Synthesis, Chemical Characterization, and Molecular Structures of $Ag_8Fe_4(CO)_{16}(dppm)_2$ and $Ag_4Au_4Fe_4(CO)_{16}(dppe)_2$

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The new $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ ($P^\wedge P$ = dppm, dppe) neutral cluster compounds have been isolated in good yields by condensation in CH_3CN or THF of $M_2(P^\wedge P)^{2+}$ (M = Ag, Au) cations with $[Ag_4\{Fe(CO)_4\}_4]^{4-}$ anions and characterized by IR, NMR, and microanalyses. The structure of both $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ has been determined by X-ray diffraction studies. The former represents a very rare example of a neutral Ag−Fe cluster containing phosphine as ancillary ligand for silver.

Introduction

The chemistry of Ag−Fe clusters containing phosphines as ancillary ligands for silver is very poor.[1−3] No neutral compound is known, besides $Ag_6Fe_3(CO)_{12}\{(PPh_2)_3CH\}$, which contains the tridentate *triphos* ligand.[4] A few addition products of AgL^+ moieties to anionic iron carbonyl compounds have also been reported, but none of them have been structurally characterized.[1−3] The paucity of Ag−Fe−phosphine compounds is in contrast with the existence of several anionic silver clusters stabilized uniquely by $Fe(CO)_4$ groups[5−8] and the wide variety of Au−Fe clusters in which gold is coordinated by phosphine ligands.[9−15]

We now report the synthesis of the new $Ag_8\{Fe(CO)_4\}_4(dppm)_2$, $Ag_4Au_4\{Fe(CO)_4\}_4(dppm)_2$, and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ compounds (dppm = bis(diphenylphosphine)methane, dppe = bis(diphenylphosphine)ethane). The molecular structures of two of them, namely, $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$, have been determined by X-ray diffraction studies. To our knowledge, $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ represents the second example of a neutral Ag−Fe cluster containing phosphine as ancillary ligand for silver. Moreover, its structure suggests that the nature of the elusive $[Ag_6Fe_4(CO)_{16}]^{2-7}$ could be different from that of the $[Cu_6Fe_4(CO)_{16}]^{2-}$ congener[16,17] and points out a possible reaction pathway from $[Ag_4Fe_4(CO)_{16}]^{4-}$ to $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ that preserves the favored ν_2-square $Ag_4\{Fe(CO)_4\}_4$ motif throughout the reaction.

Results and Discussion

The exploitation of the additional bonding capability of the μ_2-$Fe(CO)_4$ groups of $[Ag_4Fe_4(CO)_{16}]^{4-}$ leading to the synthesis of $[Ag_5Fe_4(CO)_{16}]^{3-}$ has demonstrated that the former can act as an 8-crown-2 ligand for Ag^+ ions.[6] The consideration that pinning of M^+ ions with an ancillary ligand could trigger outward rather than inward bonding capability of the μ_2-$Fe(CO)_4$ groups of $[Ag_4Fe_4(CO)_{16}]^{4-}$ (see Scheme 1) led us to investigate the potential of the latter as a tetradentate ligand toward $M_2(P^\wedge P)^{2+}$ (M = Ag, Au) moieties.

The reaction of $[Ag_4Fe_4(CO)_{16}]^{4-}$ salts with $M_2(P^\wedge P)^{2+}$ species greatly depends on the nature of the coinage metal, the ancillary phosphine ligand, and the reaction solvent. For instance, mixing of ca. 2 mol of $Ag_2(dppm)(NO_3)_2$ per mole of $[NEt_4]_4[Ag_4Fe_4(CO)_{16}]$ in acetonitrile affords a mixture containing the neutral $Ag_8\{\mu_3\text{-}Fe(CO)_4\}_4(dppm)_2$ species and comparable amounts of the $[Ag_{13}Fe_8(CO)_{32}]^{3-/4-}$ and $[Ag_6Fe_4(CO)_{16}]^{2-}$ salts. The red

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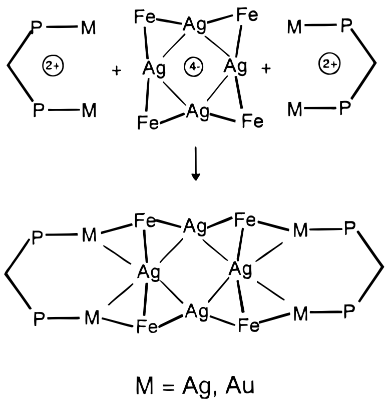
Scheme 1



