

Supramolecular Structures in [Ag(dppf)] Complexes [dppf = 1,1'-Bis(diphenylphosphanyl)ferrocene] Stabilized by Coordinatively Versatile Trifluoroacetate (TFA) Ligands

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The interaction of silver(I) trifluoroacetate and dppf in different molar equivalents has led to the isolation of dinuclear complexes [Ag₂(μ-O₂CCF₃)₂(μ-dppf)] (**1**) and [Ag₂(η¹-O₂CCF₃)₂(dppf)₂] (**2**). Treatment of **1** with excess dppf gave a coordination polymeric compound [Ag(η²-O₂CCF₃)(dppf)]_n (**3**). Reaction of **1** with PMe₂Ph in MeOH in the presence of NH₄PF₆ led to displacement of trifluoroacetate, forming the mononuclear compound [Ag(PMe₂Ph)₂(η²-dppf)]PF₆ (**4**). All compounds have been characterized by microanalytical and spectroscopic analyses [IR, MS and NMR (¹H, ¹⁹F and ³¹P{¹H})] as well as X-ray diffraction studies. Molecular structures of the solvates of **1**, viz. **1A** (1·0.5THF) and **1B**

(1·0.5CH₂Cl₂), **2** and **3** show that they contain trifluoroacetate in bridging, monodentate and bidentate bonding modes, respectively, with dppf as a bridging co-ligand. Compound **3** is an infinite linear [-dppf-Ag-dppf-Ag-dppf-Ag-]_n coordination polymer. Interestingly, **1A** and **1B** form two different supramolecular network structures through C-H...F and C-H...O hydrogen-bonding interactions. Such secondary bonding interactions also lead to the formation of a 3D supramolecular structure in **3**.

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Introduction

Transition-metal-mediated self-assembly is emerging as a new and pragmatic strategy for the design of nanostructures, supramolecular two- or three-dimensional network structures and coordination polymers.^[1] Nitrogen-donor ligands have dominated these molecular designs.^[1b–1d,1f,1h,2] Among the metals, the use of silver in this line of crystal engineering has escalated in the last decade^[2,3] due to its rich structural diversity, which may be further tuned by numerous factors such as metal-to-ligand stoichiometry, counterions, ligand conformation, intra- and intermolecular H-bonding and solvents. Surprisingly, phosphanes have rarely been used in such assemblies until very recently, when some helices, rings, cages and polymers began to emerge in silver(I) systems containing (2-furyl)phosphane^[3a] and some diphosphanes.^[3b,3d] In particular, the role of the metallodiphosphane 1,1'-bis(diphenylphosphanyl)ferrocene (dppf) in supramolecular assemblies has not been investigated. We expect that the variable conformation modes of dppf in combination with coordinatively flexible ligands, such as acetate or nitrate as ancillary ligands,^[4] will give a multitude of molecular and crystal structural possibilities with a metal like silver, which can adopt variable geometries, especially

when assisted by intermolecular forces such as H-bonding. We describe here the results of such a study.

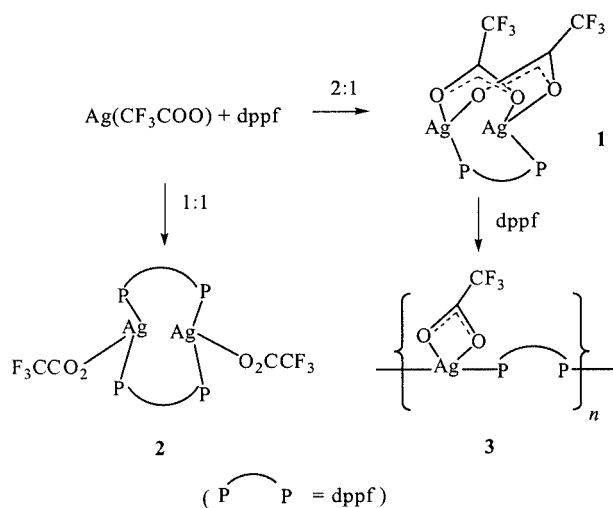
Results and Discussion

Synthesis

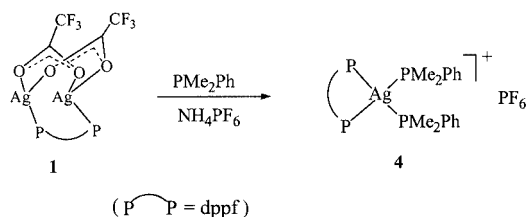
Treatment of Ag(O₂CCF₃) with dppf (2:1 molar ratio) in THF/MeOH for 8 h afforded an air-stable, non-light-sensitive yellow crystalline solid of a THF solvate of the disilver complex [Ag₂(O₂CCF₃)₂(dppf)] (**1**) in 34% yield. Workup of the supernatant of **1** in CH₂Cl₂/ether gave the solvate 1·0.5CH₂Cl₂ (30% yield). This solvate was obtained in 90% yield directly from a 6 h reaction in CH₂Cl₂. Recrystallization of **1** from THF/MeOH gave diffraction-quality crystals of 1·0.5THF (**1A**) after 1 d at ambient temperature, while the same process in CH₂Cl₂/diethyl ether gave diffraction-quality crystals of 1·0.5CH₂Cl₂ (**1B**). Treatment of Ag(O₂CCF₃) with 1 mol-equiv. of dppf in CH₂Cl₂ for 3 h at room temperature yielded a yellow solid of the dinuclear complex [Ag₂(O₂CCF₃)₂(dppf)] (**2**) in 87% yield. The reaction of **1** with 1 mol-equiv. of dppf in CH₂Cl₂ for 3.5 h afforded orange solids of the polymeric complex [Ag(O₂CCF₃)(dppf)]_n (**3**) in 88% yield. These reactions are shown in Scheme 1. When monitored in an NMR tube in CDCl₃, the latter reaction showed no evidence of **2** (see Exp. Sect.); **2** is, though, very stable in CDCl₃. Reaction of **1** with PMe₂Ph in MeOH in the presence of NH₄PF₆ led to displacement of the O₂CCF₃ ligand and isolation of the

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mononuclear complex [Ag(dppf)(PMe₂Ph)₂](PF₆) (**4**) in 48% yield (Scheme 2).



Scheme 1



Scheme 2

Structural Studies

[Ag₂(μ-O₂CCF₃)₂(μ-dppf)] (**1**)

The solvate molecules 1·0.5C₄H₈O (**1A**) and 1·0.5CH₂Cl₂ (**1B**) are isostructural; two views of the molecular structure of **1A** are illustrated in Figure 1. The structure consists of a dinuclear Ag₂ core bridged by two trifluoroacetate groups and a dppf ligand, similar to the structure of [Ag₂(-O₂CR)₂(dppf)] (R = H, CH₃, Ph).^[4] The Ag...Ag distances [3.156(2) Å in **1A** and 3.2434(4) Å in **1B**] agree with reported non-bond distances of 3.104(1) Å in [Ag₂(-O₂CCH₃)₂(dppf)] and 3.346(4) Å in [Ag₂(-O₂CPh)₂(dppf)].^[4b] With three bridging ligands and no formal M–M bond, we can view this as two macrocycles hinged at the two Ag^I centers. A twofold axis passes through the mid-point of the Ag(1)···Ag(1A) axis and the Fe(2) atom of the dppf ligand in **1A**. Selected bond parameters (Table 1) show that the equivalent bond lengths of **1A** and **1B** are very similar, but their bond angles deviate significantly, viz. the O–Ag–O, O–Ag–Ag, O–Ag–P, P–Ag–Ag and O–C–O angles.

