5928 *Inorg. Chem.* **2001,** *40,* 5928−5933

2,6-Bis(diphenylphosphino)pyridine-Bridged Hetero-Polynuclear Complexes Consolidated by Fe→M (M = Ag, Hg) Dative Bonding

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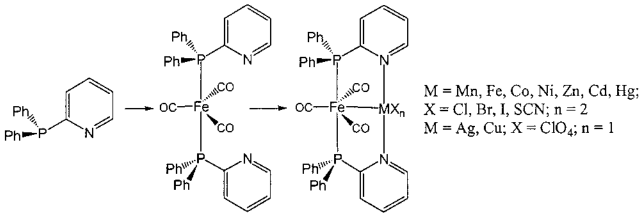
Received April 24, 2001

The bridging phosphine ligand 2,6-bis(diphenylphosphino)pyridine (L) was used to synthesize a new, neutral organometallic ligand $\{Fe(CO)_4\}_2(\mu\text{-L})$ **1**, which exhibits eclipsed and staggered conformations in two crystalline forms. This Fe,N,Fe-tridentate ligand reacts with silver perchlorate to form the hetero-trinuclear complex $[\{Fe(CO)_4\}_2Ag(\mu\text{-L})](ClO_4)$ **2**, in which the central silver(I) atom bridges a pair of iron(0) atoms at Fe−Ag distances of 2.627(3) and 2.652(3) Å; the Fe−Ag−Fe angle is 170.98(9)°. The reaction of **1** with mercury(II) chloride gives $\{Fe(CO)_4\}_2Hg_2Cl_4(\mu\text{-L})$, **3**. The ligand also reacts with mercury(II) acetate to form a hetero-octanuclear complex $[\{Fe(CO)_3Hg\}_2(\mu\text{-L})]_2$ **4** and a novel hetero-heptanuclear complex $Fe_3(CO)_8Hg_4(\mu\text{-L})_2(MeCO_2)_2$ **5**. Complex **4** displays a square metallic core in which the iron and mercury atoms occupy the corners and the centers of the edges, respectively. The metal atoms in **5** are linked to form a kinky line with bends at the iron atoms.

Introduction

For many years pyridyl−phosphine ligands have been widely used to synthesize hetero- or homo-nuclear metal complexes,[1] as electronic differentiation associated with the hard (N) and soft (P) donor atoms dictates their unique reactivities and coordination modes. One important property of these ligands is that they can stabilize metal ions in a variety of valence states and geometries. Hence, a metal−metal bond between an electron-rich metal (soft base) and a high oxidation-state metal (Lewis acid) is easy formed, and some homogeneous catalytic applications, including hydrogenation, hydroformylation, carbonylation, and alkene insertion, have been investigated.[2] Recent work from our laboratories has explored the use of bifunctional pyridyl−phosphine ligands typified by 2-(diphenylphosphino)-pyridine, Ph_2Ppy, for the construction of hetero-binuclear transition-metal complexes that are consolidated by a donor−acceptor metal−metal bond (Scheme 1).[3]

Scheme 1



The neutral ligand 2,6-bis(diphenylphosphino)pyridine, $(Ph_2P)_2$-py (L), first synthesized by Newkome and Hager,[4] has been shown to form various novel binuclear and polynuclear palladium, platinum, rhodium, iridium, silver, gold, copper, rhenium, and molybdenum complexes.[5] The rigidity of this ligand governs the P···N···P ligand bite distance so that binding a metal to each donor site places the metal ions in very close proximity (about 2.6−2.8 Å). This restriction on metal−metal separation appears to limit the range of complexes that can be generated from this ligand, and to date only two trinuclear ($Pd_3Cl_6(\mu\text{-L})_3$ and $[Ir_2Cu(CO)_2Cl_2(MeCN)(\mu\text{-L})_2](ClO_4)\cdot 2MeCN$) and two tetranuclear ($[Rh_4(\mu\text{-Cl})_2Cl_2(\mu\text{-L})_2(\mu\text{-CO})(CO)_2]\cdot 2CH_2Cl_2$ and

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10.1021/ic010426u CCC: $20.00 © 2001 American Chemical Society
Published on Web 10/11/2001