$Ag_8\{\mu_3\text{-}Fe(CO)_4\}_4(dppm)_2$ species has been separated by differential solubility in organic solvents and crystallized from acetone−isopropyl alcohol (ν_{CO} in THF at 1982 s, 1920 sh, and 1902 s cm^{-1}). Although its absorption wavenumbers are very close to those of the $[Ag_{13}Fe_8(CO)_{32}]^{4-}$ tetraanion,[5,7] the two are readily distinguishable on the basis of their different IR pattern and solubility in THF. The $^{31}P\{^1H\}$ NMR spectrum of $Ag_8\{\mu_3\text{-}Fe(CO)_4\}_4(dppm)_2$ displays a AA′XX′ signal centered at δ +8.4 ppm from H_3PO_4 with a pattern very similar to that of $Ag_2(dppm)_2X_2$ (X= R−COO, BF_4)[18] and has been correspondingly interpreted, obtaining the parameters given in the Experimental Section.

The $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ species has also been obtained by reacting $Na_2[Fe(CO)_4]\cdot x$THF with $Ag_2(dppm)(NO_3)_2$ in a ca. 1:1 molar ratio in THF as solvent. Even if this reaction gives rise to $[Ag_4Fe_4(CO)_{16}]^{4-}$ as initial product, the composition of the final reaction mixture is even more complicated than above due to the additional presence of some $[Ag_3Fe(CO)_4(dppm)_3][NO_3]$,[19] which further hampers separation and purification of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$. Formation of the above cation is due to the too high dppm/Ag ratio of this alternative reagent mixture and can be avoided by in situ preparation of $[Ag_4Fe_4(CO)_{16}]^{4-}$ from a 1:1 molar mixture of $Na_2[Fe(CO)_4]\cdot x$THF and $AgNO_3$, followed by addition of a further equivalent of silver as $Ag_2(dppm)(NO_3)_2$ salt. However, under these conditions the $[Ag_{13}Fe_8(CO)_{32}]^{3-/4-}$ and $[Ag_6Fe_4(CO)_{16}]^{2-}$ side products were present as sodium salts, and their solubility was too similar to that of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ to allow a convenient separation. This could only be achieved by metathesis of the mixture with tetraethylammonium chloride.

Once isolated in a pure state, $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ is stable in several organic solvents, such as THF and acetone, under an inert atmosphere, even in the presence of free dppm added in 5-fold molar excess. This suggests that the $[Ag_{13}Fe_8(CO)_{32}]^{3-/4-}$ and $[Ag_6Fe_4(CO)_{16}]^{2-}$ side products arise either from disproportionation of an intermediate species such as the expected $[Ag_6\{Fe(CO)_4\}_4(dppm)]^{2-}$ or from side reactions of the starting $[Ag_4Fe_4(CO)_{16}]^{4-}$ salt with Ag^+ ions set free by $Ag_2(dppm)(NO_3)_2$. On the contrary, $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ readily disproportionates to $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ and $[Ag_2(dppm)_2]^{2+}$ in dichloromethane solution.

The corresponding reaction of $[NEt_4]_4[Ag_4Fe_4(CO)_{16}]$ with 2 mol of $Ag_2(dppe)(NO_3)_2$ gives rise to a red-brown solution, from which only the $[Ag(dppe)_2]^+$ salt of the $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ trianion could be isolated upon precipitation. IR monitoring of the above reaction suggests that labile Ag−Fe clusters containing phosphines as ancillary ligands may be intermediately obtained. Unfortunately, these decompose to the most stable $[Ag(dppe)_2]_3[Ag_{13}Fe_8(CO)_{32}]$ salt with time or upon precipitation. It is worth mentioning that also all attempts to obtain an $Ag_2Fe(CO)_4(PPh_3)_2$ species, corresponding to the well-known $Au_2Fe(CO)_4(PPh_3)_2$ compound,[9,10] or $Ag_8Fe_4(CO)_{16}(PPh_3)_4$, by reaction of $Ag(PPh_3)NO_3$ with either $Na_2[Fe(CO)_4]\cdot x$THF or $[NEt_4]_4[Ag_4Fe_4(CO)_{16}]$ in the required stoichiometric ratios, afforded only $[Ag(PPh_3)_4]_3[Ag_{13}Fe_8(CO)_{32}]$. The ionic nature of this product showing an $Ag_2Fe(CO)_4(PPh_3)_{1.5}$ empirical formula has been confirmed by an X-ray diffraction study.[20]