The crystal packing of **1A** and **1B** shows weak C–H···O and C–H···F hydrogen-bonding interactions, resulting in H···O distances of 2.62–2.63 Å in **1A** and 2.48–2.63 Å in

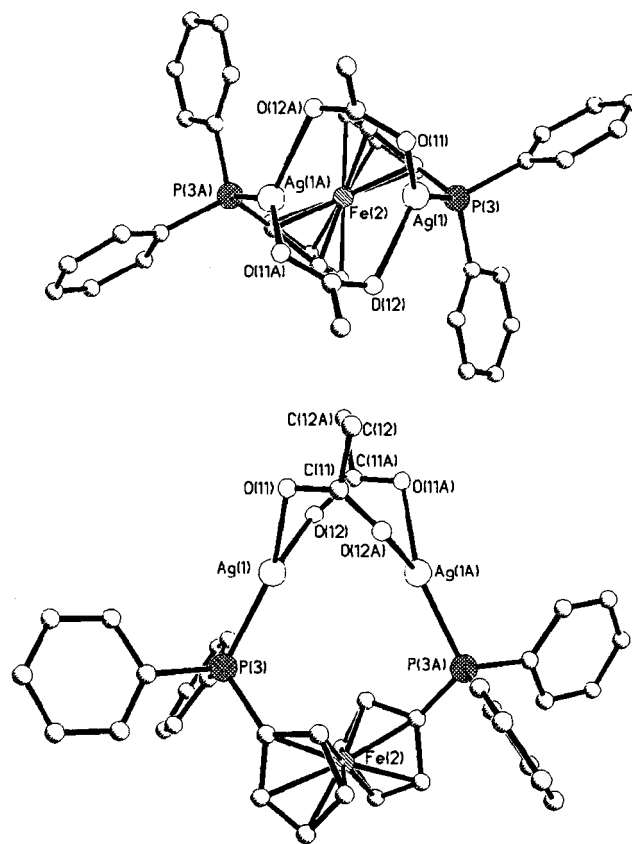
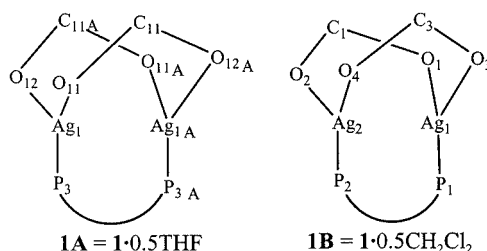


Figure 1. Two views of the molecular structure of [Ag₂(O₂CCF₃)₂(dppf)]·0.5THF (**1A**); hydrogen and fluorine atoms omitted for clarity

1B, H···F distances of 2.50–2.54 Å in **1A** and 2.37–2.69 Å in **1B** (Table 2). The H···O and C···O distances, and C–H–O angles, fall within the reported ranges, viz. 2.52–2.70 Å, 3.32–3.60 Å and 128–155°, respectively, found in a CpFe half-sandwich and related carbonyl complexes of first-row transition metals, reported by Desiraju and co-workers. Likewise, the H···F distances and C–H–F angles are found in the range reported for in C₆H_{6–x}F_x (x = 1–5), viz. 2.41–2.87 Å and 120–174°, respectively.^[5] Packing diagrams of the supramolecular networks in **1A** and **1B** viewed from the z and x axis, respectively, are illustrated in Figures 2 and 3. In **1A**, there is close packing of four molecules through two types of hydrogen bonds: C–H(Ph)···O and C–H(Cp)···F–C. The Figure shows four Ag₂ units clustering around a “central” region, which is effectively surrounded by four phenyl rings, one from each Ag₂ unit; molecules of THF are discernible in the lattice. In **1B**, the elementary prototype shows four molecular units connected by four types of H-bonds, viz. C–H(Cp)···O, C–H(Ph)···O, C–H(Cp)···F–C and C–H(Ph)···F–C. Figure 3 shows the relative orientation of three pairs of Ag₂ units; considering the dppf ligand as the “head” end of the unit and the bridging TFA ligands as the “tail” end, there is one pair pointing “head-to-head” towards each other such that their Cp rings come close to the two CH₂Cl₂ molecules in the central portion of the molecule, while the other

Table 1. Selected bond lengths [$\text{\AA}$] and bond angles [$^\circ$] for solvates of $\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})$ (**1**); symmetry transformations used to generate the "A" atoms: $x + 0$, $-y + 1.5$, $-z + 0.25$ Equivalent bond lengths [$\text{\AA}$] in the two molecules

	1A	1B		1A	1B
Ag1–P3/Ag1–P1	2.358(3)	2.3539(8)	Ag1–Ag1A/Ag1–Ag2	3.156(2)	3.2434(4)
Ag2–P2	–	2.3459(9)	Ag1–O11/Ag1–O1	2.248(9)	2.315(3)
Ag1–O12/Ag1–O3	2.407(11)	2.222(3)	Ag2–O2	–	2.309(4)
Ag2–O4	–	2.204(3)	C11–O11/C1–O1	1.219(16)	1.209(5)
C11A–O(12)/C1–O2	1.219(15)	1.221(6)	C11–O12A/C3–O3	1.219(15)	1.204(5)
C11–O11/C3–O4	1.219(15)	1.237(5)			

Equivalent bond angles [$^\circ$] in the two molecules

1A		1B	
O11–Ag1–O12	87.6(4)	O4–Ag2–O2	98.99(18)
O11–Ag1–P3	146.7(3)	O4–Ag2–P2	138.43(12)
P3–Ag1–O12	124.4(3)	P2–Ag2–O2	121.11(12)
O11–Ag1–Ag1A	83.2(2)	O4–Ag2–Ag1	76.29(9)
P3–Ag1–Ag1A	116.33(8)	P2–Ag2–Ag1	123.19(2)
O12–Ag1–Ag1A	65.9(3)	O2–Ag2–Ag1	72.86(9)
O11–C11–O12A	129.9(14)	O4–C3–O3	131.1(4)
O11A–C11A–O12	113.0(10)	O1–C1–O2	129.6(4)

two pairs orientate tail-to-tail towards each other, such that their CF_3 groups radiate towards the CH_2Cl_2 molecules. Adjacent molecules are linked into a 2D layer network by H-bonding ($\text{C}-\text{H}\cdots\text{F}$ and $\text{C}-\text{H}\cdots\text{O}$), and these layers are linked into a 3D network through interlayer H-bond interactions.

The different crystal packing encountered in these two solvates of **1** must be associated with their different bond parameters, as well as the presence and location of the solvent molecules in the crystal lattice, factors that influence the nature and strength of hydrogen bonds supporting the network.

