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Metal–Metal Cooperation via 1,1′-Bis(diphenylphosphino)ferrocene (Dppf). 1. Structurally Distinctive Silver(I) Dppf Complexes of Nitrato and Carboxylato Ligands in Variable Coordination Modes. Crystal Structures of $[Ag(NO_3)(dppf)]_2{\cdot}2CHCl_3$, $[Ag_2(HCO_2)_2(dppf)_3]{\cdot}2CH_2Cl_2$, $[Ag_2(CH_3CO_2)_2(dppf)]_2$, and $Ag_2(C_6H_5CO_2)_2(dppf)$

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Reaction between $AgNO_3$ and 1,1′-bis(diphenylphosphino)ferrocene (dppf) gives the dimeric $[Ag(NO_3)(dppf)]_2$ (**1**). In the presence of Na^+X^-, where X = CH_3CO_2, $C_6H_5CO_2$, and HCO_2, $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**), $[Ag_2(C_6H_5CO_2)_2(dppf)]$ (**3**), and $[Ag_2(HCO_2)_2(dppf)_3]$, (**4**), respectively, are formed. X-ray crystallographic studies of these compounds revealed that they are all structurally distinct. Compound **1** consists of an unprecedented $\{Ag_2(\mu\text{-dppf})_2\}$ metallacyclic framework stabilized by two "semibridging–semichelate" nitrato ligands. Compound **2** consists of a chair-conformation arrangement of four tetrahedral Ag(I) centers interlinked by two bridging *syn*-dppf, and two chelate-bridging (μ_2-(η^2-O, η^1-O′)) and two triply bridging (μ_3-(η^2-O, η^1-O′)) acetato ligands. Compound **3** consists of two trigonal planar Ag(I) moieties triply bridged by dppf (syn) and two benzoato fragments. Both **2** and **3** are examples of molecules stabilized by only bridging ligands. The structure of **2** may be viewed as a dimer of **3**. Compound **4** uniquely contains a unidentate formato ligand and both chelating (syn) and bridging (anti) dppf in a dinuclear framework. Molecules **1**, **2**, and **4** are centrosymmetric. The structures of **2**–**4** illustrate the variability of carboxylates in their ligation modes, their abilities to stabilize 18- and 16-electron silver(I) in its tetrahedral and trigonal planar geometries, and their influence on the nuclearity of the complexes. All the structures demonstrate the adaptability of dppf in its coexistence with ligands of much smaller bite size. Crystal data: for **1**, space group = $P2_1/n$ (No. 14), a = 13.908 (5) Å, b = 15.626 (9) Å, c = 18.674 (9) Å, β = 102.07 (2)°, Z = 2, 3579 reflections, R = 0.079; for **2**, space group = $P2_1/n$ (No. 14), a = 10.373 (2) Å, b = 17.593 (5) Å, c = 19.754 (8) Å, β = 100.66 (2)°, Z = 2, 4580 reflections, R = 0.042; for **3**, space group = $Pbca$ (No. 61), a = 10.532 (2) Å, b = 18.851 (9) Å, c = 41.74 (2) Å, Z = 8, 3059 reflections, R = 0.0312; for **4**, space group = $C2/c$ (No. 15), a = 41.79 (1) Å, b = 10.70 (1) Å, c = 24.73 (1) Å, β = 110.43 (3)°, Z = 4, 3986 reflections, R = 0.070.

Introduction

The versatile nature of 1,1′-bis(diphenylphosphino)ferrocene (dppf) as a ligand has attracted considerable attention recently because of its possible relevance to the catalytic activities of many of its complexes.[1] The unique ability of this metalloligand to modify its steric bite by ring twisting and tilting in order to adapt to different geometric requirements of the metal centers to which it is attached has led to its stabilization of not only the usual chelates[2] but also the open,[3] half-closed,[4] and closed[5] bridging systems. Recent findings have further reiterated the ability for dppf to span over a wide range of metal–metal distances, ranging from over 7 Å in $M_2(CO)_{10}$ (μ-dppf) (M = Cr, Mo)[3b] to 2.520 Å in the $Co_3(CCH_3)(CO)_7(dppf)$ cluster.[3a] The high tendency for Ag(I) to show a variable nuclearity in its phosphine complexes[6] and the geometrical variations of the metal itself make it an attractive model for structural studies. To date there has been no report describing the behavior of Ag(I) toward dppf. Herein reported are the molecular structures of the products from the reactions of dppf with Ag^+X^-, where X = NO_3, CH_3CO_2, $C_6H_5CO_2$, and HCO_2. It is our interest to examine if the sterically demanding dppf and ligands of much smaller bites such as NO_3^- and carboxylates can coexist as bridging ligands, if such cobridging can induce a greater cooperation between the otherwise unperturbed metal spheres, if dppf can give isostructural complexes to some known dppm and PPh_3 complexes of Ag(I), and if one can observe different ligating forms of the carboxylates and nitrate

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by tuning the torsional angle of the Cp rings, and hence the coordination mode, of dppf in these Ag(I) complexes.

Experimental Section

General Procedures. All reactions were performed shielded from light under pure dry argon using standard Schlenk techniques. Chemical reagents were supplied from commercial sources and used without further purification. All solvents were Analar grade and freshly distilled dried before use. Elemental analyses were performed by the analytical service of the Chemistry Department in the National University of Singapore (NUS). ^1H NMR spectra were recorded using a JOEL FX 90Q spectrometer at 89.55 MHz with Me_4Si as internal standard or a Bruker WM-250 instrument at 250.13 MHz referenced to the residual solvent (CD_2Cl_2) peak. ^{31}P spectra were recorded on the same spectrometers at 36.23 and 101.26 MHz, respectively. Chemical shifts are reported in ppm to high frequency of external 85% H_3PO_4. $^{13}C\{^1H\}$ spectra were measured by the WM-250 at 62.81 MHz referenced to solvent CD_2Cl_2 peak. Infrared spectra in KBr disc were run on a FT-IR Perkin-Elmer 1710 spectrometer. Conductivities were measured using a conductivity 1000 electronic conductiometer with a cell constant of 0.55 cm^{-1}. Molecular weight measurements were carried out at Galbraith Laboratories, Inc., Knoxville, TN, using vapor pressure osmometry.

Synthesis of [Ag(NO$_3$)(dppf)]$_2$ (1) and [Ag$_2$(NO$_3$)$_2$(dppf)]$_n$. $AgNO_3$ (0.306 g, 1.8 mmol) in MeOH (30 cm^3) was transferred dropwise via a PTFE delivery tube to a thf solution (20 cm^3) of dppf (0.502 g, 0.9 mmol). A yellow precipitate began to form halfway through the addition. Upon completion of addition, the resultant suspension was stirred at rt for 30 min. The yellow precipitate thus obtained was isolated by filtration and recrystallized from CH_2Cl_2/MeOH to give yellow [Ag(NO$_3$)(dppf)]$_2$·0.5CH$_2$Cl$_2$ (0.153 g, 24%). Anal. Found: C, 55.68; H, 3.86; N, 1.93; Ag, 14.62; Fe, 7.44; P, 8.53. Calcd for $C_{68.5}Hg_{57}Ag_2ClFe_2N_2O_6P_4$: C, 55.12; H, 3.85; N, 1.88; Ag, 14.47; Fe, 7.49, P, 8.31%. IR: $\nu_{max}(NO_3^-)$ 1385 s, 1284 m cm^{-1} (KBr). NMR: $\delta_H(CDCl_3)$ 7.67–7.43 (m, 40 H, Ph), 4.29 (s, 16 H, Cp); $\delta_P(CDCl_3)$ –0.94 (s). Molar conductivity Λ_m: 96.4 (CH_3NO_2), 94.6 Ω^{-1} cm^2 M^{-1} (DMSO). The filtrate was concentrated in vacuo to ca. 5 cm^3. The orange precipitate thus formed was filtered out and recrystallized from MeOH solution to give [Ag$_2$(NO$_3$)$_2$(dppf)]$_n$ (0.256 g). Anal. Found: C, 45.64; H, 3.21; N, 3.11; Ag, 23.27; Fe, 6.11; P, 6.96. Calcd for $C_{34}H_{28}Ag_2FeN_2O_6P_2$: C, 45.67; H, 3.16; N, 3.13; Ag, 24.13; Fe, 6.25, P, 6.93. IR: $\nu_{max}(NO_3^-)$ 1385 s, 1280 m cm^{-1} (KBr). NMR: $\delta_H(CDCl_3)$ 7.58–7.32 (m, 20 H, Ph), 4.44 (br, s, 4 H, Cp), 4.11 (br, s, 4 H, Cp); $\delta_P(CDCl_3)$ 5.79 (s, br).