These results, as well as the synthesis of $Ag_6Fe_3(CO)_{12}\{(PPh_2)_3CH\}$[4] and $[Ag_3Fe(CO)_4(dppm)_3]^+$,[19] outline the importance of a polydentate nonchelating phosphine, as well as the concomitant presence of the highest possible fractional positive charge on silver, in stabilizing Ag−Fe carbonyl clusters containing phosphine as ancillary ligand for the latter.

The nature of the diphosphine ligand in the $M_2(P^\wedge P)^{2+}$ fragment is less relevant upon substitution of silver with gold, even if the resulting $Ag_4Au_4\{\mu_3\text{-}Fe(CO)_4\}_4(P^\wedge P)_2$ is less stable. Indeed, the condensation reaction of $Au_2(P^\wedge P)^{2+}$ moieties onto $[Ag_4Fe_4(CO)_{16}]^{4-}$ is much more simple and can be carried out by using $[Ag_4Fe_4(CO)_{16}]^{4-}$ as sodium salt (obtained in situ by reaction of $Na_2[Fe(CO)_4]\cdot x$THF and $AgNO_3$) both in THF and acetonitrile. In THF solution the condensation reaction of $Na_4[Ag_4Fe_4(CO)_{16}]$ with 2 equiv of $Au_2(P^\wedge P)Cl_2$ ($P^\wedge P$ = dppm and dppe) gives $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ in almost quantitative yields, and the compound has been isolated in 65−70% yields (based on gold) by filtration of the reaction solution and crystallization by precipitation with toluene. The corresponding condensation in acetonitrile directly leads to a red precipitate of the $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ neutral derivative and a solution that shows the additional presence of a species displaying infrared carbonyl absorptions in CH_3CN at 1973 and 1895 cm^{-1}. The latter might be either the $[Ag_4Au_2\{Fe(CO)_4\}_4(P^\wedge P)]^{2-}$ 1:1 condensation product or, more likely, $[Ag_4Au_2Fe_4(CO)_{16}]^{4-}$. Indeed, a species showing coincident infrared carbonyl absorptions has also been obtained by addition of 2 equiv of $Au(SEt_2)Cl$ to $[Ag_4Fe_4(CO)_{16}]^{2-}$. Owing to the presence of the above side product, under these experimental conditions $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ could be recovered by filtration only in 40−50% yields.

Both $Ag_4Au_4\{Fe(CO)_4\}_4(dppm)_2$ (ν_{CO} in THF at 1992 s, 1922 s cm^{-1}) and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ (ν_{CO} in THF at 1991 s, 1921 s cm^{-1}) have been conveniently crystallized as dark red crystals by extraction in THF and precipitation with toluene. Crystallization in other solvent mixtures results in $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ crystalline precipitates contaminated by other species and partial decomposition. For instance, crystallization of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ in acetone−isopropyl alcohol leads to mixtures of red crystals of the starting material, smaller amounts of yellow crystals of Au$_4$\{Fe-

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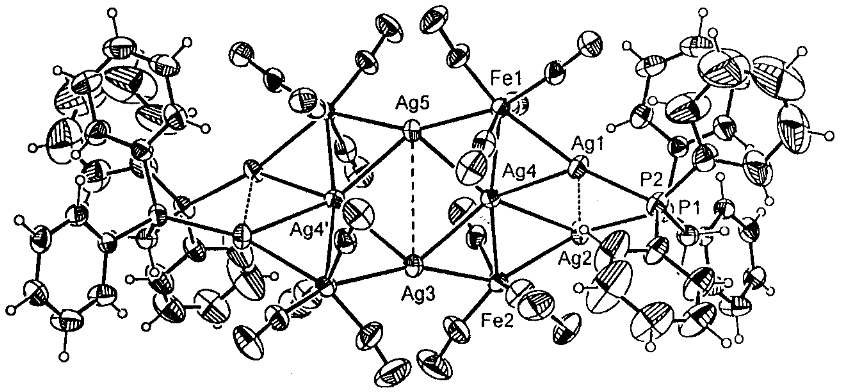

Figure 1. Molecular geometry of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and labeling of the independent atoms. The molecule sits on a 2-fold rotation axis lying along the short diagonal of the central Ag_4 rhombus. Contacts between coinage atoms are shown by dashed lines.

