

JOM 23853

# Nitrato displacement in $[\text{Ag}_2(\text{NO}_3)_2(\mu\text{-dppf})_2]$ . Molecular structure of a homoleptic dppf complex, $[\text{Ag}_2(\mu\text{-dppf})(\text{dppf})_2](\text{PF}_6)_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene)

Soh-Ping Neo, T.S. Andy Hor

*Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511 (Singapore)*

Zhong-Yuan Zhou and Thomas C.W. Mak

*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)*

(Received March 12, 1993; in revised form May 19, 1993)

## Abstract

Addition of 1,1'-bis(diphenylphosphino)ferrocene (dppf) to  $\text{AgNO}_3$  or  $[\text{Ag}_2(\text{NO}_3)_2(\mu\text{-dppf})_2]$  at room temperature gives rise to a homoleptic dppf complex  $[\text{Ag}_2(\mu\text{-dppf})(\text{dppf})_2]^{2+}$  (1). Single-crystal X-ray diffractometric analysis of its  $\text{PF}_6^-$  salt revealed a dinuclear structure with dppf singly and symmetrically bridging two trigonal planar  $\text{Ag}^I$  centres each of which contains a chelating dppf. The chelate angle  $[105.6(2)^\circ]$  is significantly more acute than the P–Ag–P angles subtended between the chelate and the bridging ligands  $[127.2(2)^\circ]$ . Complex 1 reacts further with dppf to yield a bis(chelate) complex  $[\text{Ag}(\text{dppf})_2](\text{PF}_6)$ . Metathetic reactions of  $[\text{Ag}_2(\text{NO}_3)_2(\mu\text{-dppf})_2]$  with  $\text{Na}^+$  or  $\text{K}^+$  salts of  $\text{X}^-$  ( $\text{X} = \text{Cl}, \text{OCN}, \text{SCN}, \text{Et}_2\text{NCS}_2$ ) at room temperature readily give good yields of, respectively,  $[\text{Ag}(\mu\text{-Cl})(\mu\text{-dppf})_4]$ ,  $[\text{Ag}_2(\mu\text{-NCO}, N)_2(\mu\text{-dppf})_2]$ ,  $[\text{Ag}_2(\mu\text{-SCN}, S, N)_2(\text{dppf})_2]$ , and  $[\text{Ag}_2(\text{S}_2\text{CNEt}_2)_2(\mu\text{-dppf})_2]$ .

*Key words:* Silver; Ferrocene; Nitrate

## 1. Introduction

The complexity of  $\text{Ag}^I$  diphosphine complexes is accentuated by the variable coordination modes of the ligand and geometries of the metal [1]. Numerous structural variations may result especially when the diphosphine [*e.g.* 1,1'-bis(diphenylphosphino)ferrocene (dppf)] responds to the geometrical constraints of the co-ligands [2]. A typical example is found in the recently isolated  $[\text{Ag}_2(\text{NO}_3)_2(\mu\text{-dppf})_2]$  whereby two  $\text{Ag}^I$  centres are bridged by two dppf and chelate-bridged by two nitrato groups [2]. The potential lability of the latter also renders this complex a facile precursor for disilver dppf complexes. In order to examine such dissociation, and the stability and rigidity of the resultant  $[\text{Ag}_2(\text{dppf})_2]^{2+}$  metallacyclic ring, we report here some metathetic reactions of the complex with a series of coordinating and non-coordinating anions. No re-

lated work has been reported on other  $\text{Ag}^I$  diphosphine complexes, though similar chemistry of  $\text{Ag}^I$  monophosphine complexes is known [3].

## 2. Results and discussion

A new dicationic complex formulated as  $[\text{Ag}_2(\mu\text{-dppf})(\text{dppf})_2]^{2+}$  (1) is isolated from a mixture containing molar equivalents of dppf and  $[\text{Ag}_2(\text{NO}_3)_2(\mu\text{-dppf})_2]$ . The same complex can be obtained by adding dppf to a methanol solution of  $\text{AgNO}_3$  in a ratio of 1.5:1.0. Anionic exchange with  $\text{NH}_4\text{PF}_6$  or  $\text{NaBF}_4$  gives rise to corresponding salts of 1. Single-crystal X-ray diffractometry was carried out on the  $\text{PF}_6^-$  complex of 1, and revealed a dicationic molecular core comprising two  $\{\text{Ag}(\text{dppf})\}$  moieties singly bridged by a dppf group (Fig. 1). This complex represents another example of the coexistence of chelating and bridging dppf. A survey of literature work on dppf complexes unveiled a host of chelates [4], and, more recently, bridges [5] and less prominently, unidentates [6]. Coex-

Correspondence to: Dr. T.S.A. Hor or Dr. T.C.W. Mak.

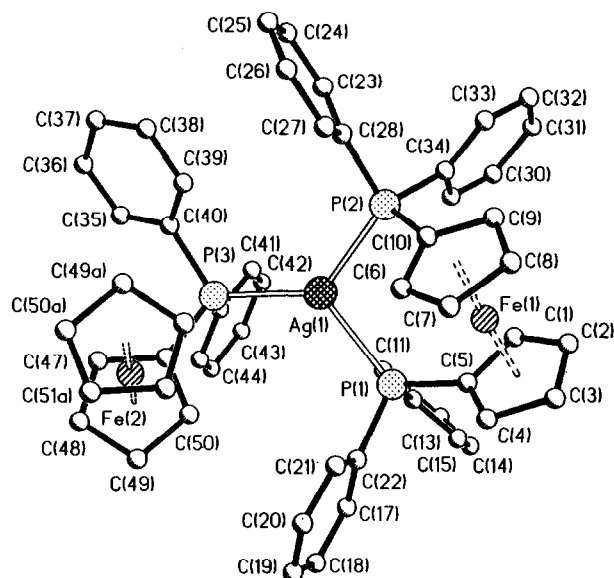
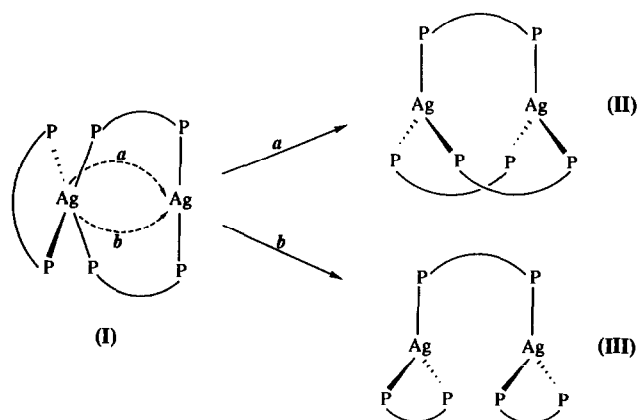