Synthesis of [Ag$_2$(CH$_3$CO$_2$)$_2$(dppf)]$_2$ (2). $NaCH_3CO_2$ (0.148 g, 1.8 mmol) in MeOH (20 cm^3) was added to a MeOH solution (20 cm^3) of $AgNO_3$ (0.306 g, 1.8 mmol) to give a white suspension of $AgCH_3CO_2$. A thf solution (20 cm^3) of dppf (0.501 g, 0.9 mmol) was introduced dropwise via a delivery tube to this suspension. The white $AgCH_3CO_2$ rapidly dissolved to give an orange solution, which was then heated to a gentle reflux for 30 min. Evaporation to ca. 5 cm^3 in vacuo gave an orange precipitate, which was recrystallized from MeOH to give [Ag$_2$(CH$_3$CO$_2$)$_2$(dppf)]$_2$ (0.578 g, 72%). Anal. Found: C, 50.99; H, 3.82; Ag, 22.46; Fe, 5.56; P, 7.67. Calcd for $C_{76}H_{68}Ag_4Fe_2O_8P_4$: C, 51.38; H, 3.87; Ag, 24.28; Fe, 6.29, P, 6.97. MW: 925 ($CHCl_3$, 1.77×10^{-2} M), 915 (CH_2Cl_2, 1.46×10^{-2} M). IR: ν_{max} ($CH_3CO_2^-$) 1548 s (br), 1408 m, 1398 m (sh) (KBr), 1572 vs, 1415 m, 1388 m cm^{-1} ($CHCl_3$). NMR: δ_H (2.82×10^{-2} M, CD_2Cl_2) 7.51–7.37 (m, Ph), 5.24 (s, Cp), 4.58 (s, Cp), 4.51 (s, Cp), 4.46 (s, Cp), 3.92 (s, Cp), 3.86 (s, Cp), 3.80 (s, Cp), 2.12 (s, AcO), 2.08 (s, AcO), 2.00 (s, AcO), 1.94 (s, AcO) (23 °C); 7.40 (s, br, Ph), 4.43 (s, br, Cp), 3.68 (s, br, Cp), 2.00 (s, AcO), 1.98 (s, AcO) (–55 °C); δ_H (1.52×10^{-1} M, CD_2Cl_2) 7.60–7.40 (m, Ph), 4.54 (s, Cp), 3.89 (s, Cp), 2.01 (s, AcO) (23 °C); 7.41–7.38 (m, Ph), 4.45 (s, br, Cp), 3.72 (s, br, Cp), 2.01 (s, AcO), 1.98 (s, AcO) (–18 °C); 7.41–7.38 (m, Ph), 4.45 (s, br, Cp), 3.72 (s, br, Cp), 2.01 (s, AcO), 1.98 (s, AcO) (–40 °C); 7.37 (s, br, Ph), 4.40 (s, br, Cp), 3.65 (s, br, Cp), 2.01 (s, AcO), 1.92 (s, AcO) (–55 °C); 7.34 (s, br, Ph), 4.32 (v br, Cp), 3.55 (v br, Cp), 2.00 (s, AcO), 1.88 (s, AcO) (–65 °C); 7.71–7.09 (m, Ph), 4.78 (s, br, Cp), 4.25 (s, br, Cp), 4.01 (s, br, Cp), 2.96 (s, br, Cp), 2.00 (s, br, AcO) (–90 °C); δ_P (2.82×10^{-2} M, CD_2Cl_2) 4.98 (s, Br), 4.78 (d, br; J(AgP) = 630 Hz) (23 °C); 4.31 (dd; $J(^{107}AgP)$ = 660 Hz, $J(^{109}AgP)$ = 759 Hz) (–55 °C); δ_P (1.52×10^{-1} M, CD_2Cl_2) 4.91 (s, br) (23 °C); 4.5 (s, br), 4.49 (d; J(AgP) = 699 Hz) (–5 °C); 4.43 (d; J(AgP) = 703 Hz) (–18 °C); 4.29 (dd; $J(^{107}AgP)$ = 661 Hz) (–40 °C); 4.17 (dd; $J(^{107}AgP)$ = 661 Hz) (–55 °C); 4.10 (dd; $J(^{107}AgP)$ = 661 Hz) (–65 °C); 4.67 (dd; $J(^{107}AgP)$ = 660 Hz) (–90 °C); $\delta_C\{^1H\}(CD_2Cl_2)$ 179.50 ($CH_3\mathit{C}O_2$), 134.46, 134.17, 131.43, 129.72, 129.59 (Ph), 77.01, 76.76, 74.02 ($Ph_2P\mathit{Cp}$), 24.09 ($\mathit{C}H_3CO_2$); $\delta_P(CDCl_3)$ 6.86 (br). Molar conductivity Λ_m: 7.3 Ω^{-1} cm^2 mol^{-1} ($C_6H_5NO_2$).

Synthesis of Ag$_2$(C$_6$H$_5$CO$_2$)$_2$(dppf) (3). $NaC_6H_5CO_2$ (0.169 g, 1.17 mmol) was added to a methanolic solution (20 cm^3) of $AgNO_3$ (0.199 g, 1.17 mmol) to give a white suspension of $AgC_6H_5CO_2$. A thf solution (17 cm^3) of dppf (0.325 g, 0.586 mmol) was added dropwise to this suspension, and the reaction was stirred at rt for 0.5 h. The only product, a yellow precipitate, isolated was recrystallized from CH_2Cl_2/MeOH. Yield: 0.282 g (48%). Anal. Found: C, 56.88; H, 3.69; Ag, 21.98; Fe, 5.72; P, 6.55. $C_{48}H_{38}Ag_2FeO_4P_2$: C, 56.95; H, 3.79; Ag, 21.31; Fe, 5.52; P, 6.12. IR: $\nu_{max}(C_6H_5CO_2^-)$ 1544 s, 1375 s cm^{-1} (KBr). NMR: $\delta_H(CDCl_3)$ 8.095–7.220 (m, 38 H, Ph), 4.618 (br, 4 H, Cp); 3.945 (br, 4 H, Cp); $\delta_P(CDCl_3)$ 6.326 (s, br), 6.192 (d, br; J(AgP) = 703 Hz).