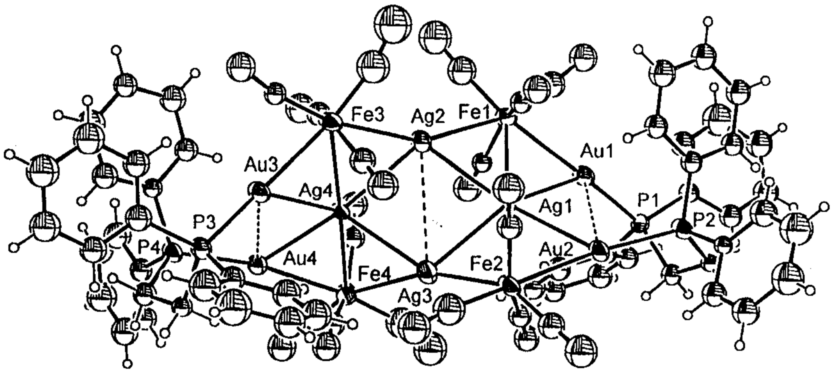

Figure 2. Molecular geometry and atom labeling of one of the two independent molecules (A) of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$.

$(CO)_4\}_2(dppe)_2$,[15] and a silver mirror. Moreover, $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ is rapidly decomposed by contact with air or upon deliberate addition of chloride ions. IR monitoring of the latter reaction shows the formation of $[Au_3\{Fe(CO)_4\}_2(P^\wedge P)]^-$ [11] and $[HFe(CO)_4]^-$; concomitantly, a precipitate of silver chloride and a silver mirror separates out.

The $^{31}P\{^1H\}$ NMR spectrum of $Ag_4Au_4\{\mu_3\text{-}Fe(CO)_4\}_4(P^\wedge P)_2$ in THF or acetone solution is more complicated than expected. It consists of two poorly resolved doublets and one singlet ($P^\wedge P$ = dppm, THF, δ +42.8 (d, 1.0), +42.7 (d, 4.1), and +37.6 (s, 1.1); $P^\wedge P$ = dppe, acetone, δ +48.2 (d, 1.0), +47.7 (d, 3.5), and +38.3 (s, 1.1) ppm; figures in parentheses represent the relative intensities). The apparent coupling constants of the doublets are comprised in the 2−3.8 Hz range of values and can only be due to coupling with the $^{107/109}Ag$ atoms at formal two (P−Au−Ag) or three (P−Au−Fe−Ag) bond distance from phosphorus. Conformational isomers are very unlikely owing to the preference for linear Fe−M−Fe and Fe−M−P coordination of both gold and silver. The observed multiplicity of the signals and their relative intensities indicate the coexistence in solution of $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ (most intense doublet) and solvent-separated or -unseparated $[Ag_4Au_2\{Fe(CO)_4\}_4(P^\wedge P)]^{2-}$ (least intense doublet) and $[Au_2(P^\wedge P)]^{2+}$ (singlet) ion pairs. Indeed, a stretching of the Au−Fe bonds of one $[Au_2(P^\wedge P)]^{2+}$ unit could be sufficient to lose the above very weak coupling. Moreover, the known ^{31}P chemical shifts of $Au_2(dppm)Cl_2$ (δ +23.5 in $CDCl_3$)[21] and $Au_2(dppe)Cl_2$ (δ +31.5 in $CDCl_3$)[22] are of little help in making the assignment. Solvent-unseparated ion pairs seem, however, more likely since the IR spectra do not display any new feature. Variable-temperature NMR and solvent effect studies have been precluded by their limited solubility and stability. Furthermore, addition of chloride ions in the NMR tube, aimed at trapping the $[Au_2(P^\wedge P)]^{2+}$ unit, led to decomposition.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$