Fig. 1. Perspective view of the structure of  $[Ag_2(\mu\text{-dppf})(\text{dppf})_2](PF_6)_2$  (I) showing only the cation and half of the molecule which is centrosymmetric at the iron centre Fe(2) of the bridging dppf ligand.

instances are also occasionally reported of two or more of the above coordination modes in a single complex [2,7].

The crystallographically imposed  $C_2$  symmetry of the structure implies a symmetrical disposition of the bridging dppf ligand with respect to the two  $Ag^I$  moieties ( $C_p \cdots C_p$  torsional twist  $180^\circ$ ). The different steric demands of dppf's in bridging and chelating modes impose some significant distortions on the trigonal planar  $Ag^I$  centres ( $P\text{-}Ag\text{-}P$  bond angles range from  $105.6(2)$  to  $130.7(2)^\circ$ ). The biting of a dppf chelate on a trigonal planar metal centre was not anticipated since virtually all the dppf chelates found in the literature are associated with metals in tetrahedral, octahedral or pyramidal geometry [4]. The bite angle  $[P(1)\text{-}Ag(1)\text{-}P(2), 105.6(2)^\circ]$  resembles more of a tetrahedral angle [8] and probably approaches the maximum for a dppf chelate. This unusual bite on a trigonal planar  $Ag^I$  is made possible by a facile torsional twist of the ferrocenyl skeleton and achieved without any apparent strain on the substituted cyclopentadienyl (Cp) rings. The  $Ag\text{-}P$  lengths (mean  $2.500(7)$  Å) for the chelate are only marginally longer than the bridging  $Ag\text{-}P$  link ( $2.458(6)$  Å). A similar difference was observed between the bridging and chelating phosphines in  $[Ag_2(\text{HCO}_2)(\mu\text{-dppf})(\eta^2\text{-dppf})_2]$  [2] whereby the  $Ag^I$  geometry is tetrahedral. The co-planarity of the phosphorus atoms with the Cp rings is essentially maintained.

Of special interest is the preferred singly-bridging arrangement to a triply-bridging skeleton proposed for



Scheme 1.

other  $[Ag_2(P\text{-}P)_3]^{2+}$  ( $P\text{-}P = \text{dppm}$  [9] and  $\text{dmpm}$  [10]) complexes. Molecular cores of the latter type have been witnessed in other metal systems such as  $Pd^{II}$  [11],  $Pt^{II}$  [12] and  $Au^I$  [13]. Despite the many characteristics shared between dppf and the hydrocarbon-based diphosphines, the bulky backbone of the former does not appear to favour a triply-bridging arrangement. A dppf chelate is also more sustainable than a 4-membered  $\text{dmpm}/\text{dppm}$  chelate. That the  $[(\text{dppf})M(\mu\text{-dppf})M(\text{dppf})]^{2+}$  core is preferred to  $[M(\mu\text{-dppf})_3M]^{2+}$ , independent of the size of the metal, is demonstrated in the recent characterization of the analogous  $[Cu_2(\mu\text{-dppf})(\text{dppf})_2]X_2$  ( $X = ClO_4, BF_4$ ) [14]. Several workers have identified an "end-over-end" intramolecular mechanism through which one of the phosphorus atoms in the chelate in  $(\eta^2\text{-P-P})Ag(\mu\text{-P-P})_2Ag$  [(I) in Scheme 1] flips across to the adjacent metal [9]. This form of chelate to bridge transformation is probably responsible for the formation of many tribridged-complexes (II). On the contrary, formation of complex 1 can be viewed as a result of a migration of the tetrahedrally-bound P atom of one of the bridges to the 2-coordination metal (III). This form of bridge to chelate transformation as a form of steric release appears to have no literature precedence but should favour the bulky phosphines like dppf. The chelate angles observed in 1 and other  $Ag^I$  complexes indicate that dppf is geometrically suited to both chelate and bridging states whilst phosphines with a small bite such as  $\text{dppm}$  would favour a bridging mode in a  $d^{10}$  system. The  $^{31}P$  NMR spectrum of 1 comprises a major species [15\*] with the expected  $[AB_2X]_2$  spin for 1 [ $\delta P_A$  1.35,  $\delta P_B$  2.22 ppm;  $J(P_A\text{-}Ag_X) \approx J(P_B\text{-}Ag_X) \approx 328$ ,  $J(P_A\text{-}P_B) \approx 22$  Hz]. The  $P\text{-}Ag$  coupling is typical of an  $sp^2$

\* Reference number with asterisk indicates a note in the list of references.

Ag I [16]. This spectrum is essentially unchanged from r.t. to - 50°C.