Table 2. Hydrogen bond lengths [$\text{\AA}$] and bond angles [$^\circ$] for **1A** and **1B**

D–H	D–H [$\text{\AA}$]	A	H $\cdots$ A [$\text{\AA}$]	D–A [$\text{\AA}$]	$\angle\text{DHA}$	Symmetry
1A:						
C326–H326	0.94	O11	2.63	3.441(19)	146	$1 - y, x, -z$
C315–H315	0.94	O12	2.62	3.399(19)	141	$1 - y, x, -z$
C2–H2	0.93	F11	2.54	3.094(24)	119	$1 - y, x, -z$
C2–H2	0.93	F13	2.50	3.251(6)	138	$1 - y, x, -z$
1B:						
C4A–H4A	0.94	F1	2.61	3.344(6)	136	$2 - x, 1 - y, 2 - z$
C3C–H3C	0.94	F1	2.69	3.420(8)	135	$x - 1, y, z$
C13–H13	0.99	F3	2.68	3.250(5)	117	$2 - x, y - 0.5, 1.5 - z$
C11–H11	0.99	F4	2.48	3.079(7)	119	$x, 1.5 - y, -0.5 + z$
C11–H11	0.99	F4A	2.67	3.182(10)	113	$x, 1.5 - y, -0.5 + z$
C12–H12	0.99	F5A	2.37	3.071(11)	127	$1 - x, y - 0.5, 1.5 - z$
C6C–H6C	0.94	F6A	2.64	3.225(15)	121	$x, 1.5 - y, -0.5 + z$
C3D–H3D	0.94	O1	2.54	3.205(6)	128	$x, 1.5 - y, -0.5 + z$
C3B–H3B	0.94	O2	2.63	3.403(6)	139	$2 - x, y - 0.5, 1.5 - z$
C7–H7	0.99	O4	2.48	3.468(6)	178	$1 - x, y - 0.5, 1.5 - z$

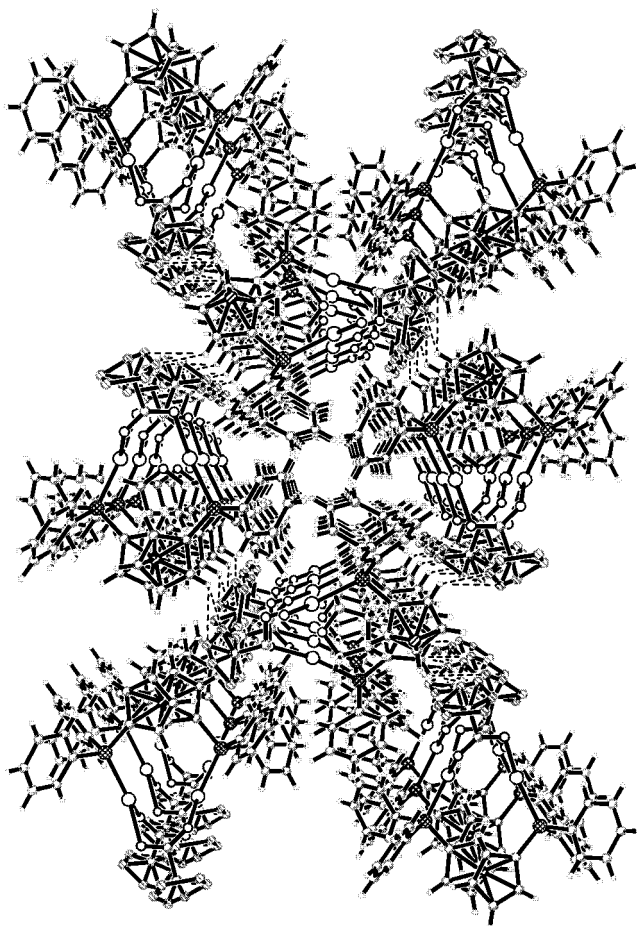


Figure 2. Packing diagram of the supramolecular network in **1A** viewed from the *z* axis, showing C–H(Ph)⋯O and C–H(Cp)⋯F–C hydrogen bonds; the four THF molecules in each layer are visible

[Ag₂(O₂CCF₃)₂(dppf)₂] (**2**)

[Ag₂(O₂CCF₃)₂(dppf)₂] (**2**) (Figure 4) contains two three-coordinate silver atoms doubly bridged by two dppf ligands; being η¹-coordinated to an oxygen atom of trifluoroacetate anions, each Ag atom achieves a 16e configuration. Selected bond parameters of **2** are given in Table 3. Similar structures have been reported for [Ag₂(NO₃)₂(dpm)₂] and [Ag₂(dpm)₂(O₂CCH₂Ph)₂] (dpm = Ph₂PCH₂PPh₂) with monodentate nitrate and carboxylate ligands, respectively,^[6a,6b] which possess Ag⋯Ag distances of 3.085(1) and 3.080(1) Å, respectively; however, there is no metal–metal interaction in **2** (Ag⋯Ag = 3.781 Å), as with Ag₂(NO₃)₂(dppf)₂ [Ag⋯Ag = 3.936(2) Å].^[4b] The Ag–P distances are also very close to those reported for Ag₂(NO₃)₂(dppf)₂.^[4b] Except for a H-bond between the CHCl₃ solvent molecule and an oxygen atom of TFA, viz. C1–H1S(CHCl₃)⋯O2 (2.12 Å), there are no secondary bonding interactions of the types observed in **1A**, **1B** and **3**.

The structures of **1** and **2** illustrate a preference of the 16e Ag^I center in these dinuclear species for a trigonal-planar configuration, with the diphosphane adopting a bridging coordination mode, while the weakly coordinating car-

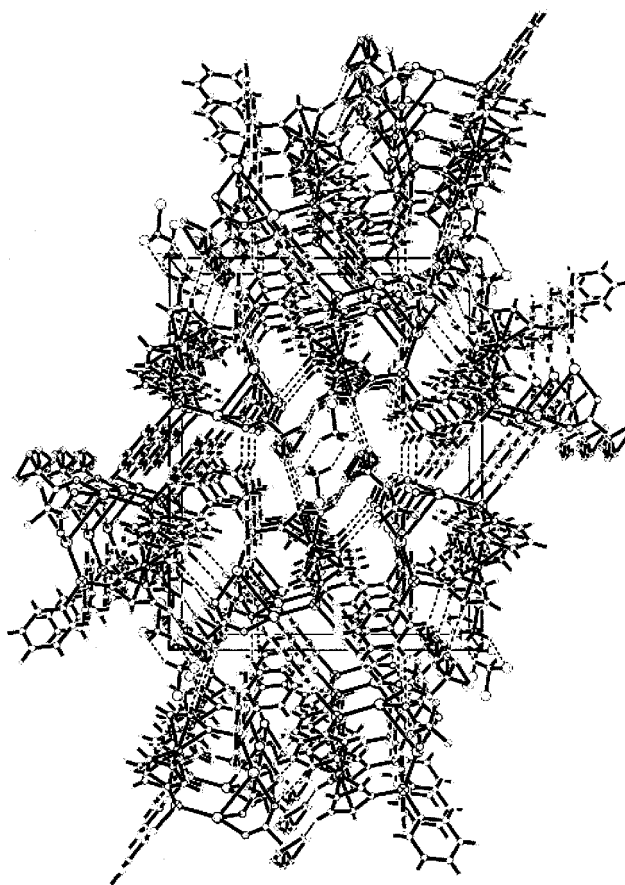


Figure 3. Packing diagram of the supramolecular network in [Ag₂(O₂CCF₃)₂(dppf)]·0.5CH₂Cl₂ (**1B**) viewed from the *x* axis; four types of H-bonds are illustrated: C–H(Cp)⋯O, C–H(Ph)⋯O, C–H(Cp)⋯F–C and C–H(Ph)⋯F–C

