Direct Ag−Pt_2 Interactions in Pentafluorophenyl A-Frame Complexes Containing Halide or OH^- and Bis(diphenylphosphino)methane (dppm) as Bridging Ligands. Crystal Structures of $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]\cdot C_7H_8$ and $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-dppm})Pt(C_6F_5)_2]\cdot {}^1/_2C_6H_{14}$

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Complexes $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2]$ (X = Cl, Br) react with $AgClO_4$ and $[Ag(OClO_3)L]$ (L = PPh_3, SC_4H_8), yielding different compounds depending on the silver reagent used. The reactions with $AgClO_4$ in wet solvents lead to the syntheses of the complexes $[(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})\{Ag(H_2O)\}Pt(C_6F_5)_2]$ [X = Cl (**1**), Br (**2**)] in which the existence of two Pt−Ag bonds is postulated. The reactions with $[Ag(OClO_3)(PPh_3)]$ give similar complexes $[(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ [X = Cl (**3**), Br (**4**)]. The presence of silver coordinated to the platinum atoms activates the substitution of the halogen bridge; thus, **3** reacts with water, yielding the complex $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**). Complex **5** can be prepared as well by reaction of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-dppm})Pt(C_6F_5)_2]$ (**6**) with $[Ag(OClO_3)(PPh_3)]$. Nevertheless, the reaction of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-dppm})Pt(C_6F_5)_2]$ with the complex $[Ag(OClO_3)(SC_4H_8)]$ does not render the analogous complex to **3**, but AgCl precipitates and $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-dppm})Pt(C_6F_5)_2]$ (**7**) is formed. This different behavior depending on the ligand present in the silver complex is probably due to the ability of the tetrahydrothiophene ligand to act as a bridge. Single-crystal X-ray studies of **5** and **7** have been carried out. For **5**, the existence of two Pt−Ag bonds with distances 2.791(1) and 2.832(1) Å has been confirmed. Complex **7** shows a distorted six-membered ring skeleton formed by the metal atoms, dppm ligand, and sulfur atom of the SC_4H_8 group. Compound $\mathbf{5}\cdot C_7H_8$ ($C_{74}H_{46}AgF_{20}OP_3Pt_2$) crystallizes in the monoclinic system, space group $P2_1/n$: $a = 14.360(1)$ Å, $b = 21.590(1)$ Å, $c = 21.585(2)$ Å, $\beta = 90.85(1)°$, $V = 6691.3(8)$ Å^3, $Z = 4$. Compound $\mathbf{7}\cdot{}^1/_2C_6H_{14}$ ($C_{56}H_{37}F_{20}P_2Pt_2S$) crystallizes in the monoclinic system, space group $P2_1/n$: $a = 22.258(6)$ Å, $b = 11.351(3)$ Å, $c = 22.268(5)$ Å, $\beta = 106.21(3)°$, $V = 5402.6(16)$ Å^3, $Z = 4$.

Introduction

Anionic perhalophenyl platinate complexes act as Lewis bases toward metal (M) complexes or metal salts forming polynuclear derivatives with donor−acceptor Pt→M bonds.[1] When the platinate substrates are dinuclear in character, their reactions with silver salts usually render trinuclear complexes with two Pt→Ag bonds and in which the platinate substrate acts as a didentate chelating ligand.[2] The resulting trinuclear complexes are rather stable, and not only do the Pt→Ag bonds seem to be preserved in solutions of donor solvents but in some cases the complexes react with neutral ligands producing displacement reactions at the silver center without cleavage of the Pt→Ag bonds. For instance, $[NBu_4][(\mu\text{-}C_6F_5)_2(C_6F_5)_4Pt_2Ag(OEt_2)]$ reacts with ligands L, yielding $[NBu_4][(\mu\text{-}C_6F_5)_2(C_6F_5)_4Pt_2Ag(L)]$ [L = PPh_3, SC_4H_8 (tetrahydrothiophene), $C_6H_{11}CN$].[2b] However, there are few such dinuclear platinate substrates, and hence this type of trinuclear complex with chelating platinate ligands is rather scarce as well.

In the course of our current research, we have recently described the syntheses and structural characterization of the anionic dinuclear platinum(II) complexes $\{[NBu_4][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2]$ [X = Cl (**A**), Br (**B**), I (**C**)]} with two very different bridging ligands: bis(diphenylphosphino)methane (dppm = $Ph_2PCH_2PPh_2$) and a halide ligand.[3] This is not a common situation since most of the complexes containing dppm acting as an exodidentate ligand are formed by two metal centers which are joined by two dppm ligands; and in many cases metal−metal bonds are present as well.[4] In addition, dinuclear derivatives with such different ligands bridging the metal centers at the same time are also rather unusual.[4]

These dinuclear systems (**A**−**C**) are inert toward Lewis bases such as X^-, NCMe, SC_4H_8, and PPh_3, which are not even able to produce the cleavage of the Pt(μ-X)Pt bridging system.

The X-ray structure of the iodo derivative (**C**) indicates that the large space requirements of the phenyl rings of the dppm ligand and the pentafluorophenyl rings seem to produce steric overcrowding, which results in long Pt···Pt distances [4.446(1) Å][3] and probably in the lack of reactivity due to the difficulties of the reactants (Lewis bases in all cases) in reaching the Pt(μ-X)(μ-dppm)Pt bridging system.

All these facts prompted us to study the reactivity of this type of complex toward Lewis acids such as $AgClO_4$ or $[Ag(OClO_3)(L)]$ (L = PPh_3, SC_4H_8) in order to explore the ability

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of these asymmetric dinuclear platinum complexes to act as didentate metallo ligands. Such reactions result in the formation of the corresponding trinuclear Pt_2Ag complexes which are more reactive than the dinuclear platinum starting materials.