Formation of 1 from [Ag<sub>2</sub>(NO<sub>3</sub>)E(/Z-dppf)<sub>2</sub>] and NH<sub>4</sub>PF<sub>6</sub> is evidenced even in the absence of added dppf. This points to the instability of the electron deficient [Ag<sub>2</sub>(g,-dppf)<sub>2</sub>]<sup>2+</sup> core especially in the solid state and requires intermolecular transfer of dppf to achieve stabilization. A recent report on the formation of [Ag(dppf)](ClO<sub>4</sub>) from AgClO<sub>4</sub> and the dppf ligand [17] would require further experimental support. The cation formed could be dimeric and hence identical to that generated from [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dppf)<sub>2</sub>]. Despite the bulk of the phosphine environment, complex 1 is susceptible to coordination expansion. This is exemplified by its reaction with excess dppf to give the sterically congested complex [Ag(dppf)E](PF<sub>6</sub>) (2). Structure of the analogous [Ag(dppe)E](NO<sub>3</sub>) has been reported [18] but the dppe analogue is too unstable to be isolated [9]. Unlike the dppe complex, complex 2 exhibits well-resolved Ag-P couplings in its alp NMR spectrum at r.t. The observed I°<sup>9</sup>Ag-P direct coupling of 248 Hz is consistent with a phosphine-bound tetrahedral AgI [16]. Similar bis(dppf) chelates have been reported in [Hg(dppf)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> [19] and [Ir(dppf)<sub>2</sub>]BPh<sub>4</sub>, the latter showing that the diphosphine ligands exert a severe steric distortion from planarity on the central metal [20]. The NO<sub>3</sub><sup>-</sup> salt of I easily metathesizes with Cl<sup>-</sup> or NCS<sup>-</sup> to give the covalent [AgEXE(/t-dppf)(dppf)<sub>2</sub>] (X = Cl or SCN respectively) which are only sparingly soluble in common organic solvents except in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>. Conductivity data also point to complex neutrality with some slight dissociation. The {(dppf)Ag(/~dppf)Ag(dppf)} skeleton is presumably retained in the process of ligand exchange. IR spectrum of the latter suggests the thiocyanato to be N-bonded [3a].

Metathetic reactions of [AgE(NO<sub>3</sub>)E(/~dppf)<sub>2</sub>] with other coordinating anionic salts M<sup>+</sup>X<sup>-</sup> (M = Na, K; X = Cl, OCN, SCN, Et<sub>2</sub>NCS<sub>2</sub>) at r.t. readily give rise to [Ag(/z-Cl)(~dppf)<sub>4</sub>] (3), [Ag<sub>2</sub>(/z-NCO,N)<sub>2</sub>(~dppf)<sub>2</sub>] (4), [Ag<sub>2</sub>(/x-SCN-S,N)E(dppf)<sub>2</sub>] (5) and [AgE(SECNEtE)(/J,-dppf)<sub>2</sub>] (6) respectively in good yields. Molecular-weight measurement of 3 (mw 2545) suggested it to be tetrameric in solution. Similar tetranuclear structures have been found in Ag<sub>4</sub>(/~O-2-CCHa)<sub>4</sub>(/z-dppf)<sub>2</sub> [2] and [Ag<sub>4</sub>(/x-NOa)z(/x-dppm)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> [21]. Complex 4 shows a strong ν(CN)str at 2153 cm<sup>-1</sup> which is indicative of a bridging -NCO group [22]. Molecular weight measurement suggested it to be dimeric in solution. Complex 5 shows the ν(CN)-tr at 2100 cm<sup>-1</sup> (with a shoulder peak at 2087 cm<sup>-1</sup>) and a weaker ν<sub>2</sub>(CS)str at 812 cm<sup>-1</sup>. The former implies a terminally S-bonded thiocyanate [3a] but the latter is more consistent with an N-bonded ligand [3a]. Though

the affinity of Ag I for soft donor ligands (e.g. S-donors) is well-known [23], M-NCS bonding predominates in thiocyanato phosphine complexes of AgI [24]. We favour a dimeric structure for 5 with dppf in a chelating and the thiocyanato in an end-to-end bridging mode. A similar structure is found in [Ag<sub>2</sub>(/~SCN-S,N)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] which consists of a quasiplanar {Ag<sub>2</sub>(SCN)<sub>2</sub>} core [25]. Dithiocarbamate monophosphine complexes of AgI have been reported [26]. Complex 6 gives a ν(CN)str at 1478 and ν(CS)str at 988 with a shoulder peak at 997 cm<sup>-1</sup>. These data are incompatible with either a unidentate [27] or a typical chelating dithiocarbamate ligand [27]. We propose a semi-bridging ligating mode with one S donor for each ligand anchored onto each AgI site, and the other S weakly linked to both metal sites. A related coordination mode has been found in [Ag(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sub>6</sub> [28]. The dppf bridges thus remain intact in the molecular core.

### 3. Conclusion

This study demonstrates the lability of the nitrate ligands in [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(/x-dppf)<sub>2</sub>]. Whether the resultant metallacycle {AgE(/~dppf)<sub>2</sub>} is sustainable depends on the nature of the incoming ligand. Since interconversion of bridging and chelating coordination modes for dppf is facile, dimerization or fragmentation of the disilver complex is easily envisaged. The present report also established the identity of the [Ag<sub>2</sub>(P-P)<sub>3</sub>]<sub>2</sub><sup>+</sup> molecular core. Surprisingly, though such a cation was inferred in a recent stability study of Ag(I)/dppm in solution, it is notably absent in dppe and dppp solutions [29].

### 4. Experimental section

#### 4.1. General

All reactions were performed under pure dry argon using standard Schlenk techniques. The reaction flasks were generally shielded by Al foil from direct laboratory light. [Ag<sub>2</sub>(NO<sub>3</sub>)E(/~dppf)<sub>2</sub>] was prepared as earlier described [2]. dppf was prepared either by a literature method [30] or purchased commercially. All other chemical reagents were commercial products and used as received. The procedures and instruments used were as described previously [2]. All NMR spectra were recorded in CDCl<sub>3</sub> solution. The <sup>31</sup>P shifts are externally referenced to 85% H<sub>3</sub>PO<sub>4</sub>. All infrared spectra were recorded in KBr disc. Molecular weight measurements were carried out by Galbraith Laboratories, Inc. in Knoxville, TN, USA using Vapour Pressure Osmometry with a Knauer-Dampfdruck osmometer with CH<sub>2</sub>Cl<sub>2</sub> as solvent. Conductivities were measured us-

ing a Conductivity 1000 electronic conductimeter with a cell constant of 0.55 cm<sup>-1</sup>. Elemental analysis was carried out in the Microanalytical Laboratory of our Department in NUS. The presence of solvates in crystalline samples was confirmed by <sup>1</sup>H-NMR analysis.

