consequence of an electrostatic interaction.[14]

This close contact in the solid state needs not to be maintained in solution: The ^{19}F NMR spectra of compound **1** at varying concentrations in acetone-d_6 (up to saturated solution) show no changes; therefore, the dynamic behavior of one of the perfluorobenzenethiolato rings must be ascribed to intramolecular interactions, which hinder the rotation around the C−S bond.

It is worth noting that compound **1** is stable to light and that no silver halide precipitates when **1** is treated with diluted HX (X = F, Cl, Br, or I).

Acknowledgment. This work was supported by the Dirección General de Investigación Científica y Técnica (Grant PB94-0597). S.H. thanks the Ministerio de Educación y Ciencia for the award of an FPI scholarship.

Supporting Information Available: ^{31}P NMR spectra of **1** in CD_2Cl_2 at −95 and 20.5 °C (1 page). An X-ray crystallographic file, in CIF format, for complex **1** is available on the Internet only. Ordering and access information is given on any current masthead page.

IC970457I

---

[14] Hunter, C. A. *Chem Soc. Rev.* **1994**, *23*, 101. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.