Ag(1)−Ag(2)	3.138(1)	Ag(1)−Ag(4)	2.833(1)
Ag(2)−Ag(4)	2.829(1)	Ag(3)−Ag(4)	2.796(1)
Ag(4)−Ag(5)	2.802(1)	Ag(4)···Ag(4′)	4.201(2)
Ag(3)···Ag(5)	3.701(1)	Ag(2)−P(1)	2.400(2)
Ag(1)−P(2)	2.404(2)	Ag(1)−Fe(1)	2.617(1)
Ag(4)−Fe(1)	2.660(2)	Ag(5)−Fe(1)	2.644(1)
Ag(2)−Fe(2)	2.608(1)	Ag(4)−Fe(2)	2.664(1)
Ag(3)−Fe(2)	2.666(1)	Ag···C(CO)	2.58−2.79
Fe(2)−Ag(3)−Fe(2′)	158.69(6)	Fe(1)−Ag(5)−Fe(1′)	154.99(6)
P(1)−Ag(2)−Fe(2)	162.06(7)	P(2)−Ag(1)−Fe(1)	163.97(7)

The molecular structures of both $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ have been investigated by X-ray diffraction studies and are reported in Figures 1 and 2, respectively. The most relevant interatomic distances are reported in Tables 1 and 2. The molecular connectivity and conformation in the two species are strictly comparable, and the metal atom framework can be described as a two-dimensional triangulated ribbon twisted around the elongation direction. This confor-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for A and B Independent Molecules of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$

	A	B		A	B
Ag(1)−Ag(2)	2.782(4)	2.751(4)	Ag(1)−Ag(3)	2.768(4)	2.762(4)
Ag(3)−Ag(4)	2.767(4)	2.765(4)	Ag(2)−Ag(4)	2.791(4)	2.773(4)
Ag(1)−Au(1)	2.793(2)	2.767(2)	Ag(1)−Au(2)	2.815(3)	2.824(3)
Au(1)−Au(2)	3.381(2)	3.518(2)	Ag(4)−Au(4)	2.792(3)	2.794(3)
Ag(4)−Au(3)	2.793(3)	2.786(2)	Au(3)−Au(4)	3.367(2)	3.488(2)
Ag(2)···Ag(3)	3.473(4)	3.294(4)	Ag(1)···Ag(4)	4.334(4)	4.434(4)
Au(4)−P(4)	2.265(9)	2.272(9)	Au(3)−P(3)	2.300(8)	2.295(8)
Au(1)−P(1)	2.304(8)	2.308(8)	Au(2)−P(2)	2.256(9)	2.27(1)
Ag(3)−Fe(2)	2.679(7)	2.708(7)	Ag(1)−Fe(2)	2.681(5)	2.657(5)
Au(2)−Fe(2)	2.551(5)	2.546(5)	Ag(2)−Fe(1)	2.669(5)	2.691(5)
Ag(1)−Fe(1)	2.648(5)	2.650(5)	Au(1)−Fe(1)	2.621(5)	2.605(5)
Ag(3)−Fe(4)	2.691(7)	2.711(7)	Ag(4)−Fe(4)	2.708(5)	2.691(5)
Au(4)−Fe(4)	2.565(5)	2.561(5)	Ag(2)−Fe(3)	2.674(5)	2.695(5)
Ag(4)−Fe(3)	2.665(5)	2.643(5)	Au(3)−Fe(3)	2.621(5)	2.608(5)
Ag/Au···C(CO)	2.53−2.85	2.53−2.85			
P(2)−Au(2)−Fe(2)	169.9(3)	172.9(3)	P(1)−Au(1)−Fe(1)	162.5(3)	162.7(3)
P(4)−Au(4)−Fe(4)	169.4(3)	171.1(3)	P(3)−Au(3)−Fe(3)	163.4(3)	165.7(3)
Fe(2)−Ag(3)−Fe(4)	160.0(2)	160.3(2)	Fe(1)−Ag(2)−Fe(3)	155.3(2)	154.9(2)