Synthesis of Ag$_2$(HCO$_2$)$_2$(dppf)$_3$ (4). A similar procedure was adopted from the acetato complex by using $NaHCO_2$ (0.049 g, 0.75 mmol), $AgNO_3$ (0.128 g, 0.5 mmol), and dppf (0.446 g, 0.75 mmol) as the substrates in a MeOH/thf solvent mixture. The product could be purified, as CH_2Cl_2 solvate, by recrystallization from MeOH alone or CH_2Cl_2/hexane. Yield: 0.208 g (59%). Anal. Found: C, 60.90; H, 4.20; Ag, 10.35; Fe, 8.85; P, 7.97. Calcd for $C_{105}H_{88}Ag_2Cl_2Fe_3O_4P_6$: C, 61.33; H, 4.28; Ag, 10.50; Fe, 8.16, P, 9.05%. NMR $\nu_{max}(HCO_2^-)$ 1628 w, 1296 m cm^{-1} (KBr); $\delta_H(CDCl_3)$ 7.26–7.07 (m, 60 H, Ph), 4.34 (br, 12 H, Cp); 4.08 (br, 12 H, Cp); $\delta_P(CDCl_3)$ 0.27 (br), –4.71 (br).

Crystallographic Analysis. Crystals of compound **1** were grown by a layering method with hexane on the sample solution in chloroform at rt (25 °C). Crystals of compounds **2**–**4** were grown under similar conditions with hexane on dichloromethane solutions. All data crystals were mounted in thin-walled Lindemann glass capillaries under an atmosphere of nitrogen. Diffraction measurements were made at rt. Compounds **2** and **3** were mounted in an inert matrix of nitrogen. Compounds **1**–**3** were sealed in their mother liquor. Diffraction measurements were made on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation. Determination of the crystal class, orientation matrices, and cell dimensions were performed according to established procedures.[7] Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a DEC Micro VAX-II computer with the SHELXTL-PLUS program package.[8] Analytical expressions of neutral-atom scattering factors were employed, and anomalous corrections were incorporated.[9] The raw data were processed with the learnt-profile procedure,[10] and absorption corrections were applied by fitting a pseudoellipsoid to the ω-scan data of selected reflections over a range of 2θ angles.[11]

All the structures were solved with the Patterson superposition method. The positions of all hydrogen atoms were generated geometrically (C–H bonds fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms. In the course of the analysis, **1** and **4** were found to contain two independent solvent molecules (of $CHCl_3$ and CH_2Cl_2, respectively) of half site occupancy. They were included in the analysis and satisfactorily refined. Atomic positional parameters of compounds **1**–**4** are listed in Tables II, IV, VI, and VIII, and selected interatomic distances and bond angles, in Tables III, V, VII, and IX, respectively. Tables of hydrogen atom positional parameters and anisotropic thermal parameters for structures **1**–**4** are available with the supplementary material.

Results

Reaction between $AgNO_3$ and dppf in a 2:1 molar ratio led to the isolation of yellow [Ag(NO$_3$)(dppf)]$_2$ (**1**) and orange [Ag$_2$(dppf)(NO$_3$)$_2$]$_n$ (**1a**) as two principal products. The structure of the latter is unknown as its single crystals decomposed readily upon X-ray irradiation in the process of data collection. Complex **1** partially ionizes to give a 1:1 electrolyte in nitromethane. There is no apparent equilibrium between **1** and **1a** in the medium of synthesis.

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Table I. Crystallographic Data for $[Ag(NO_3)(dppf)]_2\cdot 2CHCl_3$ (**1**), $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**), $Ag_2(C_6H_5CO_2)_2(dppf)$ (**3**), and $[Ag_2(HCO_2)_2(dppf)_3]\cdot 2CH_2Cl_2$ (**4**)

	1	2	3	4
formula	$C_{68}H_{56}N_2Ag_2Fe_2O_6P_4\cdot C_2H_2Cl_6$	$C_{76}H_{68}Ag_4Fe_2O_2P_2$	$C_{48}H_{38}Ag_2FeO_4P_2$	$C_{104}H_{86}Ag_2Fe_3O_4P_6\cdot C_2H_4Cl_4$
fw	1687.29	888.25	1012.39	2138.87
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic
lattice params				
a, Å	13.908 (5)	10.373 (2)	10.532 (2)	41.79 (1)
b, Å	15.626 (9)	17.593 (5)	18.851 (9)	10.70 (1)
c, Å	18.674 (9)	19.754 (8)	41.74 (2)	90.0
α, deg	90.0	90.0	90.0	90.0
β, deg	102.07 (2)	100.66 (2)	90.0	110.43 (3)
γ, deg	90.0	90.0	90.0	90.0
V, $Å^3$	3969 (3)	3542 (2)	8287.01 (5.8)	10367 (14)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	*C*2/*c* (No. 15)
Z	22	2	8	4
ρ_{calcd}, g/cm^3	1.412	1.665	1.621	1.37
μ(Mo Kα), cm^{-1}	11.68	16.15	13.92	10.20
T, °C	21	21	21	21
R^a	0.079	0.042	0.0312	0.070
$R_w{}^b$	0.090^c	0.053^d	0.0299^e	0.099^f

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} $w = [1 - \exp(-10 \sin \theta)^2/\lambda^2]/[\sigma^2|F_o| + 0.0005|F_o|^2]$. ^{d} $w = [\sigma^2|F_o| + 0.0010|F_o|^2]^{-1}$. ^{e} $w = [\sigma^2|F_o| + 0.0002|F_o|^2]^{-1}$. ^{f} $w = [\sigma^2|F_o| + 0.0018|F_o|^2]^{-1}$.

Table II. Atomic Coordinates (×10^5 for Ag; ×10^4 for Other Atoms) and Equivalent Isotropic Temperature Factors^a ($Å^2 \times 10^4$ for Ag, Fe, and P; $Å^2 \times 10^3$ for Other Atoms) for $[Ag(dppf)NO_3]_2\cdot 2CHCl_3$ (**1**)

atom	*x*	*y*	*z*	U_{eq}
Ag(1)	9121 (6)	9571 (6)	3090 (6)	742 (4)
Fe(1)	−2492 (1)	1546 (1)	385 (1)	552 (5)
P(1)	−2505 (2)	−610 (2)	−40 (2)	541 (8)
P(2)	−59 (2)	2196 (2)	511 (2)	547 (8)
O(1)	341 (5)	−249 (5)	974 (4)	59 (1)
O(2)	1333 (10)	417 (9)	1770 (6)	147 (2)
O(3)	579 (9)	−627 (8)	2055 (6)	130 (2)
N(1)	686 (9)	−167 (7)	1511 (9)	97 (2)
C(1)	−2923 (7)	482 (7)	−206 (5)	50 (1)
C(2)	−2489 (8)	1070 (7)	−627 (5)	58 (1)
C(3)	−3048 (8)	1833 (8)	−690 (6)	69 (2)
C(4)	−3807 (8)	1716 (8)	−322 (7)	73 (2)
C(5)	−3736 (7)	892 (7)	0 (6)	64 (2)
C(18)	−1153 (7)	2037 (7)	869 (5)	56 (1)
C(19)	−1914 (8)	2638 (8)	879 (7)	78 (2)
C(20)	−2572 (9)	2256 (9)	1281 (7)	88 (2)
C(21)	−2245 (8)	1440 (10)	1495 (6)	87 (2)
C(22)	−1343 (7)	1294 (7)	1248 (5)	59 (1)

^{a} U_{eq} defined as one-third of the trace of the orthogonalized U tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Ag(NO_3)(dppf)]_2\cdot 2CHCl_3$ (**1**)^a