#### 4.2. Synthesis of [Ag<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (1)

This complex can be prepared from [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(μ-dppf)<sub>2</sub>] and dppf in 1:1 molar ratio in MeOH but the following direct method was adopted because of its ease and better yield.

AgNO<sub>3</sub> (0.020 g, 0.120 mmol) in MeOH (15 cm<sup>3</sup>) was transferred dropwise via a teflon delivery tube to a solution of dppf (0.100 g, 0.18 mmol) in THF (15 cm<sup>3</sup>). The mixture was stirred for 45 min after which excess NH<sub>4</sub>PF<sub>6</sub> (ca. 0.05 g) in H<sub>2</sub>O (5 cm<sup>3</sup>) was introduced. The resultant suspension was stirred further for 3 h, filtered, and the precipitated solid washed with copious H<sub>2</sub>O to remove all the simple salts. The dried crude sample was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture to give **1**. (0.11 g; 85%). (Found C, 54.85; H, 3.80; Ag, 9.18; F, 10.03; Fe, 6.93; P, 9.60%, C<sub>102</sub>H<sub>84</sub>Ag<sub>2</sub>F<sub>12</sub>Fe<sub>3</sub>P<sub>8</sub> requires C, 54.89; H, 3.85; Ag, 9.57, F, 10.12; Fe, 7.44, P, 10.99%). ν<sub>max</sub>(PF<sub>6</sub><sup>-</sup>) (cm<sup>-1</sup>): 837s; δ<sub>H</sub> 7.49–7.06 (m, 60H, Ph), 4.49 (s, 8H, Cp), 4.24 (s, 8H, Cp), 4.04 (s, 4H, Cp), 3.55 (s, 4H, Cp); δ<sub>P</sub> (233 K) –144.33 (s, 2P; J(PF) 713 Hz), 1.35 (dt, 2P; J(AgP) 328 Hz, J(PP) 21 Hz), 2.22 (dd, 4P; J(AgP) 328 Hz J(PP) 23 Hz) (and weaker resonances at 6.19 (dt), = 5.5 (td), = 3.3 (dt) presently unidentified). Resolution of <sup>107</sup>Ag–P and <sup>109</sup>Ag–P couplings was not observed. The spectral pattern is essentially unchanged between 298 and 223 K).

The BF<sub>4</sub><sup>-</sup> complex can be prepared similarly by using NaBF<sub>4</sub> as the ion-exchange agent.

Metathesis of the nitrate salt of **1** with NaCl and KSCN in MeOH yielded the following products which could be purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane: [Ag<sub>2</sub>Cl<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>]·2CH<sub>2</sub>Cl<sub>2</sub> (0.042 g; 62%) (Found C, 59.75; H, 4.04; Ag, 10.58; Cl, 3.96; Fe, 8.77; P, 9.12, C<sub>104</sub>H<sub>88</sub>Ag<sub>2</sub>Cl<sub>6</sub>Fe<sub>3</sub>P<sub>6</sub> requires C, 58.93; H, 4.18; Ag, 10.18; Cl, 3.34; Fe, 7.90; P, 8.77%). Molar conductivity Λ<sub>m</sub>: 7.86 (CH<sub>2</sub>Cl<sub>2</sub>) Ω<sup>-1</sup>cm<sup>2</sup>M<sup>-1</sup>. [Ag<sub>2</sub>(SCN-N)<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>] (0.044 g; 63%) (Found C, 62.77; H, 4.17; N, 1.35; Fe, 7.75; P, 9.28; S, 4.22, C<sub>104</sub>H<sub>84</sub>N<sub>2</sub>Ag<sub>2</sub>Fe<sub>3</sub>P<sub>6</sub>S<sub>2</sub> requires C, 62.61; H, 4.24; N, 1.40; Fe, 8.40; P, 9.30; S, 3.21%). The Ag analysis was hampered by interferences. ν<sub>max</sub>(NCS) (cm<sup>-1</sup>): 2088. Molar conductivity Λ<sub>m</sub>: 15.71 (CH<sub>2</sub>Cl<sub>2</sub>) Ω<sup>-1</sup>cm<sup>2</sup>M<sup>-1</sup>.

#### 4.3. Synthesis of [Ag(dppf)<sub>2</sub>](PF<sub>6</sub>) (2)

The complex can be prepared from complex **1** and dppf in 1:1 molar ratio in THF but the following method is more direct and affords a better yield.