Experimental Section

The C, H, and N analyses and conductance measurements were performed as described elsewhere.[3] Infrared spectra (4000−200 cm^{-1}) were recorded from Nujol mulls between polyethylene sheets on a Perkin Elmer 833 or 1710 FTIR spectrophotometer. NMR measurements were done on either a Varian XL200 or a Unity 300 spectrometer. $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]$, $[NBu_4][(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})Pt(C_6F_5)_2]$ (X = Cl, Br),[3] $[Ag(OClO_3)(PPh_3)]$,[5] and $[Ag(OClO_3)(SC_4H_8)]$[6] were prepared as described elsewhere. All the reactions involving silver reagents were carried out under exclusion of light.

Safety Note. Perchlorate salts with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Syntheses of $[(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (X = Cl (1), Br (2)]. Method A. To a solution of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})Pt(C_6F_5)_2]$ (X = Cl, 0.80 g, 0.47 mmol; Br, 0.80 g, 0.45 mmol) in CH_2Cl_2 (30 mL) was added an equimolar amount of $AgClO_4$, and the mixture was stirred at room temperature for 14 h. The solution was evaporated to dryness, and the residue was extracted with diethyl ether. The insoluble NBu_4ClO_4 was filtered off, and after the solution was evaporated to dryness, the residue was treated with *n*-hexane, rendering complexes **1** and **2** (yields: 90 and 71%, respectively).

Method B. To a solution of $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]$ (X = Cl, 1.00 g, 0.50 mmol; Br, 0.400 g, 0.192 mmol) in tetrahydrofuran (30 mL) was added $AgClO_4$ in 1:2 molar ratio, and the mixture was stirred at room temperature for 45 min. The solvent was evaporated to dryness, and the residue was extracted with diethyl ether. The insoluble AgX and NBu_4ClO_4 were filtered off, and after the solution was evaporated to dryness, the residue was treated with *n*-hexane, rendering complexes **1** and **2** (yields: 72 and 67%, respectively).

Anal. Found (calcd) for $[(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**1**): C, 36.98 (36.69); H, 1.93 (1.51). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 808(s), 790(s). C_6F_5 others 1638(m), 1611(m), 1506(vs), 1060(vs), 959(vs); dppm 1100(m), 768(m), 740(m), 690(m), 623(w), 572(m), 482(m); ν(Pt-Cl) 315(d); H_2O ν(O−H) 3676(m), 3610(m).

Anal. Found (calcd) for $[(C_6F_5)_2Pt(\mu\text{-Br})(\mu\text{-dppm})\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**2**) C, 36.08 (35.70); H, 1.26 (1.47). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 807(s), 786(s), C_6F_5 others 1636(m), 1609(m), 1507(m), 1061(vs), 958(m); dppm: 1101(m), 769(sh), 691(m), 525(m), 487(m); H_2O 3605(m, br).

Syntheses of $[(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$, (X = Cl (3), Br (4), OH (5)]. To a solution of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})Pt(C_6F_5)_2]$ (X = Cl, 0.216 g, 0.126 mmol; Br, 0.100 g, 0.057 mmol; OH (see below), 0.150 g, 0.088 mmol) in CH_2Cl_2 (30 mL) was added an equimolar amount of $[Ag(OClO_3)(PPh_3)]$, and the mixture was stirred at room temperature for 5 min. The solution was evaporated to dryness, and the residue was extracted with diethyl ether. The insoluble NBu_4ClO_4 was filtered off, and after the solution was evaporated to dryness, the residue was treated with *n*-hexane, rendering complexes **3**−**5** (yields: 75, 70, and 65% respectively).

Complex **3** was also prepared as follows: To a solution of 0.200 g (0.126 mmol) of **2** in CH_2Cl_2 (30 mL) was added 0.033 g (0.126 mmol) of PPh_3, and the mixture was stirred at room temperature for 5 min. The solution was evaporated to dryness, and the residue was treated with *n*-hexane, rendering complex **3** in 73% yield.

Complex **5** can also be prepared as follows: To a solution of **3** in 30 mL of CH_2Cl_2 is added 1 mL of water. The mixture is stirred for 48 h, and then the CH_2Cl_2 is removed by evaporation. The remaining solid is filtered off and identified as **5** (80% yield).

Anal. Found (calcd) for $[(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**3**): C, 43.22 (43.54); H, 2.39 (2.02). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 809(s), 787(s), C_6F_5 others 1635(m), 1606(m), 1502(vs), 1060(vs), 960(m); dppm 1099(m), 741(m), 693(m), 522(m), 510(m), 490(m); ν(Pt−Cl) 313(w); PPh_3 absorptions not assigned due to overlap with those of dppm.

Anal. Found (calcd) for $[(C_6F_5)_2Pt(\mu\text{-Br})(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**4**): C, 42.38 (42.51); H, 2.11 (1.97). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 808(s), 789(s), C_6F_5 others 1638(m), 1608(m), 1503(vs), 1061(vs), 960(m); dppm 1099(m), 741(m), 693(m), 522(s), 510(m), 489(m); PPh_3 absorptions not assigned due to overlap with those of dppm.

Anal. Found (calcd) for $[(C_6F_5)_2Pt(\mu\text{-OH})(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**): C, 43.65 (43.98); H, 2.08 (2.09). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 806(s), 785(s), C_6F_5 others 1638(m), 1608(m), 1505(vs), 1062(vs), 960(m); dppm 1100(m), 693(m), 522(m), 491(m); ν(O−H) 3609(m); PPh_3 absorptions not assigned due to overlap with those of dppm.