mational feature makes the molecules chiral, and the crystals contain racemic mixtures of enantiomers deriving from opposite spiralization. The carbonyl ligands belong primarily to the $Fe(CO)_4$ groups in C_{2v} idealized geometry with only secondary interactions with the coinage metal atoms. The diphosphine ligands act as bidentate and saturate the terminal coinage metals, thus preventing further condensation of the constituent units (vide infra). Both molecules conform to a C_2 symmetry that is crystallographically imposed for the Ag_8 molecule and only idealized for the Ag_4Au_4 species. If carbon and oxygen atoms are ignored, the idealized symmetry of the heavy atom frames is D_2. The metal atom array is organized around a central Ag_4 diamond whose edges are spanned by $Fe(CO)_4$ groups lying alternately above and below the Ag_4 plane. The opposite vertexes defining the long diagonal of the diamond are bonded to Ag_2(dppm) and Au_2(dppe) fragments, respectively. The latter units are significantly rotated with respect to the diamond plane [55.20(3)° for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and 57.6_{av}° for $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$] according to the 2-fold symmetry axis located along the short diagonal of the diamond. This rationalization of the metal atom assembly points out that the molecules are formed by simple condensation of two $[Ag_2(dppm)]^{2+}$ or $[Au_2(dppe)]^{2+}$ dications on opposite atoms of the square tetraanion $[Ag_4Fe_4(CO)_{16}]^{4-}$.[6] No bond breaks down in the process, and a major change is a squeezing of the Ag_4 rectangle into a rhombus (contacts along the short diagonal 3.701(1) Å in the Ag_8 species and 3.473 and 3.294(4) Å in the Ag_4Au_4 species). The out-of-plane positions of the $Fe(CO)_4$ groups are caused by the tilted conformation of the $M_2(P^\wedge P)$ units. The twisted overall geometry of the molecules seems dictated by the need to achieve the preferred linear coordination of the Ag and Au atoms [P−Ag−Fe(av) 163.0° or P−Au−Fe(av) 167.2°, Fe−Ag−Fe(av) 164.3°].

Conclusions

The structure of the $Ag_8\{\mu_3\text{-}Fe(CO)_4\}_4(dppm)_2$ species envisions a possible reaction course from $[Ag_4Fe_4(CO)_{16}]^{4-}$ to $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ upon addition of Ag^+ ions, which does not implicate the intermediate formation of a purported $[Ag_6Fe_4(CO)_{16}]^{2-}$ species,[7] isostructural with $[Cu_6Fe_4(CO)_{16}]^{2-}$.[16] Indeed, the condensation of $[Ag_4Fe_4(CO)_{16}]^{4-}$ ions with nonbonded $Ag_2{}^{2+}$ moieties (as well as the rearrangement of $[Ag_5Fe_4(CO)_{16}]^{3-}$ upon addition of an Ag^+ ion) could give rise to $[\{Ag\}_{2n}\{Ag_4Fe_4(CO)_{16}\}_n]^{2n-}$ ($n \geq 1$) oligomers, which preserve the favored ν_2-square Ag_4Fe_4 motif, rather than involve the less favorable ν_2-triangular M_3Fe_3 moiety of the related $[Cu_3Fe_3(CO)_{12}]^{3-}$ and $[Cu_6Fe_4(CO)_{16}]^{2-}$ pair of compounds.[16,17] For instance, wrapping of two $[\{Ag\}_2\{Ag_4Fe_4(CO)_{16}\}]^{2-}$ moieties around an Ag^+ ion could directly give rise to the structure of $[Ag_{13}Fe_8(CO)_{32}]^{3-}$. This alternative reaction pathway would take into account the insolubility of all purported $[Ag_6Fe_4(CO)_{16}]^{2-}$ salts.[7] In conclusion, it seems reasonable to suggest that the twisted ribbonlike metal frame of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ represents a fragment of the above oligomers intercepted and stabilized by ancillary phosphine ligands. Furthermore, the present synthesis of $Ag_4Au_4\{Fe(CO)_4\}_4(P^\wedge P)_2$ from the $[Ag_4Fe_4(CO)_{16}]^{4-}$ ion and the previously reported synthesis of its $[Au_4Fe_4(CO)_{16}]^{4-}$ congener[23] may anticipate the possible existence of a related $Au_8\{Fe(CO)_4\}_4(P^\wedge P)_2$ neutral species.