A methanolic solution (25 cm<sup>3</sup>) of AgNO<sub>3</sub> (0.031 g, 0.18 mmol) was introduced by a teflon tube to a solution of dppf (0.20 g, 0.361 mmol) in THF (20 cm<sup>3</sup>). The mixture was stirred for 30 min after which it was evaporated to low volume *in vacuo*. The dark orange precipitate thus resulted was isolated by filtration and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture to give [Ag(dppf)<sub>2</sub>](NO<sub>3</sub>)·½CH<sub>2</sub>Cl<sub>2</sub> (0.20 g, 87%) (Found C, 62.57; H, 4.53; N, 1.36; Ag, 9.62; Fe, 8.53; P, 9.88%, C<sub>68.5</sub>H<sub>57</sub>NAgCl<sub>2</sub>Fe<sub>2</sub>O<sub>3</sub>P<sub>4</sub> requires C, 62.27; H, 4.35; N, 1.06; Ag, 8.16; Fe, 8.45; P, 9.38%). ν<sub>max</sub>(NO<sub>3</sub><sup>-</sup>) (cm<sup>-1</sup>): 1384s, 1333s; δ<sub>H</sub> 7.34–7.06 (m, 40H, Ph), 4.42 (s, 8H, Cp), 4.10 (s, 8H, Cp); δ<sub>P</sub> –3.46 (d; J(AgP) 248Hz). The BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> complexes can be prepared by metathesis in MeOH. [Ag(dppf)<sub>2</sub>](PF<sub>6</sub>) (Found C, 59.50; H, 4.07; Ag, 6.84; F, 7.04; Fe, 8.13; P, 11.32%, C<sub>68</sub>H<sub>56</sub>AgF<sub>6</sub>Fe<sub>2</sub>P<sub>5</sub> requires C, 59.98; H, 4.14; Ag, 7.92; F, 8.37; Fe, 8.20; P, 11.37%). ν<sub>max</sub>(PF<sub>6</sub>) (cm<sup>-1</sup>): 836s; δ<sub>H</sub> 7.36–7.07 (m, 40H, Ph), 4.44 (s, 8H, Cp), 4.10 (s, 8H, Cp); δ<sub>P</sub> –3.23 (d; J(AgP) 251 Hz), –143.64 (sep, J(PF) 712 Hz).

#### 4.4. Synthesis of [Ag<sub>2</sub>(μ-NCO)<sub>2</sub>(μ-dppf)<sub>2</sub>] (4)

An aqueous solution (3 cm<sup>3</sup>) of KNCO (0.050 g, 0.62 mmol) was delivered by a teflon tube to a MeOH solution (50 cm<sup>3</sup>) of [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(μ-dppf)<sub>2</sub>] (0.130 g, 8.97 × 10<sup>-2</sup> mmol). Precipitation rapidly occurred and the resultant suspension was stirred for 6 h. Upon settling of the precipitate, the solution was carefully filtered off and the residue dried and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture to give complex **4**. (Found C, 59.81; H, 3.93; N, 1.93; Ag, 13.97; Fe, 7.68; P, 9.43%, C<sub>70</sub>H<sub>56</sub>N<sub>2</sub>Ag<sub>2</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>4</sub> requires C, 59.69; H, 3.98; N, 1.99; Ag, 15.32; Fe, 7.93; P, 8.80%). Mw 1433. ν<sub>max</sub>(NCO) (cm<sup>-1</sup>): 2153s; δ<sub>H</sub> 7.50–7.30 (m, 40H, Ph), 4.07 (s(br), 16H, Cp); δ<sub>P</sub> 0.99 (s(br)).

#### 4.5. Syntheses of [Ag(μ-Cl)(μ-dppf)]<sub>4</sub> (3) [Ag<sub>2</sub>(μ-SCN-S)<sub>2</sub>(dppf)<sub>2</sub>] (5) and [Ag<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(μ-dppf)<sub>2</sub>] (6)

These follow the method described for **4** by using NaCl, KSCN and Na<sub>2</sub>S<sub>2</sub>CNEt<sub>2</sub> as the metathetic reagents. For **3** (0.035 g, 52%) (Found C, 58.26; H, 4.05; Ag, 14.11; Cl, 3.48; Fe, 7.47; P, 8.92, C<sub>136</sub>H<sub>112</sub>Ag<sub>4</sub>Cl<sub>4</sub>Fe<sub>2</sub>P<sub>8</sub> requires C, 58.53; H, 4.05; Ag, 15.46; Cl, 5.09; Fe, 8.00; P, 8.88%). mw 2545. δ<sub>H</sub> 7.64–7.31 (m, 80H, Ph), 4.08 (s, 32H, Cp); δ<sub>P</sub> –3.37 (s(v br)). For **5** (0.067 g, 67%) (Found C, 58.77; H, 4.00; N, 1.87; Ag, 14.17; Fe, 7.08; P, 9.48; S, 5.23%, C<sub>70</sub>H<sub>56</sub>N<sub>2</sub>Ag<sub>2</sub>Fe<sub>2</sub>P<sub>4</sub>S<sub>2</sub> requires C, 58.36; H, 3.92; N, 1.94; Ag, 14.97; Fe, 7.75; P, 8.60; S, 4.45%). MW 1244. ν<sub>max</sub>(NCS) (cm<sup>-1</sup>): 2100s, 2087sh, 812m; δ<sub>H</sub> 7.57–7.27 (m, 40H, Ph), 4.34 (s, 8H, Cp), 4.22 (s, 8H, Cp); δ<sub>P</sub> –0.94 (s(v br)). For **6**, which crystallizes as hexane solvate (0.037 g, 47%) (Found C, 59.64; H, 5.44; N, 1.58; Ag, 11.02;

Fe, 6.10; P, 7.37; S, 8.73, C<sub>84</sub>H<sub>90</sub>N<sub>2</sub>Ag<sub>2</sub>Fe<sub>2</sub>P<sub>4</sub>S<sub>4</sub> requires C, 59.10; H, 5.31; N, 1.64; Ag, 12.64; Fe, 6.54; P, 7.26; S, 7.51%).  $\nu_{\max}$  1478s (CN), 997sh, 988m (CS) (cm<sup>-1</sup>);  $\delta_{\text{H}}$  7.81–7.31 (m, 40H, Ph), 4.24 (s, 8H, Cp),