Preparation of Crystals of 5. Suitable crystals for X-ray purposes were obtained by slow evaporation of a solution of **5** in CH_2Cl_2 in a toluene atmosphere.

Synthesis of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-OH})(\mu\text{-dppm})Pt(C_6F_5)_2]$ (6). To a solution of 0.15 g (0.09 mmol) of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-Br})(\mu\text{-dppm})Pt(C_6F_5)_2]$ in a mixture of 30 mL of MeOH and 10 mL of H_2O, was added KOH in excess, and the mixture was refluxed for about 24 h. The suspension was concentrated to ca. 10 mL, and the solid precipitate was filtered off. The resulting solid was washed with 3 mL of ^{i}PrOH and treated with *n*-hexane, yielding **6**, 78% yield.

Anal. Found (calcd) for **6**: C, 45.90 (45.86); H, 3.37 (3.49); N, 0.93 (0.82). IR data (cm^{-1}): C_6F_5 X-sensitive[7] 809(s), 787(s), C_6F_5 others 1638(m), 1608(m), 1499(vs), 1058(vs), 956(vs); dppm 1101(s), 772(m), 743(s), 691(m), 678(w), 530(m), 495(m), 482(m); ν(O−H) 3621(m); NBu_4^+ 884(m).

Synthesis of $[(C_6F_5)_2Pt(\mu\text{-SC}_4H_8)(\mu\text{-dppm})Pt(C_6F_5)_2]$, (7). Method A. To a solution of 0.300 g (0.174 mmol) of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})Pt(C_6F_5)_2]$ in CH_2Cl_2 (30 mL) was added 0.052 g (0.174 mmol) of $[Ag(OClO_3)(SC_4H_8)]$, and the mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness, and the residue was extracted with diethyl ether. The insoluble AgCl and NBu_4ClO_4 were filtered off, and after the solution was evaporated to dryness, the residue was treated with *n*-hexane, giving complex **7** in 79% yield.

Method B. To a solution of 0.214 g (0.124 mmol) of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})Pt(C_6F_5)_2]$ in CH_2Cl_2 (30 mL) were added 11.0 μL (0.124 mmol) of SC_4H_8 and 0.026 g (0.124 mmol) of $AgClO_4$, and the mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness, and the residue was extracted with diethyl ether. The insoluble AgCl and NBu_4ClO_4 were filtered off, and after the solution was evaporated to dryness, the residue was treated with *n*-hexane, giving complex **7** in 74% yield.

Method C. To a solution of 0.250 g (0.158 mmol) of **2** in CH_2Cl_2 (30 mL) was added 13.9 μL (0.158 mmol) of SC_4H_8, and the mixture was stirred at room temperature for 30 min. The insoluble AgCl was filtered off, the resulting solution was evaporated to dryness, and the residue was treated with *n*-hexane, giving complex **7** in 60% yield.

Anal. Found (calcd): C, 41.34 (41.58); H, 1.88 (1.98). IR data (cm^{-1}) C_6F_5 X-sensitive[7] 806(s), 791(s), C_6F_5 others 1636(m), 1608(m), 1507(m), 1062(vs), 964(vs); dppm 1103(m), 751(m), 733(sh), 691(m), 525(m), 513(m), 484(m), 444(m), 377(m); SC_4H_8 1201(m), 888(w).

Preparation of Crystals of 7. Suitable crystals for X-ray purposes were obtained by slow diffusion of *n*−hexane into a solution of **7** in CH_2Cl_2.

Crystal Structure Determination of Compound $5\cdot C_7H_8$. Relevant crystal information is listed in Table 1. A crystal of $\mathbf{5}\cdot C_7H_8$ was mounted at the end of a glass fiber and held in place with epoxy glue. Crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer. Cell constants were refined from 2θ values of 25 reflections ($24.1 < 2\theta < 31.9°$). An absorption correction based on 540 Ψ scans was applied; transmission coefficients were in the range 0.815−0.668. Three standard reflections were measured every 160 min, and they showed no decay. The structure was solved by Patterson methods and refined against F^2 using the program SHELXL-93.[8] All non-hydrogen atoms, except for the disordered carbon atoms, were

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Table 1. Crystallographic Data[a] for $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]\cdot C_7H_8$ (**5**$\cdot C_7H_8$) and $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-dppm})Pt(C_6F_5)_2]\cdot {}^1/_2C_6H_{14}$ (**7**$\cdot {}^1/_2C_6H_{14}$)

compd	**5**$\cdot C_7H_8$	**7**$\cdot {}^1/_2C_6H_{14}$
empirical formula	$C_{74}H_{46}AgF_{20}OP_3Pt_2$	$C_{56}H_{37}F_{20}P_2Pt_2S$
formula wt	1922.07	1574.04
temp (K)	150(1)	200(1)
space group	$P2_1/n$	$P2_1/n$
unit cell dimens a (Å)	14.360(1)	22.258(6)
b (Å)	21.590(1)	11.351(3)
c (Å)	21.585(2)	22.268(5)
β (deg)	90.85(1)	106.21(3)
V (Å^3)	6691.3(8)	5402.6(16)
Z	4	4
ρ_{calc} (Mg/m^3)	1.908	1.935
abs coeff (mm^{-1})	4.635	5.379
final R indices $[I > 2\sigma(I)]$[b]	R1 = 0.0546, wR2 = 0.0846	R1 = 0.0444, wR2 = 0.1030
R indices (all data)	R1 = 0.1190, wR2 = 0.1032	R1 = 0.0761, wR2 = 0.1174

[a] Wavelength for both compounds: 0.710 73 Å. [b] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms, except the hydroxy hydrogen atom, were constrained to idealized geometries and assigned a common refined isotropic displacement parameter. Two phenyl rings of the triphenylphosphine ligand were disordered over two sets of positions and were refined with partial occupancy of 0.5/0.5 [C(50)] and 0.7/0.3 [C(62)]; and their geometry was constrained to regular hexagons. Full-matrix least-squares refinement of this model converged to final residual indices listed in Table 1. Final difference electron density maps showed no features above 1 e/Å^3, with the largest peaks lying closer than 1.1 Å to the platinum atoms.