Experimental Section

All reactions including sample manipulations were carried out using standard Schlenk techniques under nitrogen and in carefully dried solvents. The $[NEt_4]_4[Ag_4Fe_4(CO)_{16}]$ and $Na_2[Fe(CO)_4]\cdot x$THF salts have been prepared according to the literature.[7,24] Analyses of Fe, Ag, and Au were performed by atomic absorption. Infrared spectra were recorded using CaF_2 cells.

Synthesis of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$. Solid $[NEt_4]_4[Ag_4Fe_4(CO)_{16}]$ (1.51 g, 0.93 mmol) and $Ag_2(dppm)(NO_3)_2$ (1.45 g, 2.0 mmol) were mixed in a 100 mL flask under a nitrogen atmosphere. Anhydrous CH_3CN (30 mL) was added, and the suspension was stirred for 6 h. After this period of time a precipitate of $[NEt_4]_2[Ag_6Fe_4(CO)_{16}]$ is formed, and IR monitoring of the surnatant solution showed the presence of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$, $[Ag_{13}Fe_8(CO)_{32}]^{3-}$, and trace amounts of $Fe(CO)_4$(dppm). The suspension was filtered, and the resulting orange solution was evaporated to dryness under vacuum. The residue was washed with water (20 mL) and toluene (10 mL).

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Table 3. Crystal Data and Experimental Details for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$

formula	$C_{66}H_{44}Ag_8Fe_4O_{16}P_4$	$C_{68}H_{48}Ag_4Au_4Fe_4O_{16}P_4$
M	2303.25	2687.69
temp, K	293(2)	293(2)
wavelength, Å	0.71069	0.71069
crystal symmetry	tetragonal	triclinic
space group	$I4_1/a$ (No. 88)	$P\bar{1}$ (No. 2)
a, Å	19.981(5)	19.621(7)
b, Å	19.981(5)	20.672(7)
c, Å	37.024(6)	21.181(6)
α, deg	90	97.49(3)
β, deg	90	89.61(3)
γ, deg	90	114.72(2)
cell volume, Å^3	14 782(6)	7726
Z	8	4
D_c, Mg m^{-3}	2.070	2.311
μ(Mo Kα), mm^{-1}	2.976	9.421
F(000)	8864	5008
crystal size, mm	0.20 × 0.21 × 0.22	0.12 × 0.20 × 0.27
θ limits, deg	2.5−25	2.5−20
scan mode	ω	ω
no. of rflns collected	25 291($\pm h$, $\pm k$, $\pm l$)	14 743($\pm h$, $\pm k$, $+l$)
no. of unique obsd rflns [$F_o > 4\sigma(F_o)$]	3708	6467
goodness of fit on F^2	1.053	0.993
R1(F),[a] wR2(F^2)[b]	0.0449, 0.0790	0.0580, 0.1370
weighting scheme a, b	0.0244, 93.3550	0.0954, 109.2737[b]
largest diff peak and hole, e Å^{-3}	0.637 and −0.815	1.638 and −1.615

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Extraction of the residue in THF (30 mL) followed by filtration afforded a orange-red solution containing crude $Ag_8\{Fe(CO)_4\}_4(dppm)_2$. This was purified by evaporating the THF in vacuo, dissolving the residue in acetone (25 mL), and precipitation by diffusion of isopropyl alcohol (40 mL). Yields: 0.42 g of $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ as shiny red crystals. Anal. Found (Calcd): Ag 37.25 (37.47), Fe 9.54 (9.70), C 34.56 (34.39), H 1.98 (1.91). ^{1}H NMR: δ 3.7 (m, 2H, CH_2), 7.07−7.65 (m, 10H, Ph). ^{31}P {^{1}H} NMR: AA′XX′ pattern centered at δ +8.43 ($J_{P-^{109}Ag}$ 477, $J_{P-^{107}Ag}$ 414, J_{P-P} 167, $^3J_{P-^{109}Ag}$ −4.3, and $^3J_{P-^{107}Ag}$ −1.8 Hz). The compound is soluble in THF and acetone, sparingly soluble in acetonitrile, and insoluble in toluene, *n*-heptane, alcohol, and water.