TABLE 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for [Ag<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> ( $U_{\text{eq}}$  defined as one third of the trace of the orthogonalized  $U$  tensor)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Ag(1)	2077(2)	2969(2)	2742(2)	46(1)
Fe(1)	5291(3)	2843(3)	2296(3)	53(2)
Fe(2)	0	5000	5000	53(3)
P(1)	3421(5)	1561(5)	3543(5)	47(3)
P(2)	3118(6)	3697(5)	1291(5)	53(3)
P(3)	160(5)	3460(5)	3387(5)	46(3)
P(4)	5000	5000	5000	74(7)
F(1)	5284(16)	5713(13)	4018(13)	118(12)
F(2)	4082(18)	4806(20)	4654(14)	146(15)
F(3)	5753(19)	3972(15)	4602(14)	157(14)
P(5)	-1286(14)	-466(13)	229(13)	121(14)
F(4)	-1258(21)	-1421(18)	-279(16)	68(9)
F(5)	-1110(32)	366(28)	734(24)	155(17)
F(6)	-317(22)	-1023(49)	691(31)	267(31)
F(7)	-2240(21)	315(22)	-207(19)	92(11)
F(8)	-2009(15)	-790(14)	1084(12)	29(6)
F(9)	-509(28)	-94(30)	-618(22)	297(36)
C(1)	5377(25)	1302(18)	2226(20)	62(15)
C(2)	6387(28)	1454(23)	2087(30)	100(21)
C(3)	6509(25)	1770(25)	2888(29)	82(20)
C(4)	5505(22)	1840(20)	3496(22)	64(15)
C(5)	4827(20)	1544(18)	3111(20)	49(14)
C(6)	4186(22)	4223(20)	2444(20)	54(15)
C(7)	5170(27)	4348(19)	2473(22)	69(17)
C(8)	5850(23)	4097(21)	1639(23)	69(16)
C(9)	5262(22)	3841(19)	1074(20)	56(14)
C(10)	4224(19)	3949(18)	1607(19)	39(12)
C(11)	2516(14)	115(16)	3259(12)	76(17)
C(12)	2450	-897	3237	85(19)
C(13)	3249	-1778	3493	84(19)
C(14)	4114	-1648	3772	87(19)
C(15)	4180	-636	3794	61(14)
C(16)	3381	246	3538	43(13)
C(17)	2997(13)	837(11)	5454(14)	50(13)
C(18)	2805	978	6371	66(16)
C(19)	2859	1918	6587	60(14)
C(20)	3105	2717	5886	60(15)
C(21)	3297	2576	4969	57(15)
C(22)	3243	1636	4752	48(13)
C(23)	1802(16)	5020(15)	92(15)	67(16)
C(24)	1272	5997	-334	110(19)
C(25)	1404	6926	-162	174(30)
C(26)	2066	6878	436	140(30)
C(27)	2596	5901	862	72(16)
C(28)	2464	4972	690	53(14)
C(29)	3551(17)	1883(19)	503(15)	90(19)
C(30)	3990	1230	-174	116(25)
C(31)	4592	1585	-1005	117(26)
C(32)	4754	2593	-1159	91(20)
C(33)	4315	3245	-482	71(16)
C(34)	3713	2890	349	54(14)

Table 1 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C(35)	-1795(16)	4611(14)	2842(11)	54(14)
C(36)	-2424	5490	2373	65(16)
C(37)	-1960	6249	1783	69(17)
C(38)	-868	6129	1662	67(17)
C(39)	-239	5250	2131	58(14)
C(40)	-703	4491	2721	41(13)
C(41)	-162(15)	1885(19)	2637(13)	77(18)
C(42)	-390	929	2666	94(22)
C(43)	-771	376	3507	93(21)
C(44)	-923	779	4319	125(26)
C(45)	-695	1735	4291	88(19)
C(46)	-314	2288	3450	55(14)
C(47)	-1192(22)	4342(21)	5009(22)	63(16)
C(48)	-1095(27)	4315(24)	5903(22)	74(18)
C(49)	-58(25)	3678(22)	6018(24)	67(17)
C(50)	439(24)	3353(20)	5158(23)	62(15)
C(51)	-240(21)	3727(21)	4521(19)	48(13)

4.21 (s, 8H, Cp), 4.04 (q, 8H, Et;  $J(\text{HH})$  6.9 Hz), 1.32 (t, 12H, Et;  $J(\text{HH})$  6.1 Hz);  $\delta_{\text{p}}$  -6.730 (s(br)).

#### 4.6. X-ray crystallography

[Ag<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (1), mw = 2063.13, crystallizes as golden plates in space group *P1* (no. 2) with  $a = 13.410(4)$ ,  $b = 13.417(4)$ ,  $c = 15.163(5)$  Å,  $\alpha = 77.74(3)$ ,  $\beta = 75.94(3)$ ,  $\gamma = 72.58(3)^\circ$  and  $Z = 1$ . Diffraction measurements were made at 18°C on a Nicolet R3/MV system (graphite-monochromatized

TABLE 2. Selected bond lengths (Å) and angles (°).

Ag(1)–P(1)	2.518(7)	Ag(1)–P(2)	2.481(7)
Ag(1)–P(3)	2.458(6)		
Fe(1)–C(1–5)(av)	2.06(3)	Fe(1)–C(6–10)(av)	2.03(3)
Fe(2)–C(47–51)(av)	2.08(3)		
P(1)–C(5)	1.83(3)	P(1)–C(16,22)(av)	1.80(2)
P(2)–C(10)	1.81(3)	P(2)–C(28,34)(av)	1.84(2)
P(3)–C(51)	1.75(3)	P(3)–C(40,46)(av)	1.83(3)
P(4)–F(1–3)(av)	1.59(2)	P(5)–F(4–9)(av)	1.56(4)
P(1)–Ag(1)–P(2)	105.6(2)	P(1)–Ag(1)–P(3)	123.7(2)
P(2)–Ag(1)–P(3)	130.7(2)		
Ag(1)–P(1)–C(5)	116.7(8)	Ag(1)–P(1)–C(16)	114.1(7)
Ag(1)–P(1)–C(22)	113.5(5)	Ag(1)–P(2)–C(10)	106.0(9)
Ag(1)–P(2)–C(28)	117.3(7)	Ag(1)–P(2)–C(34)	119.7(8)
Ag(1)–P(3)–C(51)	118(1)	Ag(1)–P(3)–C(40)	118.2(6)
Ag(1)–P(3)–C(46)	106.0(6)		

Ag(1) atom is -0.0232 Å under plane constituted with P(1), P(2), P(3).