Table 1. X-ray Crystallographic Data and Refinement Parameters of the Complexes

complex	**1a**	**1b**	**2**	**4**·2THF	**5**·2THF
formula	$C_{37}H_{23}Fe_2NO_8P_2$	$C_{37}H_{23}Fe_2NO_8P_2$	$C_{37}H_{23}AgClFe_2NO_{12}P_2$	$C_{70}H_{46}Fe_4Hg_4N_2O_{12}P_4 \cdot 2THF$	$C_{70}H_{52}Fe_3Hg_4N_2O_{12}P_4 \cdot 2THF$
M	783.2	783.2	990.52	2400.94	2351.13
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$C2/c$(No. 15)
cryst size/mm	0.44 × 0.19 × 0.11	0.36 × 0.27 × 0.25	0.36 × 0.20 × 0.08	0.20 × 0.12 × 0.10	0.60 × 0.40 × 0.40
a/Å	14.4593(6)	13.364(2)	18.194(5)	15.606(2)	22.244(3)
b/Å	11.1013(5)	14.852(3)	11.920(4)	14.677(2)	14.429(2)
c/Å	23.1378(10)	18.063(3)	18.205(6)	18.830(3)	25.380(3)
β/°	101.1260(10)	98.363(4)	95.474(6)	111.445(3)	106.590(2)
U/Å^3	3644.2(3)	3547.2(11)	3930(2)	4014.4(10)	7801.5(16)
Z	4	4	4	2	4
D_c/g cm^{-3}	1.428	1.467	1.674	1.986	2.002
F (000)	1592	1592	1976	2280	4480
μ (Mo Kα)/mm^{-1}	0.935	0.961	1.434	8.461	8.529
GOF	0.867	0.910	1.052	0.774	0.957
no. unique reflns	8811	8607	5139	9689	9368
(R_{int})	0.0937	0.0792	0.0964	0.0742	0.0385
no. obs reflns	3149	3782	2825	5032	6970
no. variables, p	451	452	446	479	474
R1, wR2 [$I > 2\sigma(I)$]^a	0.0539, 0.1150	0.0522, 0.1097	0.0935, 0.2370	0.0380, 0.0537	0.0318, 0.0683
R1, wR2 (all data)	0.1808, 0.1557	0.1488, 0.1425	0.1600, 0.2919	0.0982, 0.0627	0.0519, 0.0738

[a] $R1 = \sum(|F_o| - |F_c|/\sum|F_o|$. $wR2 = \{w[\sum(|F_o| - |F_c|)^2]/\sum|F_o|^2\}^{1/2}$.

$[Rh_2Sn(SnCl_3)Cl_3(CO)_2(\mu\text{-}L)_2]\cdot 2CH_2Cl_2$) complexes have had their structures established by X-ray crystallography.[5a,k,l] Herein, we report the synthesis and structure of four new hetero-polynuclear complexes containing the Fe→M (M = Ag, Hg) dative bond.

Experimental Section

Synthesis of Compounds. Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. The ligand $(Ph_2P)_2py$ (L) was prepared by the published method.[4,5l]

$\{Fe(CO)_4\}_2(\mu\text{-}L)$, 1. This compound was prepared according to the published procedure for $Fe(CO)_4(Ph_2Ppy)$,[3a] except that excess $Fe(CO)_5$ and a mixed dichloromethane/ethanol solvent were used. $(Ph_2P)_2py$ (2.23 g, 5 mmol) was dissolved in 10 mL of CH_2Cl_2 and mixed with a solution of $Fe(CO)_5$ (25 mmol) in EtOH (10 mL). Me_3NO (10 mmol) dissolved in EtOH (10 mL) was then added dropwise, and the solution stirred for 2 h, yielding **1** as a yellow precipitate. Yield 50%. Found: C, 56.93; H, 3.21; N, 1.69. Calcd for **1**, $C_{37}H_{23}Fe_2NO_8P_2$: C, 56.74; H, 2.96; N, 1.79. IR(νCO): 2040m, 1987m, 1945s, 1934s cm^{-1}. $^{31}P\{^1H\}$NMR: δ 75.6 ppm. Single crystals of **1a** and **1b** were obtained from diffusion of EtOH and hexane, respectively, into a solution of **1** in CH_2Cl_2.