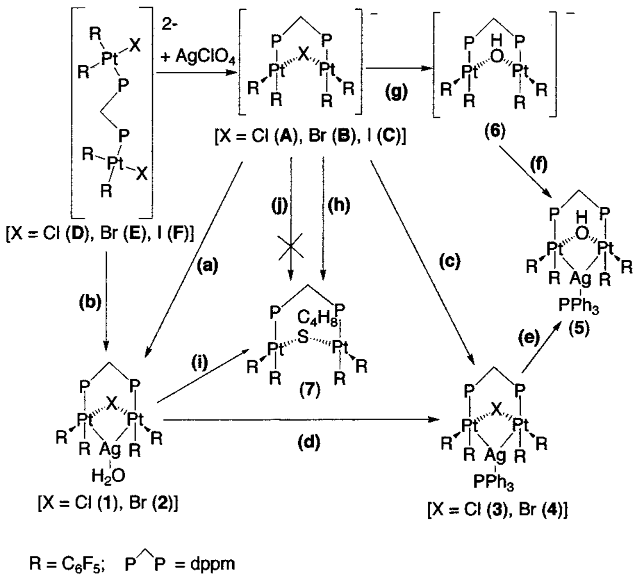
Crystal Structure Determination of Compound 7$\cdot$C$_6$H$_{14}$. Relevant crystal information is listed in Table 1. A crystal of **7**$\cdot C_6H_{14}$ was mounted at the end of a glass fiber and held in place with epoxy glue. Crystallographic data were collected on a four-circle Siemens STOE/AED2 diffractometer. Cell constants were refined from 2θ values of 48 reflections, including Friedel pairs ($21.4° < 2\theta < 33.4°$). An absorption correction based on 504 Ψ scans was applied, transmission coefficients were in the range 0.678−0.432. Three standard reflections were measured every 120 min, and they showed no decay. The structure was solved by Patterson methods and refined against F^2 using the program SHELXL-93.[8] All non-hydrogen atoms, except for the solvent atoms, were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times (1.5 for the methyl hydrogen atoms) the U_{eq} of their parent carbon atoms. The solvent atoms lie near an inversion center and were refined with a 0.5 occupancy, a common thermal parameter for all the carbon atoms and restrained geometry. Full-matrix least-squares refinement of this model converged to final residual indices listed in Table 1. Final difference electron density maps showed seven features above 1 e/Å^3 (max/min 1.89/−2.60 e/Å^3), with the largest peaks lying closer than 1.16 Å to the platinum atoms.

Results and Discussion

All the reactions presented in this paper are summarized in Scheme 1. Complexes $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2]$ [X = Cl (**A**), Br (**B**)] contain one halogen atom acting as a bridge between the two platinum centers.[3] Thus, two possible pathways for their reactivity toward silver(I) compounds could be expected: (i) elimination of the halogen atoms as the corresponding silver halide or (ii) coordination of the silver atom to the platinum center forming Pt→Ag donor−acceptor bonds.

When $AgClO_4$ is added to a CH_2Cl_2 solution of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2]$ (1:1 molar ratio), no precipitation of the corresponding AgX is observed. After several hours of stirring in the dark, the silver perchlorate dissolves completely and the solution is evaporated to dryness. The treatment of the white residue with diethyl ether allows the separation of NBu_4ClO_4 as a white solid (identified by IR). The remaining solution, after evaporation of the solvent, renders the complexes $[(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})\{Ag(H_2O)\}Pt(C_6F_5)_2]$ [X = Cl (**1**), Br (**2**)] as white solids (Scheme 1a). The presence of Ag^+ in these materials is confirmed by dissolving small amounts of them in acetone and adding some drops of a methanol solution of HCl. The immediate precipitation of AgCl is observed in both cases.

Scheme 1[a]



[a] (a) $+AgClO_4$, $-NBu_4ClO_4$, CH_2Cl_2 wet; (b) $+2AgClO_4$, $-AgCl$, $-2NBu_4ClO_4$; (c) $+[Ag(OClO_3)(PPh_3)]$, $-NBu_4ClO_4$; (d) $+PPh_3$; (e) $+H_2O$, $-HX$; (f) $+[Ag(OClO_3)(PPh_3)]$, $-NBu_4ClO_4$; (g) +KOH, reflux, −KX; (h) $+[Ag(OClO_3)(SC_4H_8)]$, −AgX, $-NBu_4ClO_4$; (i) $+SC_4H_8$, −AgX; (j) SC_4H_8.

IR spectra of complexes **1** and **2** confirm the presence of the expected ligands and show some broad signals in the 3600 cm^{-1} region, indicating the presence of water, possibly coordinated to the silver center (Scheme 1a). The presence of water can be explained by the use of solvents not perfectly dried. The ^{1}H NMR spectra of complexes **1** and **2** show signals due to the hydrogen atoms of water, besides those corresponding to the dppm ligand. The ^{19}F and ^{31}P NMR spectra are consistent with the expected geometry; the values for the chemical displacements and coupling constants with ^{195}Pt (when present) are listed in Table 2.