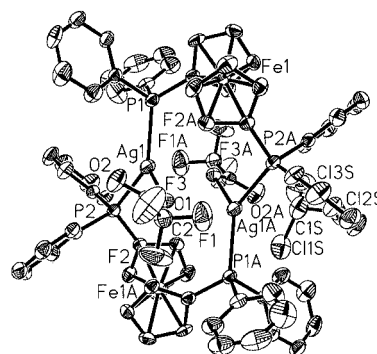


Figure 4. Molecular structure of **2**; hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability

boxylate group adapts as a bridging or monodentate ligand, forming an [Ag₂(dppf)₂] ring structure in the latter situation, as was found in Ag₂(NO₃)₂(dpm)₂ and [Ag₂(dpm)₂-(O₂CCH₂Ph)₂].^[6a,6b]

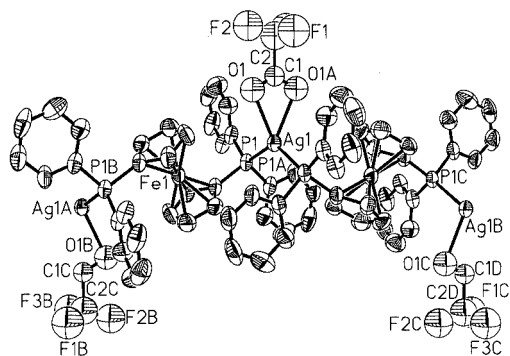
[Ag(O₂CCF₃)(dppf)]_n (**3**)

The structure of **3** consists of a polymeric chain made up of repeating units of [–PAg(η¹-O₂CCF₃)P–]_n where P–P = dppf (Figure 5). Each silver atom is four-coordi-

Table 3. Selected bond lengths [Å] and bond angles [°] for **2**

Ag1–O1	2.471(4)	Ag1–P2	2.4775(15)
Ag1–P1	2.4776(15)	C1–O1	1.239(7)
C1–O2	1.226(7)		
O1–Ag1–P2	103.23(9)	O1–Ag1–P1	117.42(9)
P2–Ag1–P1	136.45(5)	C11–P1–Ag1	121.82(18)
C111–P1–Ag1	114.31(18)	C121–P1–Ag1	110.66(19)
C1–O1–Ag1	119.3(4)	O2–C1–O1	127.0(6)
O2–C1–C2	116.3(5)	O1–C1–C2	116.7(5)

nate, being bonded to a chelating trifluoroacetate ligand and two phosphorus atoms of two different dppf ligands, thus forming a one-dimensional infinite chain, which is further reinforced by intra-chain hydrogen-bond interactions [C–H(Cp)···O 2.47 Å, 155°]. A plane of symmetry passes through the Ag atom and bisects the AgOCO ring. Notably, the chelating mode of the carboxylate ligand in Ag^I complexes is rarely encountered,^[7] in contrast to the commonly reported monodentate and μ -bridging modes.^[8] Selected bond parameters and hydrogen bond parameters are given in Table 4. The Ag–P distance [Ag(1)–P(1) 2.4270(16) Å] is intermediate between those encountered in the other Ag(dppf) complexes in this study (2.34–2.57 Å). The Ag(1)–O(1) bond is longer [2.527(7) Å] than those in **1A** and **1B** (2.21, 2.31 Å), in which TFA bridges two Ag atoms, and in **2** (2.47 Å), in which TFA is monodentate. While no inter-chain hydrogen-bonding interactions are found between adjacent polymeric chains viewed from the *x* axis, they do exist between adjacent chains viewed from the *y* axis (Table 5 and packing diagram in Figure 6).

Figure 5. Section of the polymeric chain of **3**; hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probabilityTable 4. Selected bond lengths [Å] and bond angles [°] for complex **3**; symmetry transformations used to generate the “A” atoms: $-x, y, -z + 0.5$

Ag1–P1	2.4267(17)	Ag1–O1	2.518(8)	Ag1–P1A	2.4267(17)
Ag1–O1A	2.518(8)	C1–O1	1.190(9)	C1–C2	1.67(3)
C1–O1A	1.190(9)				
P1–Ag1–P1A	129.58(9)	P1–Ag1–O1A	115.47(18)	P1A–Ag1–O1A	110.07(18)
P1–Ag1–O1	110.07(18)	P1A–Ag1–O1	115.47(18)	O1A–Ag1–O1	49.6(3)
C1–O1–Ag1	92.6(8)	O1–C1–C2	117.4(7)	O1–C1–O1A	125.2(14)

In the above complexes the participation of weak hydrogen bonding between C–H(Cp/Ph) bonds to O and/or F–C of coordinated ligands stabilizes supramolecular structures, the nature of which is further influenced by the presence of solvent molecules in the crystal lattice, as in **1A** and **1B**. The role of such weak hydrogen-bonding interactions in such phenomena has been reported frequently in recent years in organic systems^[5,9] and coordination compounds^[2g,10–12] though less frequently in organometallic complexes,^[12–15] e.g. in the bonding of C–H(arene) to O(carbonyl) in a chromium complex,^[12] of C–H(arene) to F of the anions, BF₄[–] [13] or PF₆[–] [16] and of C–F of C₆F₅ to O(carbonyl) in complexes of Fe, Co, Mn and Re.^[15]

[Ag(PMe₂Ph)₂(dppf)]PF₆ (**4**)

This molecule possesses a mononuclear structure in which the silver atom assumes a distorted tetrahedral geometry with coordination to a chelating dppf and two monodentate dimethyl(phenyl)phosphane ligands (Figure 7). Selected bond parameters are given in Table 6. The bite angle of the dppf ligand, P(1)–Ag(1)–P(2) 105.96(4)°, is similar to that in [Ag(dppf)₂]ClO₄ [105.71(4)°]; the other angles at Ag [P(3)–Ag(1)–P(4) 105.87(5)°, P(3)–Ag(1)–P(1) 113.80(4)°, P(4)–Ag(1)–P(2) 107.58(4)°] show small deviations from those in [Ag(dppf)₂]ClO₄ [98.39(4)°, 113.15(4)°, 114.54(4)°].^[17]

Spectral Characteristics

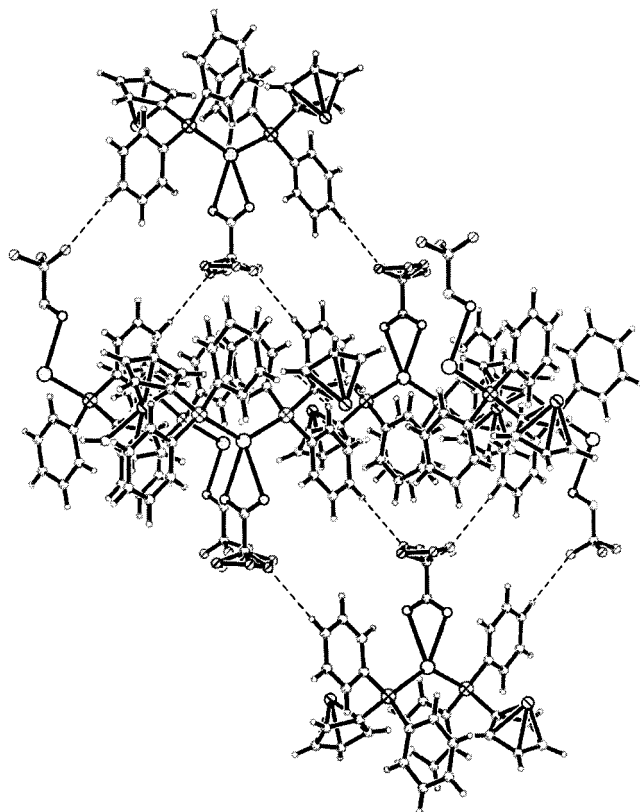
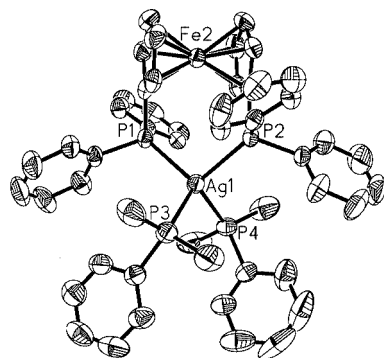
VT-¹H NMR Spectral Features