Ag(1)···Ag(2)	3.936 (2)	Ag(1)–P(2)	2.435 (3)
Ag(1)–O(1)	2.476 (8)	Ag(1)–O(2)	2.80 (1)
Ag(1)–P(1a)	2.433 (3)	Ag(1)–O(1a)	2.873 (7)
O(1)–N(1)	1.03 (2)	O(2)–N(1)	1.30 (2)
O(3)–N(1)	1.28 (2)	Fe(1)–C(Cp1)(av)	2.03 (1)
Fe(1)–C(Cp2)(av)	2.04 (9)	Fe(1)–Cp(1)^b	1.63 (1)
Fe(1)–Cp(2)	1.64 (1)		
P(2)–Ag(1)–O(1)	106.3 (2)	P(2)–Ag(1)–O(2)	95.6 (3)
O(1)–Ag(1)–O(2)	46.0 (3)	P(2)–Ag(1)–P(1a)	140.1 (1)
O(1)–Ag(1)–P(1a)	109.6 (2)	O(1)–Ag(1)–P(1a)	97.0 (3)
P(2)–Ag(1)–O(1)	100.2 (2)	O(1)–Ag(1)–O(1a)	85.5 (2)
O(2)–Ag(1)–O(1a)	131.6 (3)	P(1a)–Ag(1)–O(1a)	99.3 (2)
Ag(1)–O(1)–N(1)	105.2 (8)	Ag(1)–O(1)–Ag(1a)	94.5 (2)
N(1)–O(1)–Ag(1a)	160.4 (9)	Ag(1)–O(2)–N(1)	82.0 (8)
O(1)–N(1)–O(2)	127 (1)	O(1)–N(1)–O(3)	127 (1)
O(2)–N(1)–O(3)	107 (1)		

^{a} Symmetry transformation: a (−*x*, −*y*, −*z*). ^{b} Cp(1) is the center of the ring composed of carbon atoms C(1)–C(5), and Cp(2) is the center of the C(18)–C(22) ring.

Table IV. Atomic Coordinates (×10^5 for Ag; ×10^4 for Other Atoms) and Equivalent Isotropic Temperature Factors^a ($Å^2 \times 10^4$ for Ag, Fe, and P; $Å^2 \times 10^3$ for Other Atoms) for $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**)

atom	*x*	*y*	*z*	U_{eq}
Ag(1)	4393 (5)	5807 (2)	43065 (1)	461 (2)
Ag(2)	4499 (6)	−5447 (3)	30976 (2)	653 (2)
Fe(1)	9183 (7)	17407 (4)	22714 (4)	378 (3)
P(1)	218 (1)	1830 (1)	3888 (1)	345 (4)
P(2)	858 (2)	−192 (1)	2001 (1)	421 (5)
O(1)	−885 (4)	−402 (2)	4470 (2)	55 (2)
O(2)	−1611 (5)	−611 (3)	3366 (2)	76 (2)
O(3)	1797 (6)	−1329 (3)	3918 (3)	89 (2)
O(4)	2323 (5)	−136 (3)	4149 (3)	74 (2)
C(1)	−1686 (6)	−692 (3)	3976 (3)	48 (2)
C(2)	−2791 (7)	−1150 (4)	4160 (4)	79 (3)
C(3)	2465 (7)	−830 (4}	4270 (4)	63 (3)
C(4)	3476 (9)	−1050 (6)	4861 (5)	129 (5)
C(5)	1292 (5)	2053 (3)	3290 (3)	37 (2)
C(6)	2271 (5)	1539 (3)	3151 (3)	46 (2)
C(7)	2874 (5)	1863 (4)	2626 (3)	55 (2)
C(8)	2289 (6)	2582 (3)	2444 (3)	57 (2)
C(9)	1308 (6)	2703 (3)	2846 (3)	44 (2)
C(22)	290 (5)	757 (3)	1765 (3)	43 (2)
C(23)	716 (7)	1285 (3)	1313 (3)	55 (2)
C(24)	−71 (7)	1945 (4)	1297 (3)	64 (3)
C(25)	−955 (6)	1831 (4)	1741 (3)	57 (2)
C(26)	−752 (5)	1108 (3)	2030 (3)	48 (2)

^{a} U_{eq} defined as one-third of the trace of the orthogonalized U tensor.

When $NaCH_3CO_2$ was added to a methanolic solution of $AgNO_3$ prior to the addition of dppf, an orange product isolated in 36% yield was formulated as $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**). This complex remains essentially as a nonelectrolyte in nitrobenzene but ionizes significantly in methanol, which is reversible upon crystallization from the solvent. The IR band at 1548 cm^{-1} is attributable to the antisymmetric C–O stretch, while the bands at 1408 and 1398 cm^{-1} are attributable to symmetry stretches. Such a small separation compared to that for free acetate ion is characteristic for bridging acetato ligand.[12]

The benzoato complex $Ag_2(\mu\text{-}(\eta^1\text{-O},\eta^1\text{-O}')C_6H_5CO_2)_2(\mu\text{-dppf})$ (**3**) is isolated in 48% yield when $AgC_6H_5CO_2$, generated in situ from $AgNO_3$ and $NaC_6H_5CO_2$, is mixed with dppf in a 1.0:0.5 ratio.

The reaction of $AgNO_3$ with $NaHCO_2$ and dppf yielded a sterically congested compound $Ag_2(\sigma\text{-}HCO_2)_2(\eta^2\text{-dppf})_2(\mu\text{-dppf})$ (**4**) as the principal product. The unidentate mode of the formato ligand is characterized by its high-frequency band at 1628 cm^{-1}, attributable to the antisymmetric (C=O), and a high separation

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(12) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 232. (c) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**)[a]

Ag(1)···Ag(2)	3.104 (1)	Ag(1)–P(1)	2.344 (2)
Ag(2)–P(2)	2.365 (2)	Ag(1)–O(1)	2.268 (2)
Ag(2)–O(2)	2.298 (5)	Ag(1)–O(4)	2.393 (5)
Ag(2)–O(3)	2.376 (5)	Ag(1)–O(1a)	2.396 (4)
Ag(2)–O(4)	2.667 (5)	O(1)–C(1)	1.265 (7)
O(2)–C(1)	1.231 (7)	O(3)–C(3)	1.248 (9)
O(4)–C(3)	1.248 (9)	C(1)–C(2)	1.50 (1)
C(3)–C(4)	1.47 (1)	Fe(1)–C(Cp1)(av)	2.04 (6)
Fe(1)–C(Cp2)(av)	2.04 (6)	Fe(1)–Cp(1)[b]	1.642 (6)
Fe(1)–Cp(2)	1.648 (6)		