As expected, complexes **1** and **2** can also be prepared by reacting the precursors of **A** and **B**, $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]$ [X = Cl (**D**), Br (**E**)][3] with $AgClO_4$ in

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(8) Sheldrick, G. M. *SHELXL-93, a program for crystal structure refinement*; University of Göttingen: Germany, 1993.

Table 2. ^{19}F and ^{31}P NMR Data for Complexes **1-7**

	^{19}F NMR [a]				^{31}P NMR [a]	
complex	$\delta(F_o)$	$\delta(F_m)$	$\delta(F_p)$	$^3J_{Pt-Fo}$ (Hz)	δ(dppm)	$^1J_{Pt-P}$ (Hz)
$[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**1**)	−117.35	−163.56	−160.14	513.9	9.72	2147
	−119.31	[b]	−162.18	391.4		
$[(C_6F_5)_2Pt(\mu\text{-}Br)(\mu\text{-}dppm)\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**2**)	−116.76	−161.00	−157.47	538.8	8.81	2169
	[c]	−161.41	−159.78	[c]		
$[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**3**)	−116.89	[f]		339.0	13.22	2460
	−118.18			511.2	$PPh_3 = 13.15$	$^1J_{Ag-P} = 693, 800$
$[(C_6F_5)_2Pt(\mu\text{-}Br)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**4**)	−116.18	−165.05	−160.24	330.7	13.00	2447
	−118.31	−163.33		479.5	$PPh_3 = 13.40$	$^1J_{Ag-P} = 670, 774$
$[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**)	−118.34	[d]		451.9	9.38	2420
	−119.56			[e]	$PPh_3 =$ ca. 9	$^1J_{Ag-P}$ [e]
$[NBu_4][(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**6**)	−118.30	−165.32	−163.64	501.2	8.68	2691
	−119.44	−167.65	−167.47	351.3		
$[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**7**)	−117.88	−161.75	−158.36	281.2		
	−118.33	−163.99	−162.10	338.7		

[a] In $CDCl_3$ solution. [b] Both signals appear overlapped. [c] Broad signal at −117.9 ppm with poor resolution. [d] Several signals at ca. −164 ppm. [e] Due to the poor resolution of the signal it is not possible to measure the value of the coupling constant. [f] Two broad signals at −163.6 and −165.6 ppm with poor resolution.

tetrahydrofuran in a 1:2 molar ratio (Scheme 1b). In this case we can observe the formation of the silver halide AgX as well.

When the complex $[Ag(OClO_3)(PPh_3)]$ is added to a solution of **A** or **B** in CH_2Cl_2 in a 1:1 molar ratio, no change in the color of the solution is observed. After 5 min of stirring, the solvent is eliminated and the residue is treated with diethyl ether. The NBu_4ClO_4, insoluble in this solvent, is filtered off, and from the solution, complexes $[(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ [X = Cl (**3**), Br (**4**)] are isolated as white solids (Scheme 1c). The IR spectra of **3** and **4** show absorptions assignable to PPh_3. ^{1}H, ^{19}F, and ^{31}P NMR spectra of **3** and **4** are in accordance with the proposed geometry; the chemical shifts of their signals are collected in Table 2.

On the other hand, water coordinated to the silver center in $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**1**) can be displaced by PPh_3 without cleavage of the Pt→Ag bond. When **1** is reacted with an equimolar amount of PPh_3 in CH_2Cl_2, the complex $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**3**) is obtained from the solution (Scheme 1d).

When some drops of water are added to a CH_2Cl_2 solution of **3** and the mixture is stirred for several days, it is possible to obtain a material the infrared spectrum of which shows a sharp absorption at 3609 cm^{-1}, typical for ν(O−H).[9] Further investigation of this solid leads to its identification as $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**, Scheme 1e). This is a noteworthy result, since in our previous work[3] we observed that the halogen bridges in complexes **A**−**C** are very inert and do not react with halides, PPh_3, SC_4H_8, or NCMe. The substitution of the bridging chloride in **3** under such mild conditions suggests that the donor−acceptor Pt→Ag bonds activate this substitution. The donation of electron density by the platinum atom to silver causes the withdrawal of metal electron density from the Pt−Cl bonds, increasing their reactivity. Nevertheless, when the substitution on **3** is attempted by using NBu_4OH, we observe the immediate precipitation of black Ag_2O and the chloride bridging complex **A** is recovered from the resulting solution. As can be seen, the substitution of the bridging Cl can only be achieved with very weak bases, such as water.

Complex **5** can also be prepared straightforwardly by reacting $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**6**) with $[Ag(OClO_3)(PPh_3)]$ (1:1 molar ratio) in CH_2Cl_2 (Scheme 1f). However, the synthesis of the starting material **6** involves some peculiarities which are worth commenting on. First of all, we have tried to prepare **6** by using a procedure similar to the one used for the syntheses of **A**−**C**. The first step in the syntheses of complexes **A**−**C** involves the cleavage of the halogen bridges in the complexes $[NBu_4]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ with dppm. In short reaction times (10 min) the precursors to complexes **A**−**C**, $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-}dppm)PtX(C_6F_5)_2]$ [X = Cl (**D**), Br (**E**), I (**F**)], can be obtained with good yields (ca. 90%), whereas when longer periods are allowed, a mixture of starting material and $[Pt(C_6F_5)_2(dppm)]$ is formed. This behavior indicates that the complexes $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-}dppm)PtX(C_6F_5)_2]$ are the kinetic products of the cleavage of the bridges. Nevertheless, dppm is not able to cleave the OH bridges in complex $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$,[9] since even with long reaction periods the unaltered starting material is recovered.