At 328 K the ¹H NMR spectrum of **1** in CDCl₃ shows two singlets at δ = 3.96 and 4.45 ppm for the α - and β -protons of the Cp rings of dppf and a multiplet at δ = 7.39–7.54 ppm (unresolved δ = 7.39, 7.41, 7.44, 7.47, 7.50, 7.52 and 7.54 ppm) for the Ph protons of dppf. These features vary little upon lowering the temperature to 243 K – there is mainly a loss of resolution in the Ph multiplet and slight broadening of the β -CpH signal (δ = 4.39 ppm) with concurrent greater broadening of the α -CpH signal (δ = 3.85 ppm); below 243 K both α and β signals undergo extensive broadening.

The ¹H NMR spectrum of **2** in (CD₃)₂CO at 300 K and above shows only one peak, at δ = 4.44 ppm, for the Cp protons of dppf and two multiples, δ = 7.45–7.50 and 7.68–7.70 ppm, for the Ph protons of dppf. Below 273 K, the Cp singlet transforms into a broad unresolved multiplet,

Table 5. Hydrogen-bond lengths [Å] and bond angles [°] for **3**

D–H	D–H [Å]	A	H⋯A [Å]	D–A [Å]	∠DHA [°]	Symmetry
C4A–H4A	0.94	F2	2.63	3.479(19)	149	0.5 – x, 0.5 – y, 1 – z
C5–H5	0.94	O1	2.47	3.351(10)	155	–x, 1 – y, 1 – z

Figure 6. Packing diagram of **3** viewed from the *y* axis, showing two layers in the central chain, and inter-chain [C–H(Ph)⋯F–C] hydrogen-bonding interactionsFigure 7. Molecular structure of cationic **4**; hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability

which at 223 K, is centered at $\delta = 4.50$ ppm, while the multiplicity of the phenyl protons is also drastically changed.

In CDCl_3 at 300 K, the Ph protons of **3** are seen as a broad peak at $\delta = 7.52$ ppm and a multiplet centered at

Table 6. Selected bond lengths [Å] and bond angles [°] for complex **4**

Ag(1)–P(1)	2.5474(12)	Ag(1)–P(2)	2.5700(12)
Ag(1)–P(3)	2.5371(13)	Ag(1)–P(4)	2.5212(13)
P(1)–C(101)	1.08(5)	P(2)–C(201)	1.808(5)
P(3)–C(301)	1.820(5)	P(4)–C(401)	1.816(5)
P(3)–C(31)	1.821(5)	P(3)–C(32)	1.829(5)
P(4)–C(41)	1.812(5)	P(4)–C(42)	1.817(6)
P(1)–Ag(1)–P(2)	105.96(4)	P(3)–Ag(1)–P(4)	105.87(5)
P(4)–Ag(1)–P(1)	112.47(4)	P(3)–Ag(1)–P(1)	113.80(4)
P(4)–Ag(1)–P(2)	107.5(4)	P(3)–Ag(1)–P(2)	111.07(4)

$\delta = 7.37$ ppm, and the Cp signals as two broad singlets at $\delta = 4.34$ and 4.25 ppm; at lower temperatures these were transformed into several unassignable broad peaks at $\delta = 2.5$ –6.3 ppm.

VT- ^{19}F NMR Spectral Features

The sharp ^{19}F signal of **1** in CDCl_3 varies slightly, from $\delta = 1.6$ ppm at 300 K to $\delta = 1.7$ ppm at 223 K, while that of complex **2** in $(\text{CD}_3)_2\text{CO}$ undergoes a greater downfield shift, from $\delta = 2.4$ ppm at 323 K to $\delta = 2.7$ ppm at 223 K, with increasing line-width broadening. Below this, the peak transformed into two broad overlapping peaks, which at 183 K are seen at $\delta = 3.1$ and 2.8 ppm (relative intensity ca. 1:2); these overlapping peaks indicate the presence of trifluoroacetate ligands in different coordination environments, most probably caused by different denticities of the ligands. This is accompanied by complex variations in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

The VT- ^{19}F NMR spectrum of **3** in CDCl_3 shows only one sharp peak ($\delta = 1.2$ ppm) in the range 300–223 K, while at 213 K a minor peak (ca. 10%) emerges at $\delta = 1.7$ ppm, indicating two types of coordinated trifluoroacetate ligands, as in **2** above.

VT- $^{31}\text{P}\{^1\text{H}\}$ NMR Spectral Features

The variations of **1** in CDCl_3 are shown in Figure 8. A broad peak at $\delta = 6.6$ ppm ($\nu_{1/2} = 405$ Hz) at 328 K broadens further at 313 K ($\delta = 6.5$ ppm, $\nu_{1/2} = 607$ Hz). At 296 K, three overlapping broad peaks appear at $\delta = 10.1$, 7.4 and 4.2 ppm ($\nu_{1/2} = 146$, 255 and 146 Hz, with relative intensity ca. 1:2:1); these gradually transform into two pairs of sharp doublets at 223 K, being centered at $\delta = 7.6$ ppm ($J^{107/109}\text{Ag–P} = 695$ and 805 Hz), indicative of coordination of one P atom to an Ag atom,^[18] which is in agreement with its solid-state structure. These VT features can be rationalized in terms of $^{31}\text{P}–^{107}\text{Ag}/^{109}\text{Ag}$ inter- and intramolecular exchange processes first observed by Dean

and co-workers in dinuclear Ag complexes containing bridging diphosphanes.^[19]

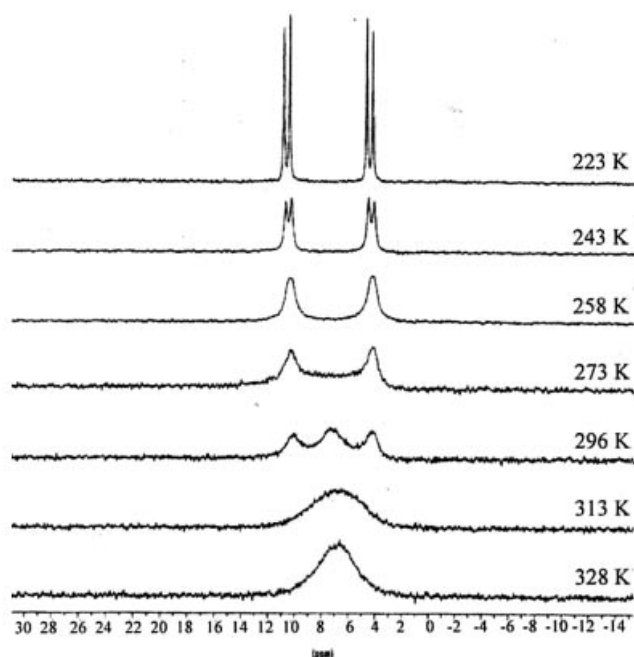


Figure 8. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** in CDCl_3

^{31}P NMR spectra in $(\text{CD}_3)_2\text{CO}$ of **2** show a very broad peak at $\delta = -1.2$ ppm ($\nu_{1/2} \approx 300$ Hz) at 300 K. As the temperature is lowered to 183 K, a combination of broad bands and $^{107/109}\text{Ag}$ -coupled doublets appear. With **3**, a decrease of temperature causes the broad ambient-temperature signal [$\delta = -1.5$ ppm ($\nu_{1/2} = 600$ Hz)] to transform into a very complex pattern, consisting of several broad “humps”, which can not be rationalized. The only distinctive feature is a doublet at $\delta = -3.45$ ppm, which is observable at 223 K and below with $J^{107/109}\text{Ag-P}$ couplings of 418 and 482 Hz, indicative of coordination of two P atoms per Ag atom, which is consistent with its solid-state linear polymeric structure.