Ag(2)–Ag(1)–P(1)	109.9 (1)	Ag(1)–Ag(2)–P(2)	124.3 (1)
Ag(2)–Ag(1)–O(1)	73.2 (1)	Ag(1)–Ag(2)–O(2)	73.7 (1)
P(1)–Ag(1)–O(1)	137.9 (1)	P(2)–Ag(2)–O(2)	123.8 (1)
Ag(2)–Ag(1)–O(4)	56.3 (1)	Ag(1)–Ag(2)–O(3)	86.1 (1)
P(1)–Ag(1)–O(4)	118.5 (1)	P(2)–Ag(2)–O(3)	126.5 (2)
O(1)–Ag(1)–O(4)	98.5 (2)	O(2)–Ag(2)–O(3)	105.6 (2)
Ag(2)–Ag(1)–O(1a)	131.7 (1)	Ag(1)–Ag(2)–O(4)	48.3 (1)
P(1)–Ag(1)–O(1a)	117.8 (1)	P(2)–Ag(2)–O(4)	114.5 (1)
O(1)–Ag(1)–O(1a)	76.4 (1)	O(2)–Ag(2)–O(4)	114.1 (2)
O(4)–Ag(1)–O(1a)	93.0 (2)	O(3)–Ag(2)–O(4)	51.2 (2)
Ag(1)–O(1)–C(1)	121.7 (4)	Ag(1)–O(1)–Ag(1a)	103.6 (1)
C(1)–O(1)–Ag(1a)	134.5 (4)	Ag(2)–O(2)–C(1)	117.5 (4)
Ag(2)–O(3)–C(3)	99.6 (4)	Ag(1)–O(4)–Ag(2)	75.5 (1)
Ag(1)–O(4)–C(3)	124.1 (5)	Ag(2)–O(4)–C(3)	85.9 (4)
O(1)–C(1)–O(2)	123.8 (6)	O(1)–C(1)–C(2)	116.9 (5)
O(2)–C(1)–C(2)	119.2 (5)	O(3)–C(3)–O(4)	123.3 (6)
O(3)–C(3)–C(4)	119.9 (7)	O(4)–C(3)–C(4)	116.9 (7)

[a] Symmetry transformation: a (−*x*, −*y*, −*z*). [b] Cp(1) is the center of the ring composed of carbon atoms C(5)–C(9), and Cp(2) is the center of the C(22)–C(26) ring.

Table VI. Atomic Coordinates (×10^5 for Ag, Fe; ×10^4 for Other Atoms) and Equivalent Isotropic Temperature Factors[a] (Å^2 × 10^4 for Ag, Fe; Å^2 × 10^3 for Other Atoms) for $[Ag_2(C_6H_5CO_2)_2(dppf)]$ (3)

atom	*x*	*y*	*z*	U_{eq}
Ag(1)	15777 (12)	160283 (2)	−36374 (4)	516 (6)
Ag(2)	10972 (11)	9221 (2)	5318 (4)	492 (6)
Fe(1)	50587 (20)	10754 (3)	−342 (7)	392 (9)
P(1)	3654 (4)	1814 (1)	−297 (1)	42 (2)
P(2)	2701 (4)	538 (1)	419 (1)	33 (2)
O(1)	−113 (9)	1459 (2)	−986 (4)	60 (4)
O(2)	531 (10)	969 (2)	−735 (4)	54 (5)
O(3)	744 (12)	1578 (2)	815 (5)	81 (6)
O(4)	−400 (9)	1163 (2)	1125 (4)	66 (5)
C(1)	−142 (16)	1157 (3)	−1049 (6)	50 (8)
C(2)	−1096 (15)	1027 (2)	−1577 (6)	40 (7)
C(3)	−1065 (13)	704 (2)	−1767 (5)	40 (7)
C(4)	−1919 (15)	574 (3)	−2253 (7)	58 (8)
C(5)	−2777 (16)	768 (4)	−2565 (7)	73 (8)
C(6)	−2857 (13)	1094 (3)	−2389 (7)	56 (7)
C(7)	−2031 (14)	1214 (3)	−1887 (6)	44 (7)
C(8)	−118 (18)	1453 (3)	1143 (7)	48 (9)
C(9)	−916 (16)	1661 (3)	1613 (6)	47 (7)
C(10)	−1804 (16)	1530 (3)	2046 (7)	77 (9)
C(11)	−2528 (16)	1725 (4)	2477 (8)	110 (9)
C(12)	−2396 (22)	2054 (5)	2479 (10)	141 (14)
C(13)	−1481 (20)	2179 (3)	2051 (10)	102 (12)
C(14)	−739 (14)	1988 (3)	1630 (7)	75 (8)
C(39)	4758 (19)	1551 (3)	143 (6)	31 (10)
C(40)	6067 (20)	1490 (3)	24 (7)	48 (11)
C(41)	6560 (18)	1272 (3)	513 (8)	70 (10)
C(42)	5552 (21)	1197 (3)	976 (7)	59 (10)
C(43)	4403 (16)	1365 (2)	766 (6)	41 (9)
C(44)	3923 (20)	679 (3)	−134 (6)	45 (11)
C(45)	3734 (17)	899 (2)	−732 (5)	25 (9)
C(46)	4941 (19)	932 (3)	−1071 (7)	34 (9)
C(47)	5884 (15)	750 (3)	−718 (6)	53 (8)
C(48)	5227 (21)	595 (3)	−154 (6)	56 (11)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

between this band and the lower frequency symmetric band (C–O) at 1296 cm^{-1} compared to that of free formate ion.[13]

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[Ag_2(C_6H_5CO_2)_2(dppf)]$ (**3**)[a]

Ag(1)···Ag(2)	3.346 (4)	Ag(1)–P(1)	2.364 (5)
Ag(1)–O(1)	2.219 (9)	Ag(1)–O(3)	2.400 (1)
Ag(2)–P(2)	2.340 (4)	Ag(2)–O(2)	2.477 (8)
Ag(2)–O(4)	2.182 (9)	O(1)–C(1)	1.27 (1)
O(2)–C(1)	1.22 (2)	O(3)–C(8)	1.22 (2)
O(4)–C(8)	1.25 (2)	Fe(1)–C(Cp1)(av)	2.05 (2)
Fe(1)–C(Cp2)(av)	2.05 (2)		

Ag(2)–Ag(1)–P(1)	115.4 (1)	Ag(2)–Ag(1)–O(1)	85.3 (2)
Ag(2)–Ag(1)–O(3)	55.8 (2)	Ag(1)–Ag(2)–P(2)	115.2 (1)
Ag(1)–Ag(2)–O(2)	58.6 (2)	Ag(1)–Ag(2)–O(4)	88.8 (2)
Ag(1)–O(1)–C(1)	109.7 (9)	Ag(2)–O(2)–C(1)	131.8 (8)
Ag(1)–O(3)–C(8)	139.9 (9)	Ag(2)–O(4)–C(8)	107.0 (9)
P(1)–Ag(1)–O(1)	150.9 (2)	P(1)–Ag(1)–O(3)	107.8 (3)
O(1)–Ag(1)–O(3)	100.7 (4)	P(2)–Ag(2)–O(2)	98.1 (2)
P(2)–Ag(2)–O(4)	152.3 (2)	O(2)–Ag(2)–O(4)	106.7 (3)
O(1)–C(1)–O(2)	126 (1)	O(3)–C(8)–O(4)	125 (1)

[a] Cp(1) is the center of the ring composed of carbon atoms C(39)–C(43), and Cp(2) is the center of the C(44)–C(48) ring.