$[\{Fe(CO)_4\}_2Ag(\mu\text{-}L)](ClO_4)$, 2. A solution of $AgClO_4$ (0.053 g, 0.13 mmol) in benzene (5 mL) was added to a solution of compound **1** (0.10 g, 0.13 mmol) in benzene (5 mL), and the mixture was stirred for 10 min. The yellow precipitate was collected and dried under vacuum. Single crystals of **2**, which were obtained by slow diffusion of benzene into a solution in THF, were thin plates of poor quality that were barely acceptable for X-ray analysis. Yield 85%. Found: C, 44.90; H, 2.48; N, 1.34. Calcd for **2**, $C_{37}H_{23}O_{12}NP_2ClAgFe_2$: C, 44.86; H, 2.34; N, 1.41. IR(νCO): 2055s, 2000s, 1970s, 1950s cm^{-1}. $^{31}P\{^1H\}$NMR: δ 73.6, 73.8 ppm.

$\{Fe(CO)_4\}_2Hg_2Cl_4(\mu\text{-}L)$, 3. To a solution of compound **1** (0.10 g, 0.13 mmol) in dichloromethane (5 mL) was added $HgCl_2$ (0.071 g, 0.26 mmol). The mixture was stirred for 3 h and filtered. The solution was precipitated by addition of hexane (10 mL) to give $[Fe(CO)_4]_2Hg_2Cl_4(\mu\text{-}L)$ as a pale yellow powder. Yield 65%. Found: C, 33.10; H, 1.85; N, 0.90. Calcd for **3**, $C_{37}H_{23}O_8NP_2Cl_4Fe_2Hg_2$: C, 33.51; H, 1.75; N, 1.06. IR(νCO): 2077w, 2030s, 1982m, 1940s, 1930s cm^{-1}. $^{31}P\{^1H\}$NMR: δ 69.0 ppm.

$[\{Fe(CO)_3Hg\}_2(\mu\text{-}L)]_2$, 4. To a solution of compound **1** (0.1 g, 0.13 mmol) in THF (5 mL) was added $Hg(MeCO_2)_2$ (0.083 g, 0.26 mmol). The mixture was stirred for a few hours and then filtered to remove the insoluble material. The filtrate was allowed to stand for two weeks, and the well-developed orange crystals of **4**·2THF that appeared were collected by filtration and used in subsequent X-ray crystal analysis. The product was then dried in a vacuum and used for elemental analysis. Yield 60%. Found: C, 37.28, H, 2.46, N, 1.09. Calcd for **4**, $C_{70}H_{46}Fe_4Hg_4N_2O_{12}P_4$: C, 37.26, H, 2.05, N, 1.24. IR(νCO): 1972s, 1908s cm^{-1}.

$Fe_3(CO)_8Hg_4(\mu\text{-}L)_2(\mu\text{-}MeCO_2)_2$, 5. To a solution of compound **1** (0.1 g, 0.13 mmol) in THF (5 mL) was added $Hg(MeCO_2)_2$ (0.083 g, 0.26 mmol) and Ag_2CO_3 (0.018 g, 0.065 mmol). The mixture was stirred for 1 day, during which time the Ag_2CO_3 was slowly dissolved by acetic acid formed in the reaction of compound **1** and $Hg(MeCO_2)_2$, and the color changed from yellow to orange. The solution was allowed to stand for 2 weeks, and a small quantity of black metallic silver appeared. After removal of the precipitate by filtration, hexane was layered on top of the filtrate. After 2 days, dark-red diffraction-quality crystals of **5**·2THF were obtained. The product was then dried in a vacuum and used for elemental analysis. Yield 30%. Found: C, 38.50, H, 2.45, N, 1.26. Calcd for **5**, $C_{70}H_{52}N_2O_{12}P_4Fe_3Hg_4$: C, 38.10, H, 2.37, N, 1.27. IR(νCO): 1983m, 1958s, 1920s, 1904s cm^{-1}.