Mass Spectra

FAB⁺-MS spectra of **1A/1B** and **2** do not show the parent ion fragment [M^+], but fragments arising from the consecutive loss of an O_2CCF_3 ligand and an $\text{Ag}(\text{O}_2\text{CCF}_3)$ moiety, leading to $m/z = 661$ [$\text{Ag} + \text{dppf}$] as the most intense fragment. The FAB⁺-MS spectrum of **3** is identical to that of **2**. The highest mass fragment in the ESI⁺-MS spectrum of **4** arises from the addition of 1 equiv. of PMe_2Ph to the parent ion at $m/z = 1216$ [$\text{M}^+ + \text{PMe}_2\text{Ph}$], followed by fragments showing consecutive losses of PMe_2Ph to yield $m/z = 661$ as the strongest peak. The FAB⁺-MS spectrum of **5** only shows the most intense peak at $m/z = 662$.

Infrared Spectra

IR spectra of **1A/1B** show the bridging O_2CCF_3 vibration frequencies at $\tilde{\nu} = 1684$ (asymm.), 1437 (symm.), 1207 and 1133, with $\Delta\tilde{\nu}(\text{asymm.} - \text{symm.}) = 247 \text{ cm}^{-1}$ – outside the

range ($88\text{--}200 \text{ cm}^{-1}$) reported for bridging trifluoroacetate complexes.^[20] The $\Delta\tilde{\nu}(\text{asymm.} - \text{symm.}) = 231 \text{ cm}^{-1}$ of **2** for monodentate trifluoroacetates is similar to 232 cm^{-1} in $\text{PhHg}(\text{O}_2\text{CMe})$ containing monodentate carboxylate groups.^[20] The IR stretching frequencies of **3** are close to those of **2**, with a $\Delta\tilde{\nu}(\text{asymm.} - \text{symm.})$ of 227 cm^{-1} , very close to that in **2**, even though, unlike **2**, its acetate ligand is in a chelating mode. Notably, $\Delta\tilde{\nu}(\text{asymm.} - \text{symm.})$ for the trifluoroacetate ligand in **3** far exceeds those of most chelating acetate ligands ($65\text{--}175 \text{ cm}^{-1}$), except for those of $\text{Sn}(\text{O}_2\text{CMe})_4$ ($320, 440 \text{ cm}^{-1}$).^[20] C–H stretches of the Cp and Ph rings of dppf in **2** are observed as two weak unresolved peaks at $\tilde{\nu} = 3077$ and 3058 cm^{-1} , while **1A/1B** and **3** also show two C–H stretches in the same frequency range, but in addition exhibit three other very weak peaks between $\tilde{\nu} = 2960$ and 2853 cm^{-1} . Presumably, these lower-frequency stretches pertain to C–H hydrogen-bonded to O or F of TFA, as shown in their crystal structures.

Conclusion

Facile interactions between silver trifluoroacetate and dppf afford a coordination polymer or dinuclear species possessing TFA in different bonding modes, depending on the stoichiometry of the reactants. Weak hydrogen-bonding interactions ($\text{C-H}\cdots\text{F}$ and $\text{C-H}\cdots\text{O}$) in the dinuclear compounds yield 2D supramolecular structures, the nature of which varies with solvent molecules in the crystal lattice.

Experimental Section

General: $\text{Ag}(\text{O}_2\text{CCF}_3)$, PMe_2Ph and NH_4PF_6 were purchased from Aldrich, and dppf from STREM, and used as supplied. All reactions were performed under dry nitrogen using Schlenk techniques. Solvents were freshly distilled from standard drying agents. NMR spectra were recorded with a Bruker ACF300 FT NMR spectrometer (^1H at 300.13 MHz; $^{31}\text{P}\{^1\text{H}\}$ at 121.50 MHz and ^{19}F at 282.38 MHz), with chemical shifts referenced to residual non-deuterated solvent, external H_3PO_4 and external CF_3COOH , respectively. Infrared spectra were measured in KBr pellets in the range of $400\text{--}4000 \text{ cm}^{-1}$ with a Perkin-Elmer 1600 FT-IR spectrometer. FAB and ESI mass spectra were obtained with Finnigan MAT95XL-T and MATLCQ spectrometers, respectively. All elemental analyses were carried out in-house.

Syntheses

Reactions of $\text{Ag}(\text{O}_2\text{CCF}_3)$ with dppf. Using Ag^+/dppf (2:1) in THF/MeOH. Synthesis of $[\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})]$ (1**):** Ligand dppf (0.111 g, 0.20 mmol) in THF (10 mL) was added to a solution of $\text{Ag}(\text{O}_2\text{CCF}_3)$ (0.094 g, 0.43 mmol) in MeOH (10 mL) and the resultant solution stirred for 8 h. The so-obtained orange suspension was filtered through Celite, and the orange filtrate was concentrated to ca. 2 mL. Addition of diethyl ether (5 mL) and cooling at $0\text{--}5^\circ\text{C}$ for 3 h gave yellow air-stable, non-light-sensitive crystals of a THF solvate of $[\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})]$ (**1**) (0.073 g, 0.07 mmol, 34%). $\text{C}_{38}\text{H}_{28}\text{Ag}_2\text{F}_6\text{O}_4\text{P}_2 \cdot 0.6\text{C}_4\text{H}_8\text{O}$ (1039.4): calcd. C 46.6, H 3.2, P 6.0; found C 45.9, H 2.7, P 6.0. ^1H NMR (CDCl_3 , 300 K): $\delta = 7.39\text{--}7.55$ (m, 20 H, Ph), 4.44 and 3.92 (each s, 4 H, C_5H_4)

ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 10.1, 7.4$ and 4.2 ppm ($\nu_{1/2} = 146, 255$ and 146 Hz, with relative intensity ca. 1:2:1). ^{19}F NMR: $\delta = 1.6$ ppm. FAB⁺-MS: $m/z = 883$ [$\text{M} - \text{O}_2\text{CCF}_3$]⁺, 661 [$\text{M} - \text{Ag} - 2(\text{O}_2\text{CCF}_3)$]⁺, 1437 [$\text{M} + \text{dppf}$]⁺. IR (KBr cm^{-1}): ν_{CO_2} : $1684, 1437, 1207, 1133$; ν_{others} : 3071 w, 3050 w, 2960 vwbr, 2923 vw, 2852 vwbr, 1508 w, 1021 m, 838 m, 803 s, 724 vs, 696 s, 518 w, 456 w. Concentration of the mother liquor to dryness, redissolution in CH_2Cl_2 , followed by addition of diethyl ether (3 mL) then gave an orange solid of **1**· $0.5\text{CH}_2\text{Cl}_2$ (0.065 g, 30% yield). $\text{C}_{38}\text{H}_{28}\text{Ag}_2\text{F}_6\text{FeO}_4\text{P}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (1038.6): calcd. C 44.5, H 2.8; found C 44.8, H 2.9. ^1H NMR (CDCl_3): As above with additional $\delta = 5.30$ ppm (CH_2Cl_2). ^{19}F NMR: As above. $^{31}\text{P}\{^1\text{H}\}$ NMR: With slight variations: $\delta = 10.4, 7.4, 4.3$ ppm ($\nu_{1/2} = 54, 121$ and 54 Hz, relative intensity 1:2:1). A similar reaction of $\text{Ag}(\text{O}_2\text{CCF}_3)$ (0.404 g, 1.83 mmol) and dppf (0.507 g, 0.92 mmol) in CH_2Cl_2 (20 mL) for 6 h furnished a yellow solid of **1**· CH_2Cl_2 (0.811 g, 90%). Crystallization of **1** in THF/MeOH and CH_2Cl_2 /diethyl ether gave orange diffraction-quality crystals of **1**· $0.5\text{THF} \equiv \text{1A}$ and **1**· $0.5\text{CH}_2\text{Cl}_2 \equiv \text{1B}$, respectively, after 1 d at ambient temperature.

Using Ag^+/dppf (1:1) in CH_2Cl_2 . Synthesis of $[\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})_2]$ (2**):** Ligand dppf (1.014 g, 1.83 mmol) was added to a suspension of $\text{Ag}(\text{O}_2\text{CCF}_3)$ (0.404 g, 1.83 mmol) in CH_2Cl_2 (15 mL) and the mixture stirred at room temperature for 3 h. The resultant orange homogeneous solution was concentrated to ca. 2 mL; the subsequent addition of hexane (2 mL) gave yellow solids of $[\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})_2]$ (**2**)· $0.25\text{CH}_2\text{Cl}_2$ (1.23 g, 86%). $\text{C}_{72}\text{H}_{56}\text{Ag}_2\text{F}_6\text{Fe}_2\text{O}_4\text{P}_4 \cdot 0.25\text{CH}_2\text{Cl}_2$ (1571.8): calcd. C 55.2, H 3.6; found C 55.2, H 3.95. ^1H NMR [$(\text{CD}_3)_2\text{CO}$, 300 K]: $\delta = 7.69, 7.48$ (each centered m, 8-H and 12-H, respectively, Ph), 4.44 (s, 8 H, C_5H_4) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = -1.2$ ppm ($\nu_{1/2} \approx 300$ Hz). ^{19}F NMR: $\delta = 2.4$ ppm. ^1H NMR (CDCl_3 , 300 K): $\delta = 7.41, 7.33$ (each centered m, 12-H and 8-H, respectively, Ph), 4.51 and 4.05 (each s, 4 H, C_5H_4) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = -1.0$ ppm ($\nu_{1/2} \approx 300$ Hz). ^{19}F NMR: $\delta = -0.1$ ppm. FAB⁺-MS: $m/z = 1437$ [$\text{M} - \text{O}_2\text{CCF}_3$]⁺, 1216 [$\text{M} - \text{Ag} - 2(\text{O}_2\text{CCF}_3)$]⁺, 661 [$\text{M} - \text{Ag} - 2(\text{O}_2\text{CCF}_3) - \text{dppf}$]⁺. IR (KBr, cm^{-1}): ν_{CO_2} : 1664 s, 1433 m, 1199 s, 1131 s; ν_{others} : 3077 wsh, 3058 wbr, 1480 w, 1313 vw, 1175 ssh, 1031 w, 837 m, 764 m, 697 s, 484 mbr. Diffraction-quality single crystals of **2** were obtained from a solution in CHCl_3 layered with hexane after 1 d at room temperature.

Reactions of $[\text{Ag}_2(\text{O}_2\text{CCF}_3)_2(\text{dppf})]$ (1**). Reaction with dppf. Synthesis of $[\text{Ag}(\text{O}_2\text{CCF}_3)(\text{dppf})]_n$ (**3**):** Ligand dppf (0.03 mL, 0.05 mmol) was added to a solution of **1** (0.050 g, 0.05 mmol) in CH_2Cl_2 (15 mL) and the mixture stirred for 3.5 h. The homogeneous product solution was then concentrated to ca. 1 mL, followed by addition of hexane (1.5 mL), whereupon an orange solid of $[\text{Ag}(\text{O}_2\text{CCF}_3)(\text{dppf})]_n$ (**3**) (0.034 g, 88%) separated. $\text{C}_{72}\text{H}_{56}\text{Ag}_2\text{F}_6\text{Fe}_2\text{O}_4\text{P}_4$ (1550.6): calcd. C 55.8, H 3.6; found C 55.2, H 3.95. ^1H NMR (CDCl_3 , 300 K): $\delta = 7.52$ ($\nu_{1/2} \approx 20$ Hz, 8 H, Ph), 7.37 (centered m, 12 H, Ph), 4.34 and 4.25 (each s, $\nu_{1/2} \approx 15$ Hz, 4 H, C_5H_4) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = -1.5$ ppm with sh at -3.0 (combined $\nu_{1/2} \approx 600$ Hz). ^{19}F NMR: $\delta = 1.2$ ppm. FAB⁺-MS: As in **2**. IR (KBr, cm^{-1}): ν_{CO_2} : 1662 s, 1435 m, 1200 vs, 1133 s; ν_{others} : 3081 wsh, 3051 w, 2960 w, 2923 w, 2863 vw, 1480 w, 1098 m, 1031 w, 836 w, 798 vw, 745 m, 722 vw, 696 s, 513 ssh, 487 sbr. Diffraction-quality crystals were obtained from CH_2Cl_2 , layered with hexane, after 1 d at ambient temperature. The reaction was also monitored in an NMR tube in CDCl_3 at intervals up to 5.5 h. After 15 min, the proton spectrum showed two broad overlapping Cp signals centered at $\delta = 4.35$ and 4.22 ppm, with a combined halfwidth of ca. 75 Hz. These sharpened with time and after 3.5 h were at $\delta = 4.34$ and 4.25 ppm; these then remained unchanged up

to 5 h. The ^{31}P signals varied from $\delta = -1.4$ to -1.0 ppm (ca. 400 Hz), while the F signals were seen as overlapping singlets of equal intensity at $\delta = 1.3$ and 0.9 ppm. These resonances did not appear in the region of those in the spectrum of **2**.

Reaction with PMe_2Ph : Ligand PMe_2Ph (0.04 mL, 0.26 mmol) was added to a solution of **1** (0.05 g, 0.05 mmol) in MeOH (15 mL). After stirring for 1 h, NH_4PF_6 (0.035 g, 0.21 mmol) was added. A bright yellow precipitate then began to separate, and the mixture was stirred for a further 30 min. The precipitate was filtered off and recrystallized from CH_2Cl_2 /diethyl ether to give air-stable, non-light-sensitive yellow crystals of $[\text{Ag}(\text{dppf})(\text{PMe}_2\text{Ph})_2]\text{PF}_6$ (**4**) (25.8 mg, 48%). $\text{C}_{50}\text{H}_{50}\text{AgF}_6\text{FeP}_5 \cdot \text{H}_2\text{O}$ (1101.6): calcd. C 54.5, H 4.8; found C 54.2, H 4.8. ^1H NMR (CDCl_3): $\delta = 7.60$ – 7.81 (Ph), $4.68, 4.56, 4.03$ (C_5H_4), 1.82 (d, $J = 13$ Hz, PMe_2Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 39.8$ and 3.9 (dppf), -5.5 (PMe_2Ph), -144 (sept) ppm. ESI⁺-MS: $m/z = 1216$ [$\text{M} + \text{PMe}_2\text{Ph}$]⁺, 798 [$\text{M} - \text{PMe}_2\text{Ph}$]⁺, 661 [$\text{M} - 2 \text{PMe}_2\text{Ph}$]⁺. IR (Nujol, cm^{-1}): ν_{PF_6} : 840 and 556 . Single diffraction-quality crystals were obtained by recrystallization in MeOH/diethyl ether (1:4) after 1 d at -30°C .