Table VIII. Atomic Coordinates (×10^5 for Ag; ×10^4 for Other Atoms) and Equivalent Isotropic Temperature Factors[a] (Å^2 × 10^4 for Ag; Å^2 × 10^3 for Other Atoms) for $[Ag_2(HCO_2)_2(dppf)_3]\cdot 2CH_2Cl_2$ (**4**)

atom	*x*	*y*	*z*	U_{eq}
Ag(1)	36456 (3)	38030 (11)	4686 (4)	491 (4)
Fe(1)	4367 (1)	6026 (2)	102 (1)	58 (1)
Fe(2)	2500	2500	0	49 (1)
P(1)	4246 (1)	4231 (4)	1142 (2)	52 (2)
P(2)	3563 (1)	4751 (4)	−514 (2)	49 (2)
P(3)	3179 (1)	4252 (3)	852 (2)	41 (1)
O(1)	3695 (3)	1552 (13)	57 (5)	121 (8)
O(2)	3768 (4)	1078 (13)	941 (6)	130 (9)
C(1)	3775 (4)	736 (13)	454 (6)	220 (16)
C(2)	4246 (4)	4430 (18)	−381 (6)	68 (7)
C(3)	4525 (4)	5023 (23)	−469 (7)	89 (10)
C(4)	4418 (5)	6152 (24)	−684 (7)	99 (11)
C(5)	4071 (5)	6355 (19)	−743 (6)	80 (8)
C(6)	3962 (3)	5252 (14)	−554 (6)	51 (6)
C(7)	4739 (4)	5868 (15)	906 (6)	60 (7)
C(8)	4728 (5)	7096 (18)	686 (7)	83 (9)
C(9)	4394 (5)	7619 (17)	579 (8)	84 (9)
C(10)	4197 (4)	6695 (16)	722 (6)	64 (7)
C(11)	4411 (4)	5615 (15)	923 (6)	54 (6)
C(48)	2438 (4)	3967 (13)	485 (7)	60 (7)
C(49)	2163 (4)	3921 (14)	−68 (10)	79 (9)
C(50)	2298 (5)	4023 (13)	−514 (8)	79 (8)
C(51)	2654 (4)	4148 (12)	−253 (6)	56 (6)
C(52)	2747 (3)	4106 (11)	371 (6)	44 (6)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

Despite the presence of adventitious nitrate ion in the syntheses of the carboxylato complexes, no competing reactions were evident. The richness of dppf in **4** is not stoichiometrically but thermodynamically dictated. Accordingly, the use of a dppf:Ag$^+$ substrate ratio of less than 1.5 in the synthesis of **4** would lead to an insofar unknown intermediate which rapidly decomposes to **4**.

X-ray structural determinations were carried out on all the complexes **1**–**4**. Complex **1** revealed a centrosymmetric $CHCl_3$-solvated dimeric structure with two Ag(I) centers doubly bridged by two staggered (torsional angle = 89.6°) dppf ligands. Its molecular structure is shown in Figure 1. Crystallographic data for the complex are given in Table I, and final atomic positional parameters, in Table II. Some pertinent molecular data are listed in Table III. Stabilization of the 14-electron P–Ag(I)–P fragment is achieved by the NO_3^- coordination in a semibridging and semichelating manner whereby the one-atom bridging oxygens (O(1) and O(1a)) are strongly bonded to one metal (Ag(1)–O(1) = 2.476 (8) Å) and weakly to another (Ag(1a)–O(1)) = 2.873 (7) Å) while the other nitrato oxygen atoms (O(2) and O(2a)) are weakly linked to the former metal centers (Ag(1)–O(2) and

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[13] Tso, C. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1242.

Table IX. Selected Bond Distances (Å) and Angles (deg) for $[Ag_2(HCO_2)_2(dppf)_3]\cdot 2CH_2Cl_2$ (**4**)[a]

Ag(1)–P(1)	2.523 (5)	Ag(1)–P(2)	2.544 (5)
Ag(1)–P(3)	2.496 (5)	Ag(1)–O(1)	2.65 (2)
O(2)–C(1)	1.27 (2)	O(1)–C(1)	1.27 (2)
Fe(1)–C(Cp1)(av)	2.04 (2)	Fe(1)–C(Cp2)(av)	2.05 (2)
Fe(2)–C(Cp3)(av)	2.05 (2)		
P(1)–Ag(1)–P(2)	109.3 (2)	P(1)–Ag(1)–P(3)	116.4 (1)
P(2)–Ag(1)–P(3)	115.0 (1)	P(1)–Ag(1)–O(1)	103.0 (3)
P(2)–Ag(1)–O(1)	89.9 (3)	P(3)–Ag(1)–O(1)	119.8 (3)
O(1)–C(1)–O(2)	117 (1)		

[a] Symmetry transformation: a ($^1/_2 - x$, $^1/_2 - y$, $-z$); b ($1 - x$, y, $^1/_2 - z$). Cp(1) is the center of the ring composed of carbon atoms C(7)–C(11); Cp(2) is the center of the C(2)–C(6) ring, and Cp(3) is the center of the C(48)–C(52) ring.

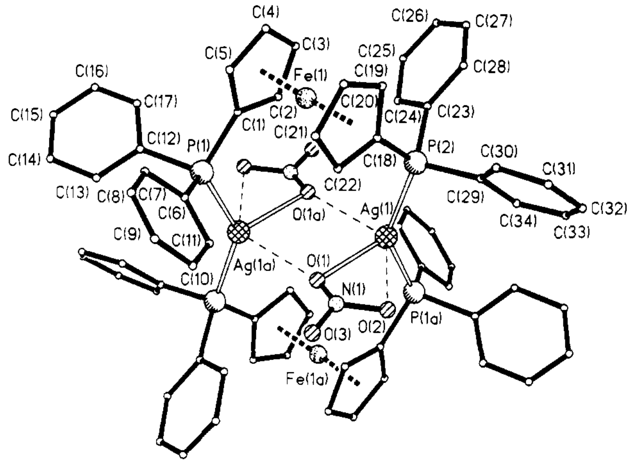

Figure 1. Molecular structure of $[Ag(NO_3)(dppf)]_2\cdot 2CHCl_3$ (**1**).

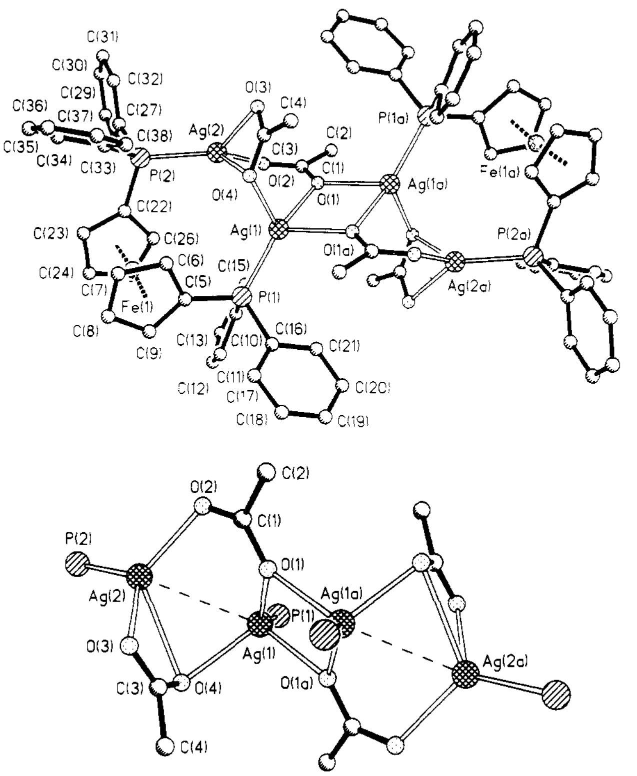

Figure 2. (a) Top: Molecular structure of $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**). (b) Bottom: Perspective view of the coordination modes of the acetato ligands in $[Ag_2(CH_3CO_2)_2(dppf)]_2$ (**2**).