The only way to prepare complex **6** is by substitution of the bromine ligand in complex **B** by the OH group. This substitution does not take place under mild conditions, since the reaction of **B** with bases such as NBu_4OH or KOH does not progress at room temperature. It is necessary to reflux a solution of **B** and an excess of KOH in a $MeOH/H_2O$ mixture for 24 h to obtain the complex $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**6**) after removal of the MeOH and addition of ^{i}PrOH, in which the product is not soluble (Scheme 1g). The yield is 78%. The severe conditions which are necessary for the substitution of the bromine ligand in **B** contrast with the facility of hydrolysis of **3** brought about by the presence of the silver bonded to the platinum centers.

The stoichiometry of **6** is confirmed by its elemental (C, H, N) analyses, IR spectrum, and ^{1}H, ^{19}F, and ^{31}P NMR spectra. The IR spectrum shows an absorption at 3621 cm^{-1} assignable to ν(O−H).[9] In the ^{1}H NMR spectrum, the hydroxyl hydrogen atom appears at 2.15 ppm. The ^{19}F and ^{31}P NMR spectra are consistent with the expected geometry; the values for the chemical shifts and coupling constants with ^{195}Pt (when present) are listed in Table 2.

We have also studied the reaction of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**A**) with $[Ag(OClO_3)(SC_4H_8)]$ in order to prepare the analogous complex to **3** with the tetrahydrothiophene ligand (SC_4H_8) coordinated to the silver atom. However, this process does not result in the formation of the expected trinuclear complex. Thus, when $[Ag(OClO_3)(SC_4H_8)]$ is added to a solution of **A** in CH_2Cl_2 (1:1 molar ratio) and the resulting solution is stirred at room temperature for 24 h, the presence of a solid is observed. The removal of the solvent and the addition of diethyl ether allow the elimination by filtration of a solid which is identified as a mixture of AgCl

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]\cdot C_7H_8$ (**5**·C_7H_8)

Pt(1)−Ag	2.791(1)	Pt(2)−Ag	2.832(1)	Pt(1)-C(1)	1.992(10)	Pt(2)-C(13)	2.015(12)
Pt(1)−O	2.100(6)	Pt(2)−O	2.084(7)	Pt(1)-C(7)	2.058(11)	Pt(2)-C(19)	2.071(11)
Pt(1)−P(1)	2.302(3)	Pt(2)−P(2)	2.296(3)	Ag−P(3)	2.422(3)	Pt(1)···Pt(2)	3.479(1)
Ag−Pt(1)−O	85.3(2)	Ag−Pt(2)−O	84.5(2)	O−Pt(1)−C(1)	176.2(4)	O−Pt(2)−C(13)	177.2(4)
Ag−Pt(1)−P(1)	95.2(1)	Ag−Pt(2)−P(2)	94.1(1)	O−Pt(1)−C(7)	89.2(3)	O−Pt(2)−C(19)	88.1(4)
Ag−Pt(1)−C(1)	98.3(3)	Ag−Pt(2)−C(13)	98.3(3)	P(1)−Pt(1)−C(1)	92.7(3)	P(2)−Pt(2)−C(13)	91.6(3)
Ag−Pt(1)−C(7)	90.4(3)	Ag−Pt(2)−C(19)	93.6(3)	P(1)−Pt(1)−C(7)	173.7(3)	P(2)−Pt(2)−C(19)	171.3(3)
Pt(1)−O−Pt(2)	112.5(3)	P(1)−C(25)−P(2)	116.0(6)	C(1)−Pt(1)−C(7)	89.5(4)	C(13)−Pt(2)−C(19)	91.4(4)
Pt(1)−P(1)−C(25)	115.8(3)	Pt(2)−P(2)−C(25)	117.0(4)	Pt(1)−Ag−P(3)	143.0(1)	Pt(2)−Ag−P(3)	140.5(1)
O−Pt(1)−P(1)	88.3(2)	O−Pt(2)−P(2)	88.5(2)	Pt(1)−Ag−Pt(2)	76.4(1)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]\cdot{}^1/_2C_6H_{14}$ (**7**·$^1/_2C_6H_{14}$)

Pt(1)−S	2.356(2)	Pt(2)−O	2.354(2)	Pt(1)-C(7)	2.054(9)	Pt(2)-C(19)	2.067(8)
Pt(1)−P(1)	2.289(2)	Pt(2)−P(2)	2.292(2)	Ag−P(3)	2.422(3)	Pt(1)...Pt(2)	4.150(1)
Pt(1)-C(1)	2.030(8)	Pt(2)-C(13)	2.008(8)				
Pt(1)−S−Pt(2)	123.6(1)	P(1)−C(25)−P(2)	117.7(4)	S−Pt(1)−C(7)	91.4(2)	S−Pt(2)−C(19)	93.6(2)
Pt(1)−P(1)−C(25)	114.8(3)	Pt(2)−P(2)−C(25)	114.3(3)	P(1)−Pt(1)−C(1)	90.4(2)	P(2)−Pt(2)−C(13)	92.0(2)
S−Pt(1)−P(1)	92.6(1)	S−Pt(2)−P(2)	91.5(1)	P(1)−Pt(1)−C(7)	175.2(2)	P(2)−Pt(2)−C(19)	174.6(2)
S−Pt(1)−C(1)	174.8(2)	S−Pt(2)−C(13)	173.8(3)	C(1)−Pt(1)−C(7)	85.3(3)	C(13)−Pt(2)−C(19)	83.0(3)