Synthesis of $Ag_4Au_4\{Fe(CO)_4\}_4(dppm)_2$. Solid $Na_2[Fe(CO)_4]\cdot x$THF ($x \sim 2$, 0.68 g, ca. 1.9 mmol) and $AgNO_3$ (0.31 g, 1.82 mmol) were mixed in a 100 mL flask under a nitrogen atmosphere. Anhydrous THF (30 mL) was added, and the suspension was rapidly stirred for 6 h. After this period of time IR monitoring showed the presence of the carbonyl absorptions of $[Ag_4Fe_4(CO)_{16}]^{4-}$. Solid $Au_2(dppm)Cl_2$ (0.77 g, 0.91 mmol) was added, and the supension was stirred for ca. 3 h until quantitative formation of $Ag_4Au_4\{Fe(CO)_4\}_4(dppm)_2$ was monitored by IR. The suspension was filtered under nitrogen, and the solution was precipitated by diffusion of toluene (40 mL) to give 0.58 g of $Ag_4Au_4\{Fe(CO)_4\}_4(dppm)_2$ as red crystals. Another 0.27 g of product was collected after crystallization of the residue obtained upon evaporation of the mother liquor of the first crystallization. Anal. Found (Calcd): Ag 16.09 (16.23), Au 29.37 (29.63), Fe 8.25 (8.40), C 29.85 (29.79), H 1.74 (1.65). The compound is soluble in THF and acetone, sparingly soluble in acetonitrile, and insoluble in toluene, *n*-heptane, alcohol, and water.

Synthesis of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$. Solid $Na_2[Fe(CO)_4]\cdot x$THF ($x \sim 2$, 0.52 g, ca. 1.45 mmol) and $AgNO_3$ (0.24 g, 1.41 mmol) were mixed in a 100 mL flask under a nitrogen atmosphere. Anhydrous THF (30 mL) was added, and the suspension was rapidly stirred for 6 h. After this period of time IR monitoring showed the presence of the carbonyl absorptions of $[Ag_4Fe_4(CO)_{16}]^{4-}$. Solid $Au_2(dppe)Cl_2$ (0.62 g, 0.72 mmol) was added, and the supension was stirred for ca. 3 h until quantitative formation of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ was monitored by IR. The suspension was filtered under nitrogen, and the solution was precipitated by diffusion of toluene (40 mL) to give 0.47 g of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ as red crystals. Another 0.18 g of product was collected by crystallization of the residue obtained upon evaporation of the mother liquor. Anal. Found (Calcd): Ag 16.18 (16.05), Au 29.16 (29.31), Fe 8.21 (8.31), C 30.43 (30.47), H 1.69 (1.79). The compound is soluble in THF and acetone, sparingly soluble in acetonitrile, and insoluble in toluene, *n*-heptane, alcohol, and water.

Crystallography. Crystal data and experimental details for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. A significant decay (40%) was observed in $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$, for which the data collection was limited at $\theta = 20°$ and corrected.

An empirical absorption correction was applied in both compounds by using the azimuthal scan method.[25] Direct methods (SHELXS 86)[26] identified the positions of the metal atoms and iterative cycles of least-squares refinement (on F^2), and difference Fourier synthesis located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions (C−H = 0.97 Å) for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$. The molecule sits around a 2-fold symmetry axis in the crystal.

Two independent molecules of $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ have been found in the crystal; they have the same stereogeometry including the conformations of the diphosphine rings. Some differences are observed only in the softer metal−metal interactions and conformational details of the phenyl rings. The final refinement (on F^2) of all positional and thermal parameters for $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ proceeded by full-matrix least-squares calculations (SHELXL 93)[27] using anisotropic thermal parameters for the heavy atoms (Au, Ag, Fe,

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[26] Sheldrick, G. M. *SHELXS 86*, Program for crystal structure solution; University of Göttingen, 1986.

[27] Sheldrick, G. M. *SHELXL 93*, Program for crystal structure refinement; University of Göttingen, 1993.

P) and isotropic for all the remaining atoms due to unfavorable observations-to-parameters ratio.

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Supporting Information Available: Tables of crystal data and data collection details, fractional coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters for $Ag_8\{Fe(CO)_4\}_4(dppm)_2$ and for $Ag_4Au_4\{Fe(CO)_4\}_4(dppe)_2$ (40 pages). Ordering information is given on any current masthead page.

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