Ag(1a)–O(2a) = 2.80 (1) Å). A similar mode of coordination for NO_3^- has been reported for $[Cu(ONO_2)_2(OH_2)_{2.5}]$,[14] but in this case the two weak M–O bonds are associated with the *same* oxygen atom, which is the bridging site. The semichelate configuration leads to a substantial narrowing of the Ag(1)–O(1)–N(1) (and Ag(1a)–O(1a)–N(1a)) angles (105.2 (8)°) from the ca. 150° expected for a unidentate NO_3^-.[15] Since molecule **1** is centrosymmetric and the P(1)–Ag(1a)···Ag(1)–P(2) torsional angle is −15.1°, the core atoms, Ag(1), Ag(1a), P(1), P(1a), P(2), and P(2a), are approximately coplanar (maximum deviation from the least-squares plane is 0.17 Å).

The molecular structure of complex **2** is shown in Figure 2a, and a perspective view of the acetato bridges, in Figure 2b. Crystallographic data are given in Table I, and positional parameters, in Table IV. Some pertinent molecular data are listed in Table V. The structure, which is centrosymmetric, comprises two $\{Ag_2(dppf)(CH_3CO_2)_2\}$ moieties linked by two oxygen sites (O(1) and O(1a), thus resulting in two triply bridging acetates. The four Ag(I) centers are arranged in an approximate chair conformation together with the four acetates. The molecule may also be viewed as a fusion of three metallacyclic rings, consisting of a planar four-membered $\{Ag_2O_2\}$ ring sandwiched by two six-membered rings. All the silver atoms are tetrahedrally coordinated by three basal oxygens and an apical phosphorus atom.

Two modes of coordination of acetate are eminent, both of which function as a six-electron donor in its anionic state. The triply bridging acetates (μ_3-(η^2-O, η^1-O′)), with a monoatom bridging site, have previous been reported.[16] The chelate-bridge coordination mode,[17] in which an oxygen atom (O(4) and O(4a) in Figure 2b) functions as a bridging and chelating site, is however uncommon and particularly interesting in view of the dominance of the μ_2-symmetrical bridge found in many acetato complexes.[18]

Molecular weight data of **2** in both $CHCl_3$ (925) and CH_2Cl_2 (915) suggested substantial dissociation in solution, possibly to the dimeric $Ag_2(\mu$-(η^1-O, η^1-O′)$CH_3CO_2)_2(\mu$-dppf) (**2a**) (MW = 888), which is isostructural to its dppm and dppe analogs[19] (discussed later). VT (23 to −90 °C) NMR (^1H and ^{31}P) studies indicated that the molecule is fluxional at rt with rapid phosphine dissociation and an intermolecular dissociation process, as evident from the concentration- and solvent-dependent spectra. The ^{31}P spectra at rt generally give a broad singlet (δ 4.98 ppm) for **2** and a broad doublet (δ 4.78) for **2a**, the relative intensities of which are concentration dependent. At ca. −18 °C, the signals sharpen to a doublet (δ 4.43). At ca. −40 °C, the characteristic double doublets ($J(^{107}Ag\text{–}P)$ = 661 Hz) emerge which are consistent with the abundance and gyromagnetic ratio for ^{107}Ag and ^{109}Ag. Though no further changes were observed in the ^{31}P spectra upon cooling to −90 °C, the ^1H spectra revealed the collapse of two singlets for the Cp protons to four broad singlets at ca. −75 °C, which may be interpreted as an $A_2B_2C_2D_2$ pattern for an asymmetrically bridged dppf. Near-equivalence of the acetate resonances is maintained till ca. −65 °C below which a broad singlet is observed. These observations pointed to a equilibrium existing between **2** and **2a** in solution. The tetranuclear complex **2** is possibly entropically favored at high sample concentration and at low temperature. A low-energy exchange process is still operational at −90 °C which equilibrates the phosphine sites in

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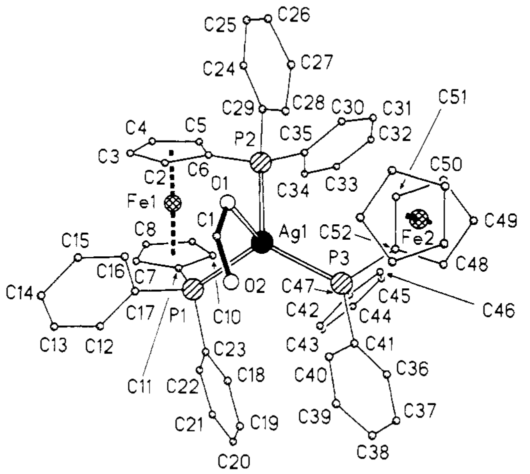

Figure 3. Perspective view of the structure of $[Ag_2(HCO_2)_2(dppf)_3]\cdot 2CH_2Cl_2$ (**4**), showing half of the molecule which is centrosymmetric at the iron center Fe(2) of the bridging dppf ligand.

2. Similarly facile fluxionality has been noted in other silver(I) phosphine complexes.[19,20]

Compound **3** consists of a dimetal structure with both 16-electron trigonal planar Ag(I) centers triply-bridged by two benzoato ligands and one dppf ligand (Figure 3). Crystallographic data are given in Table I, and positional parameters, in Table VI. Some pertinent molecular data are listed in Table VII. The structural framework can be viewed as a dissociation product of **2**, which hence is isostructural to **2a**, through the scission of four Ag–O bonds (Ag(1)–O(1a), Ag(1a)–O(1), Ag(2)–O(4), and Ag(2a)–O(4a) in Figure 2). The similarity of **2** and **3** in their ^{31}P spectra at rt is suggestive of a similar isomerization and dissociation process in solution. Their different solid-state structures are presumably steric-controlled. This structure demonstrates vividly that despite its small bite (2.2 Å),[21] a carboxylato bridge can comfortably coexist with a bulky diphosphine such as dppf with assistance from the tunable P···P separation of the latter. In **3**, the two benzoato bridges bring the two metal centers to a proximity of a mere 3.346 Å apart. While both Ag–P distances are essentially identical (average Ag–P = 2.350 (5) Å), one pair of Ag–O lengths (Ag(1)–O(1) and Ag(2)–O(4)) is significantly shorter than the other pairs by an average of 0.239 (9) Å; this is indicative of the polar nature of the longer Ag–O links. It is intriguing that the present structure of **3** prevails over an obvious alternative—$(\eta^2\text{-}C_6H_5CO_2)Ag(\mu\text{-dppf})Ag(\eta^2\text{-}C_6H_5CO_2)$ with the benzoate in its terminal chelating mode and the dppf bridge in the anti conformation. The structural preference for **3** is perhaps an indication of benzoato in its favored bridging state.[22]

Complex **4** crystallizes with two occluded CH_2Cl_2 molecules. It consists of a dppf ligand symmetrically bridged between two $\{Ag(dppf)(HCO_2)\}$ moieties. It thus represents one of the few known structurally characterized examples in which the bridging and chelating dppf coexist. The molecule is centrosymmetric, with Fe(2) lying on a center of symmetry (Figure 4). Crystallographic data are given in Table I, atomic positional parameters in Table VIII, and some pertinent molecular data in Table IX. The crystallographic symmetry requires an idealized anti conformation of the bridging ferrocenyl unit. This open form of bridging, which was previously reported,[3,23] allows a linear disposition of the phosphine groups and precludes an auxiliary bridging ligand; this differentiates **4** from the syn bridges found in **1**–**3**. The chelating dppf which is abundant in the literature is found perhaps surprisingly only in **4** among the complexes studied. The unidentate attachment of the formato ligand, which is relatively uncommon[24] compared to its chelate[25] or bridging mode,[26] completes the noble gas requirement of the metal. The syn conformation of the formate is in accordance with the higher basicity of the syn lone pair.[21]