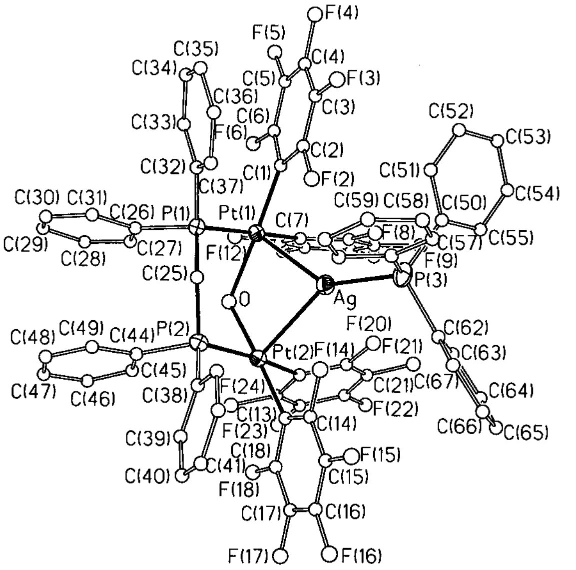

Figure 1. Drawing of the complex $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**), showing the atom-labeling scheme. Heavy atoms are represented by their 50% probability ellipsoids. For clarity, only one set of the disordered atoms is represented.

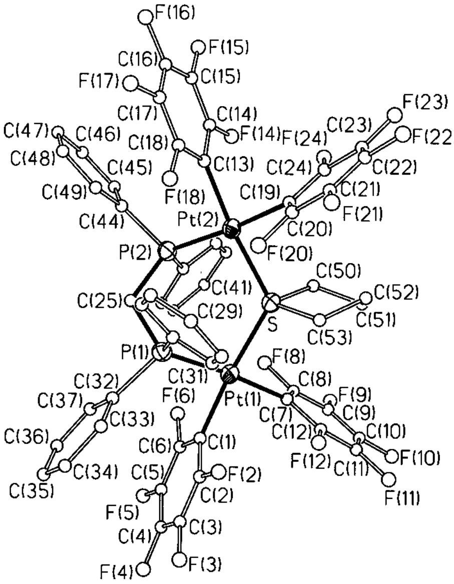

Figure 2. Drawing of the complex $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**7**), showing the atom-labeling scheme. Heavy atoms are represented by their 50% probability ellipsoids.

and NBu_4ClO_4. By evaporation of the OEt_2 from the filtrate a white solid, $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**7**), is obtained (Scheme 1h). A similar result is obtained if an equimolar mixture of $AgClO_4$ and SC_4H_8 is used instead of the complex $[Ag(OClO_3)(SC_4H_8)]$. Furthermore, the reaction of $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}dppm)\{Ag(H_2O)\}Pt(C_6F_5)_2]$ (**1**) with SC_4H_8 renders complex **7** as well (Scheme 1i). ^{1}H, ^{19}F, and ^{31}P NMR spectra for **7** (see Table 2) are in accord with the proposed structure, which has been established by X-ray diffraction.

Again, the presence of the silver atom bonded to the platinum centers activates the halogen bridge toward substitution. This replacement of the Cl atom by the tetrahydrothiophene ligand can only be achieved with the Pt−Ag compound, while the addition of SC_4H_8 to a solution of **A** does not cause any reaction after several days of stirring (Scheme 1j).[3]

The influence of the ligand L bonded to the silver center $[Ag(OClO_3)(SC_4H_8)]$ (L = PPh_3, SC_4H_8; Scheme 1f,g) on the nature of the final products is also noteworthy, since for L = PPh_3 the trinuclear system Pt_2Ag is formed or maintained, whereas for L = SC_4H_8, precipitation of AgCl and formation of **7** take place in both cases. Lower steric requirements and the ability of SC_4H_8 to act as a bridging ligand may be responsible for this differing behavior.

Crystal Structures of $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]\cdot C_7H_8$ (5·C_7H_8) *and* $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]\cdot{}^1/_2C_6H_{14}$ (7·$^1/_2C_6H_{14}$). We have carried out single-crystal X-ray diffraction studies on **5** and **7**. The structure of the neutral complex **5** is shown in Figure 1; selected bond distances and angles are listed in Table 3, and relevant crystallographic data are compiled in Table 1. The neutral complex $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ can be regarded as formed by two "$Pt(C_6F_5)_2$" fragments linked together by the dppm and hydroxy ligands and by the silver atom. The environment of each platinum atom is a square pyramid, and the two pyramids share an edge. Each platinum atom lies in the center of the base of the pyramid. Bond distances and angles are equal within experimental error for the two platinum environments and are in the range usually found in Pt(II) complexes containing these kinds of ligands.[10] The Ag−Pt−L angles are near 90°, with Ag−Pt−O smaller (*ca.* 85°), and with larger values (near 100°) for the pentafluorophenyl groups *trans* to the oxygen atom. The angles between the perpendicular to the best basal plane for each platinum and the Pt−Ag line are 7.6(1)° and 7.1(1)°, indicating that each Pt−