Symmetry transformation:  $a(-x, -y, -z)$ .

Mo K<sub>α</sub> radiation, λ = 0.71073 Å using a single crystal (0.22 × 0.20 × 0.02 mm) selected from a batch sample of generally poor quality. The intensities (2θ<sub>max</sub> = 40°, 4486 unique data) were corrected for absorption and structure solution was accomplished by Patterson and Fourier methods.

One of the two independent PF<sub>6</sub><sup>-</sup> groups is located on a site of 1 symmetry, whereas the other occupies a general position and necessarily exhibits half site occupancy. For the latter group intraatomic distance restraints of P–F = 1.54 ± 0.02 and F···F = 2.18 ± 0.03 Å were imposed in least-squares refinement. All non-hydrogen atoms except the F atoms of the second PF<sub>6</sub><sup>-</sup> group were refined anisotropically, and all hydrogen atoms were introduced in their idealized positions with assigned isotropic temperature factors. All calculations were performed on a DEC MicroVAX-II computer using the SHELXTL-PLUS system [31]. Convergence for 2764 observed data [ $|F_o| > 3\sigma(F_o)$ ] and 505 variables was reached at  $R(F) = 0.080$  and  $R(wF^2) = 0.092$  with  $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$ .

The final atomic parameters are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.

### 5. Supplementary material available

List of thermal parameters and structure factors for [Ag<sub>2</sub>(μ-dppf)(dppf)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> are available from the authors.

### Acknowledgments

We are grateful to the National University of Singapore (NUS) (RP 850030) and Hong Kong Research Grants Council (Earmarked Grant No. CUHK 22/91) for support of this work. We thank the technical staff in the Department of Chemistry at NUS for assistance, and Y.-P. Leong for help in the preparation of this manuscript. S.-P. Neo acknowledges NUS for a scholarship award.

### References and notes

- 1 A.A.M. Aly, D. Neugebauer, O. Orama, U. Schubert and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, **90** (1978) 125; A.F.M.J. van der Ploeg, G. van Koten and A.L. Spek, *Inorg. Chem.*, **18** (1979) 1052; A.F.M.J. van der Ploeg and G. van Koten, *Inorg. Chim. Acta*, **51** (1981) 225; E.R.T. Tiekink, *Acta Crystallogr., Ser. C*, **46C** (1990) 1933; H. Wagner and U. Schubert, *Chem. Ber.* **123** (1990) 2101; S.J. Berners-Price, P.J. Sadler and C. Brevard, *Magn. Reson. Chem.*, **28** (1990) 145.
- 2 T.S.A. Hor, S.P. Neo, C.S. Tan, T.C.W. Mak, K.W.P. Leung and R.-J. Wang, *Inorg. Chem.*, **31** (1992) 4510.
- 3 (a) J.L. Cox and J. Howatson, *Inorg. Chem.*, **12** (1973) 1205; (b) H.C. Brinkhoff, A.G. Matthijssen and C.G. Oomes, *Inorg. Nucl. Chem. Lett.*, **7** (1971) 87; (c) B.K. Teo and J.C. Calabrese, *J. Am. Chem. Soc.*, **97** (1975) 1256.
- 4 S. Onaka, *Bull. Chem. Soc. Jpn.*, **95** (1986) 2359; T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, **106** (1984) 158; C.E. Housecroft, S.M. Owen, P.R. Raithby and B.A.M. Shaykh, *Organometallics*, **9** (1990) 1617; A.L. Bandini, G. Banditelli, M.A. Cinelli, G. Sanna, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem.*, **28** (1989) 404; W.R. Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, *Organometallics*, **2** (1983) 714; W.R. Cullen, F.W.B. Einstein, T. Jones and T.J. Kim, *Organometallics*, **2** (1983) 741; W.R. Cullen, F.W.B. Einstein, T. Jones and T.J. Kim, *Organometallics*, **4** (1985) 346; V. Scarcia, A. Furlani, B. Longato, B. Corain and G. Pilloni, *Inorg. Chim. Acta*, **153** (1988) 67; M. Adachi, M. Kita, K. Kashiwabara, J. Fujita, N. Iitaka, S. Kurachi, S. Ohba and D. Jin, *Bull. Chem. Soc. Jpn.*, **65** (1992) 2037; G. Bandoli, G. Trovo, A. Dolmella and B. Longato, *Inorg. Chem.*, **31** (1992) 45.
- 5 S. Onaka, A. Mizuno and S. Takagi, *Chem. Lett.*, (1989) 2037; Y.K. Yan, H.S.O. Chan, T.S.A. Hor, K.-L. Tan, L.-K. Liu and Y.-S. Wen, *J. Chem. Soc., Dalton Trans.*, (1992) 423; T.S.A. Hor, H.S.O. Chan, K.-L. Tan, L.-T. Phang, Y.K. Yan, L.-K. Liu and Y.-S. Wen, *Polyhedron*, **10** (1991) 2437; T.S.A. Hor, L.-T. Phang, L.-K. Liu and Y.-S. Wen, *J. Organomet. Chem.*, **397** (1990) 29; T.S.A. Hor and L.-T. Phang, *Polyhedron*, **9** (1990) 2305; P. Kalck, C. Randrianalimanana, M. Ridmy and A. Thorez, *New J. Chem.*, **12** (1988) 679; S.T. Chacon, W.R. Cullen, M.I. Bruce, O. bin Shawkataly, F.W.B. Einstein, R.H. Jones and A.C. Willis, *Can. J. Chem.*, **68** (1990) 2001; T.J. Kim, S.C. Kwon, Y.H. Kim, N.H. Heo, M.M. Teeter and A. Yamano, *J. Organomet. Chem.*, **426** (1992) 71.
- 6 F. Neumann and G. Suss-Fink, *J. Organomet. Chem.*, **367** (1989) 175; L.-T. Phang, S.C.F. Au-Yeung, T.S.A. Hor, S.B. Khoo, Z.-Y. Zhou and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1993) 165; T.S.A. Hor and L.-T. Phang, *J. Organomet. Chem.*, **390** (1990) 345; T.S.A. Hor and L.-T. Phang, *J. Organomet. Chem.*, **373** (1989) 319; D.T. Hill, G.R. Girard, F.L. McCabe, R.K. Johnson, P.D. Stupik, J.H. Zhang, W.M. Reiff and D.S. Eggleston, *Inorg. Chem.*, **28** (1989) 3529; E.C. Alyea and A. Somogyvari, *Transition Met. Chem.*, **12** (1987) 310.
- 7 J.D. Unruh and W.J. Wells, Germany Offen. Pat. DE 2617306 (Date 761104); P.K. Baker, S.G. Fraser and P. Harding, *Inorg. Chim. Acta*, **116** (1986) L5; T.A. George and R.C. Tisdale, *J. Am. Chem. Soc.*, **107** (1985) 5157.
- 8 U. Casellato, G. Valle, D. Ajo, B. Corain, B. Longato and R. Graziani, *J. Crystallogr. Spectrosc. Res.*, **18** (1988) 583; I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, *Organometallics*, **4** (1985) 972.
- 9 D. Obendorf, M. Probst, P. Peringer, H. Falk and N. Muller, *J. Chem. Soc., Dalton Trans.* (1988) 1709, and references therein.
- 10 P.A.W. Dean, J.J. Vittal and R.S. Srivastava, *Can. J. Chem.*, **65** (1987) 2628.
- 11 E.W. Stern and P.K. Maples, *J. Catal.*, **27** (1972) 120 and 134; A.L. Balch, *Adv. Chem. Ser.*, **196** (1980) 243; C.T. Hunt and A.L. Balch, *Inorg. Chem.*, **20** (1981) 2267; A.L. Balch, C.T. Hunt, C.L. Lee, M.M. Olmstead and J.P. Farr, *J. Am. Chem. Soc.*, **103** (1981) 3764.
- 12 L. Manojlovic-Muir, K.W. Muir, M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding and K.R. Seddon, *J. Chem. Soc., Dalton Trans.*, (1986) 1955, and references therein.
- 13 W. Bensch, M. Prelati and W. Ludwig, *J. Chem. Soc., Chem. Commun.*, (1986) 1762.
- 14 G. Pilloni, R. Graziani, B. Longato and B. Corain, *Inorg. Chim. Acta*, **190** (1991) 165; U. Casellato, R. Graziani and G. Pilloni,