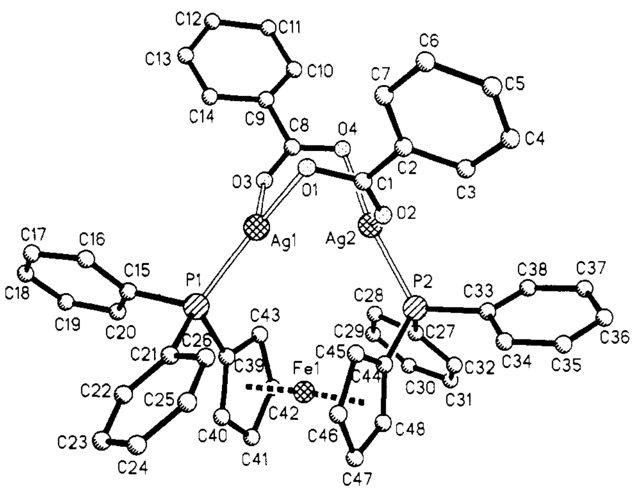

Figure 4. Molecular structure of $Ag_2(C_6H_5CO_2)_2(dppf)$ (**3**).

Discussion

The coordination mode of the nitrato ligand in **1** represents an intermediacy of a symmetrical one-atom bridging and chelating modes. The presence of four weak Ag–O linkages reflects a relief from electron oversaturation which would have resulted from an idealized triply-bridging mode (μ_3-(η^2-O, η^1-O′) for the nitrates. A peculiar feature is the short and strong N(1)–O(1) (and N(1a)–O(1a)) bonds (1.03 (2) Å) which are associated with the strong Ag(1)–O(1) (and Ag(1a)–(O1a)) interactions whereas two much longer and presumably weaker N(1)–O(2) (and N(1a)–O(1a)) bonds (1.30 (2) Å) are associated with the weak Ag(1)–O(2) (Ag(1a)–O(2a) interactions. Such an uneven distribution of N–O bond lengths in nitrato complexes is by itself very rare. The high π-character of N(1)–O(1) is perhaps indicative of a high polarity of the Ag(1)–O(1) linkages. This feature of the nitrato group is not found in the analogous dppm complex, $[Ag(NO_3)(dppm)]_2$,[27] in which case the nitrato ligand is terminally coordinated in an asymmetric chelating fashion. As a result, its syn conformation is in distinct contrast to the anti form found in **1**. This difference is attributed to the higher steric demand of the dppf bridges which not only force the nitrato bridges to adopt an anti conformation but also spans over a longer Ag···Ag separation of 3.936 (2) Å (compared to 3.099 (1) Å in the dppm dimer) and creates a large pocket for the accommodation of the nitrato bridges. The planarity of **1** also contrasts the folding nature of the dppm dimer along the Ag···Ag hinge. This may suggest a potentially rich and different A-frame chemistry for this dppf dimeric system, which so far has been undeveloped. A relatively small torsional twist of the Cp···Cp′ rings (89.6°) compared to the other open bridging systems[3b,28] ensures a close proximity of the metal centers. It would be of interest to observe

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any conformational changes to these phosphinocyclopentadienyl rings with respect to the incoming of small molecules to the metal spheres. Systems with $M_2(\mu\text{-dppm})_2$ as their molecular core are well-cited[29] and have a very rich chemistry. We are however not aware of any structurally characterized *closo*-$M_2(\mu\text{-dppf})_2$ in the literature.

The chelate-bridge acetate coordination mode in **2** is of particular interest. This form of bridging for carboxylate has been recently advocated by Lippard et al.[30] as an intermediate in the "carboxylate shift" in the transition of a monodentate bridge (μ-η^1-O) to a symmetrical bidentate (μ-η^1-O, η^1-O′) which may be of relevance to the active sites in metalloproteins. Monoatom bridging (μ-η^2-O) carboxylate has been crystallographically identified and is sometimes associated with weak interaction of the free carbonyl oxygen with one of the bridged metal centers.[31] This feature is characterized by two short and one long M–O bonds in the structure. The coordinate mode found in **2** diverges from the above usual characteristic in that the "free" oxygen (O(3) and O(3a)) interacts strongly with the metal, which as a result is only weakly bonded to the monoatom bridging oxygen. This picture hence resembles more a μ_2-symmetrical bridge than the monoatom bridge and should be considered as a more advanced intermediate step in the "carboxylate shift".

This unusual μ_3-ligation mode of acetate in **2** also represents a distinctive contrast to that found in its PPh_3 analog $[Ag(CH_3CO_2)(PPh_3)]_4$.[32] This difference can be understood in terms of the cooperative effect brought about by the bridging dppf. The gauche dppf moiety (twist angle = 88.8°) in **2** spans a Ag···Ag distance of 3.104 (1) Å, which is 0.018 Å shorter than the unaided Ag···Ag separation found in the PPh_3 analog. Such apparently insignificant shortening is however sufficient to bring Ag(2) and Ag(2a) to the close proximity of O(4) and O(4a) in **2**, thus transforming a symmetrical syn–syn bridge to an unusual chelating bridging mode. The two bonding modes of acetate allow all the Ag(I) centers to be tetrahedrally bound and in compliance with the 18-electron rule. In contrast, like most of the Ag_4 aggregates with a chair conformation in which the core atoms are characterized by their different coordination numbers and stereogeometries,[33] the analogous PPh_3 molecule is assembled from two 18-electron tetrahedral Ag(I) and two 16-electron trigonal planar Ag(I) entities. Structure **2** represents an example of polynuclear molecules with no terminal ligands.

The cubane vs chair conformation represents a characteristic feature for tetranuclear $Ag_4X_4(PR_3)_4$ complexes. The chair form is known to favor the more sterically demanding phosphines and halides. The bulkiest ligands are believed to promote further dissociation of the chair conformer to give the dinuclear complexes, though proven examples of such dissociation are rare. On the other hand, the diphosphine analogs of the Ag(I) complexes tend to give dimers rather than tetramers.[19,34] An examination of the structure of **2** revealed that, if one cleaves the weakest Ag–O link of each of the acetato bridges, viz. Ag(2)–O(4) and Ag(2a)–O(4a) (2.667 (5) Å) and Ag(1a)–O(1) and Ag(1)–O(1a) (2.396 (4) Å), a symmetrical dimer $[Ag_2(\mu\text{-}\eta^1\text{-O},\ \eta^1\text{-O}'\text{-}CH_3CO_2)_2(\mu\text{-dppf})]$ (**2a**) would result. Such a dimeric structure indeed is found in the benzoato complex **3** and provides a basis for our assignment of the dissociation process described earlier. A rapid equilibrium between the structural forms represented by **2** and **3** is thus envisaged with the acetate favoring a tetranuclear framework and the bulkier benzoate favoring a dinuclear framework.

The high variability of dppf and carboxylates in their coordination modes allows numerous structural variations to the Ag(I) complexes formed. The compatibility of dppf and RCO_2^- or NO_3^- as bridging ligands despite their contrast in bite size further reiterates that there is an insofar undeveloped A-frame chemistry[35] for dppf. The skeletal flexibility of dppf should encourage the proximal metals to be more receptive to incoming groups of differing steric requirements. Present efforts in our laboratories are directed to these objectives.

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Supplementary Material Available: Tables of crystallographic data and refinement details, positional parameters, and anisotropic thermal parameters for the structures of **1**–**4** (23 pages). Ordering information is given on any current masthead page.

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