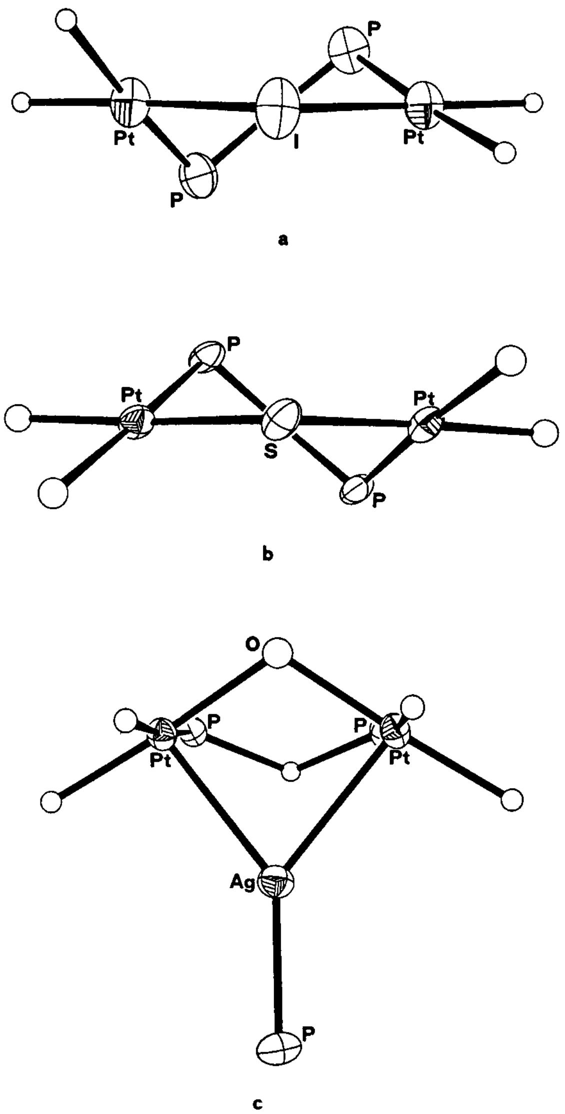

Figure 3. View of the cores of the complexes (a) $[(C_6F_5)_2Pt(\mu\text{-}I)(\mu\text{-}dppm)Pt(C_6F_5)_2]^-$ (**C**),[3] (b) $[(C_6F_5)_2Pt(\mu\text{-}SC_4H_8)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (**7**), and (c) $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}dppm)\{Ag(PPh_3)\}Pt(C_6F_5)_2]$ (**5**).

Ag bond is almost perpendicular to the base of the corresponding pyramid. The dihedral angle between the two platinum basal planes is 114.4(2)°. The short Pt−Ag distances, 2.791(1) and 2.832(1) Å, are characteristic of Pt→Ag bonds which are not supported by any other ligand covalently bonded to both metal centers. The lengths of these Pt−Ag bonds lie in the range of values previously found for other trinuclear complexes in which the silver atom is bonded simultaneously to two platinum centers, such as in $[NBu_4][(\mu\text{-}Cl)_2(C_6F_5)_4Pt_2Ag(OEt_2)]$ and $[NBu_4][(\mu\text{-}C_6F_5)_2(C_6F_5)_4Pt_2Ag(L)]$ (L = OEt_2, SC_4H_8).[2] The coordination sphere of the silver atom is completed by the triphenylphosphine ligand. The Ag−P(3) distance is 2.422(3) Å, similar to others found in the literature[11] but slightly longer that the Ag−P distance found for pentahalophenyl complexes in which only one Pt−Ag bond is present.[10] The environment of the silver atom is planar and symmetric, since the Pt−Ag−P angles are very similar (see Table 3). Finally, as has been observed previously,[1,2] the four pentafluorophenyl groups are oriented in such a way that one of their *ortho* fluorine atoms points toward the silver atom. The distances range from 2.754(8) to 2.982(6) Å and might indicate the existence of some kind of Ag···F interaction contributing to the overall stability of the complex.

The structure of neutral complex **7** is shown in Figure 2; selected bond distances and angles are listed in Table 4, and relevant crystallographic data are compiled in Table 1. As can be seen, the two "$Pt(C_6F_5)_2$" moieties are bridged by the dppm ligand and the sulfur atom of the tetrahydrothiophene ligand. Bond distances involving the platinum atoms are equal within experimental error in both moieties, and all of them are in the range usually found for this kind of complex. The metal atoms lie in the center of square planar environments, the angle between these being 133.2(1)°, greater than that corresponding to complex **5** and similar to those previously reported for the anion of complex **C** (Figure 3a), $[(C_6F_5)_2Pt(\mu\text{-}I)(\mu\text{-}dppm)Pt(C_6F_5)_2]^-$ [135.1(1)°].[3] It is noteworthy that, as in **C**, the skeleton of complex **7** is twisted (Figure 3b) and the angle formed by the Pt−Pt and P−P lines has a value of 41.0(1)° [40.4(1)° for **C**]. Nevertheless, for **5** these lines are almost parallel, the angle being 0.7(1)°, and the six-membered ring formed by the two Pt atoms, P(1), P(2), O, and C(25) has a chair conformation (Figure 3c). This "open book" symmetric disposition for **5** is probably due to the presence of the silver atom coordinated to the two platinum centers simultaneously. When this "restraint" is not present, as in **7** or **C**, the six-membered ring twists to adopt a more distorted disposition. The Pt−Pt nonbonding distances are also clearly different for **5** and **7** (and **C**). The shorter distance is found for **5**, 3.479(1) Å, probably due to the "tweezers" effect of the silver atom, whereas for **7**, the intermetallic distance is 4.150(1) Å [4.446(1) Å for **C**]. Nevertheless, the size of the bridging atom between the platinum centers cannot be rejected as a possible cause of these variations in the Pt−Pt distances.

Conclusions

The dinuclear complexes $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ (X = Cl, Br) are able to act as didentate chelating metallo ligands toward $[AgL]^+$. The formation of the Pt→Ag bonds obliges the dinuclear platinum starting material to twist its two coordination planes to reach the final "open book" disposition necessary for the formation of the Pt−Ag bonds.

Another important effect introduced by the silver coordination is an increase in the reactivity of the bridging halide, which is inert in the dinuclear platinum starting materials.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds $5\cdot C_7H_8$ and $7\cdot {}^1/_2C_6H_{14}$ are available on the Internet only. Access information is given on any current masthead page.

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