- XXVIII Int. Conf. Coord. Chem., Gera, FRG, Aug 1990, Abstr. No. 6-31.
- 15 There is at least one minor species in solution which is currently unidentified due to the partial overlapping of its  $^{31}P$  bands with the main peaks.
- 16 E.L. Muetterties and C.W. Alegranti, *J. Am. Chem. Soc.*, **92** (1970) 4114.
- 17 M. Maekawa, S. Kitagawa and M. Munakata, *Kinki Daigaku Rigogakubu Kenkyu Hokoku*, (1989) 103; *Chem. Abs.*, **113** (1990) 6489q.
- 18 C.S.W. Harker and E.R.T. Tiekink, *J. Coord. Chem.*, **21** (1990) 287; S.J. Berners-Price, C. Brevard, A. Pagelot and P.J. Sadler, *Inorg. Chem.*, **24** (1985) 4278.
- 19 K.R. Mann, W.H. Morrison Jr. and D.N. Hendrickson, *Inorg. Chem.*, **13** (1974) 1180.
- 20 U. Casellato, B. Corain, R. Graziani, B. Longato and G. Pilloni, *Inorg. Chem.*, **29** (1990) 1193.
- 21 D.M. Ho and R. Bau, *Inorg. Chem.*, **22** (1983) 4073.
- 22 A.H. Norbury, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 17, Academic Press, New York, 1975.
- 23 R.J. Lancashire in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry*, vol. 5, Pergamon Press, Oxford, 1987, ch. 54, p. 775.
- 24 A. Sabatini and I. Bertini, *Inorg. Chem.*, **4** (1965) 1665.
- 25 J. Howatson and B. Morosin, *Cryst. Struct. Commun.*, **2** (1973) 51.
- 26 C. Kowala and J.M. Swan, *Aust. J. Chem.*, **19** (1966) 555.
- 27 D.A. Brown, W.K. Glass and M.A. Burke, *Spectrochim. Acta*, **32A** (1976) 137; R. Kellner, G. St. Nikolov and N. Trendafilova, *Inorg. Chim. Acta*, **84** (1984) 233; K. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination compounds*, 4th ed., Wiley-Interscience, 1986, p. 256.
- 28 H. Yamaguchi, A. Kido, T. Uechi and K. Yasukouchi, *Bull. Chem. Soc. Jpn.*, **49** (1976) 1271.
- 29 P. Di Bernardo, G. Dolcetti, R. Portanova, M. Tolazzi, G. Tomat and P. Zanonato, *Inorg. Chem.*, **29** (1990) 2859.
- 30 G. Marr and T. Hunt, *J. Chem. Soc. (C)*, (1969) 1070.
- 31 G.M. Sheldrick in D. Sayre (ed.), *Computational Crystallography*, Oxford University Press, New York, 1982, p. 505; G.M. Sheldrick in G.M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*, Oxford University Press, New York, 1985, p. 175.