Variable-Temperature (VT) NMR Spectra: ^1H , $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F VT NMR spectra obtained for complexes **1**–**3** are described in the Results and Discussion section.

Crystal Structure Determinations: Crystals were mounted on quartz fibers. X-ray data were collected with a Bruker AXS SMART CCD diffractometer, using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 223 K (for **1**–**3**) or 293 K (for **4**) (Table 7). The program SMART^[21] was used to collect the intensity data, indexing and determination of lattice parameters, SAINT^[22] was used to integrate the intensity of reflections and scaling, SADABS^[21] was used for absorption correction and SHELXTL^[23] for space group and structure determination and least-squares refinements against F^2 . The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Cp and Ph hydrogen atoms were placed in calculated positions. For **1A**, the crystal was modeled as a racemic twin. The CF_3 groups were treated as disordered over two alternative sites with equal occupancies; the two sites were symmetry-related. C–F and F...F distances were restrained to be equal, and the F atoms were given individual isotropic thermal parameters. There was a half molecule of THF disordered about a twofold axis. This was modeled over two alternative sites of equal occupancies with the oxygen and two carbon atoms common; all the carbon atoms were given a common isotropic thermal parameter, with that for the oxygen at 1.1 times that of the carbon atoms. Appropriate restraints were placed to keep the geometry reasonable. For **2**, the CHCl_3 solvent molecule was modeled as disordered over two sites; occupancies were refined and summed to unity. C–Cl and Cl...Cl distances were restrained to be equal. Anisotropic thermal parameters for each Cl atom were paired with that of the alternative site. For **3**, the CF_3 groups were treated as disordered over two alternative sites with equal occupancies; the two sites were symmetry-related. C–F and F...F distances were restrained to be equal, and atoms were given isotropic thermal parameters. Crystal data and refinement parameters are given in Table 7. Selected bond lengths and angles for **1A**/**1B**, **2**, **3** and **4** are in Tables 1, 3, 4 and 6, respectively. Hydrogen bonds and angles of **1A**/**1B** and **3** are in Tables 2 and 5, respectively. CCDC-193074 to -193076 and -215390 to -215391 for complexes **1B**, **3**, **1A**, **2** and **4**, respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam-

Table 7. Crystal data and parameters related to the structure determination and refinement for **1–4**

	1A (1·0.5C ₄ H ₈ O)	1B (1·0.5CH ₂ Cl ₂)	2 ·CHCl ₃	3	4
Empirical formula	C ₄₀ H ₃₂ Ag ₂ F ₆ FeO _{4.50} P ₂	C _{38.5} H ₂₉ Ag ₂ ClF ₆ FeO ₄ P ₂	C ₃₇ H ₂₉ AgCl ₃ F ₃ FeO ₂ P ₂	C ₃₆ H ₂₈ AgF ₃ FeO ₂ P ₂	C ₅₀ H ₅₀ AgF ₆ FeP ₅
Formula mass	1032.19	1038.60	894.61	775.24	1083.47
Temperature [K]	223(2)	223(2)	223(2)	223(2)	293(2)
Crystal system	tetragonal	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>I</i> -42 <i>d</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Crystal size [mm]	0.32 × 0.22 × 0.16	0.40 × 0.40 × 0.38	0.22 × 0.08 × 0.04	0.30 × 0.25 × 0.15	0.30 × 0.16 × 0.09
<i>a</i> [Å]	28.3502(5)	10.2862(6)	12.1521(11)	12.790(2)	14.2739(2)
<i>b</i> [Å]	28.3502(5)	17.6488(9)	13.1192(12)	24.101(4)	20.9706(2)
<i>c</i> [Å]	10.6842(2)	22.0971(12)	13.7594(12)	16.495(3)	17.0519(2)
α [°]	90	90	118.007(2)	90	90
β [°]	90	90.6710(10)	103.871(2)	110.304(4)	106.9810(10)
γ [°]	90	90	95.312(2)	90	90
<i>V</i> [Å ³]	8587.3(3)	4011.2(4)	1825.6(3)	4768.7(15)	4881.65(10)
<i>Z</i>	8	4	2	4	4
<i>D</i> _{calcd.} [Mg·m ⁻³]	1.597	1.720	1.627	1.080	1.474
Absorption coefficient	1.376	1.536	1.289	0.817	0.919
<i>F</i> (000)	4096	2052	896	1560	2208
Θ range for data collection [°]	2.03–24.71	1.84–25.00	2.07–26.37	2.14–26.37	2.21–29.41
Index ranges	–23 ≤ <i>h</i> ≤ 23 0 ≤ <i>k</i> ≤ 33 0 ≤ <i>l</i> ≤ 12	–9 ≤ <i>h</i> ≤ 12 –19 ≤ <i>k</i> ≤ 20 –24 ≤ <i>l</i> ≤ 26	–15 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 14 0 ≤ <i>l</i> ≤ 17	–15 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 30 0 ≤ <i>l</i> ≤ 20	–19 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 28 0 ≤ <i>l</i> ≤ 23
Reflection collected	55438	22913	24654	19161	31993
Independent reflections	3619	7057	7445	4873	12074
Transmission, max./min.	0.8099/0.6673	0.5929/0.5785	0.9502/0.7646	0.8875/0.7920	0.9280 & 0.7639
Data/restraints/parameters	3619/32/243	7057/78/528	7445/30/452	4873/6/195	12074/0/568
Goodness-of-fit on <i>F</i> ²	1.254	1.037	1.082	1.132	1.027
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0784 <i>wR</i> ₂ = 0.1827	<i>R</i> ₁ = 0.0389 <i>wR</i> ₂ = 0.1117	<i>R</i> ₁ = 0.0677 <i>wR</i> ₂ = 0.1449	<i>R</i> ₁ = 0.0711 <i>wR</i> ₂ = 0.2267	<i>R</i> ₁ = 0.0612 <i>wR</i> ₂ = 0.1005
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0925 <i>wR</i> ₂ = 0.1937	<i>R</i> ₁ = 0.0422, <i>wR</i> ₂ = 0.1144	<i>R</i> ₁ = 0.0891 <i>wR</i> ₂ = 0.1559	<i>R</i> ₁ = 0.0989 <i>wR</i> ₂ = 0.2384	<i>R</i> ₁ = 0.1412 <i>wR</i> ₂ = 0.1284
Largest diff. peak/hole	0.923/–0.441	1.198/–1.055	1.865/–0.976	1.277/–0.492	0.621/–0.496
$R = (\Sigma F_o - F_c) \Sigma F_o$, $R_w = [(\Sigma w F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$, GoF = $[(\Sigma w F_o - F_c)^2 / (N_{\text{obsd.}} - N_{\text{param.}})]^{1/2}$.					

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