X-ray Crystallography. Intensity data for complexes **1a**, **1b**, **2**, **4**·2THF, and **5**·2THF were collected at 293 K on a Bruker Smart CCD

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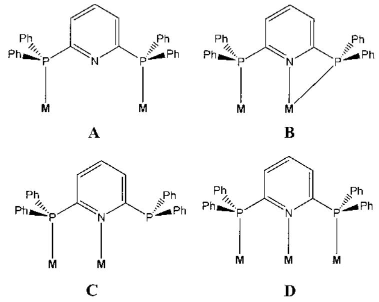
Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1A**, **1B**, **2**, **4**·2THF, and **5**·2THF

Complex **1a**		Complex **1b**	
Fe(1)−P(1)	2.237(2)	Fe(1)−P(1)	2.243(1)
Fe(2)−P(2)	2.236(2)	Fe(2)−P(2)	2.240(1)
Fe(1)−C(1)	1.782(6)	Fe(1)−C(1)	1.748(6)
Fe(1)−C(2)	1.765(7)	Fe(1)−C(2)	1.782(5)
Fe(1)−C(3)	1.779(6)	Fe(1)−C(3)	1.768(6)
Fe(1)−C(4)	1.760(6)	Fe(1)−C(4)	1.765(6)
Fe(2)−C(5)	1.772(8)	Fe(2)−C(5)	1.779(6)
Fe(2)−C(6)	1.774(8)	Fe(2)−C(6)	1.782(6)
Fe(2)−C(7)	1.746(7)	Fe(2)−C(7)	1.770(6)
Fe(2)−C(8)	1.765(7)	Fe(2)−C(8)	1.770(6)
P(1)−Fe(1)−C(1)	87.2(2)	P(1)−Fe(1)−C(1)	88.7(2)
P(1)−Fe(1)−C(2)	91.4(2)	P(1)−Fe(1)−C(2)	92.5(2)
P(1)−Fe(1)−C(3)	90.0(2)	P(1)−Fe(1)−C(3)	90.0(2)
P(1)−Fe(1)−C(4)	175.8(2)	P(1)−Fe(1)−C(4)	176.9(2)
P(2)−Fe(2)−C(5)	88.8(2)	P(2)−Fe(2)−C(5)	87.5(2)
P(2)−Fe(2)−C(6)	89.0(2)	P(2)−Fe(2)−C(6)	92.8(2)
P(2)−Fe(2)−C(7)	89.1(2)	P(2)−Fe(2)−C(7)	88.1(2)
P(2)−Fe(2)−C(8)	178.6(2)	P(2)−Fe(2)−C(8)	176.4(2)
C(1)−Fe(1)−C(2)	120.1(3)	C(1)−Fe(1)−C(2)	120.1(2)
C(1)−Fe(1)−C(3)	118.0(2)	C(1)−Fe(1)−C(3)	124.8(3)
C(1)−Fe(1)−C(4)	88.9(2)	C(1)−Fe(1)−C(4)	89.0(3)
C(2)−Fe(1)−C(3)	121.9(3)	C(2)−Fe(1)−C(3)	115.0(3)
C(2)−Fe(1)−C(4)	91.9(3)	C(2)−Fe(1)−C(4)	90.5(2)
C(3)−Fe(1)−C(4)	90.4(3)	C(3)−Fe(1)−C(4)	89.5(3)
C(5)−Fe(2)−C(6)	116.2(3)	C(5)−Fe(2)−C(6)	120.4(3)
C(5)−Fe(2)−C(7)	120.6(3)	C(5)−Fe(2)−C(7)	119.6(3)
C(5)−Fe(2)−C(8)	92.6(3)	C(5)−Fe(2)−C(8)	92.4(2)
C(6)−Fe(2)−C(7)	123.1(3)	C(6)−Fe(2)−C(7)	120.0(2)
C(6)−Fe(2)−C(8)	90.1(3)	C(7)−Fe(2)−C(8)	90.3(3)
C(7)−Fe(2)−C(8)	90.5(3)	C(7)−Fe(2)−C(8)	88.9(2)
Complex **2**			
Ag(1)−N(1)	2.42(1)	Fe(1)−P(1)	2.284(4)
Ag(1)−Fe(1)	2.627(3)	Fe(2)−P(2)	2.287(4)
Ag(1)−Fe(2)	2.652(3)		
N(1)−Ag(1)−Fe(1)	91.8(3)	P(1)−Fe(1)−C(4)	175.9(6)
N(1)−Ag(1)−Fe(2)	92.9(3)	P(2)−Fe(2)−Ag(1)	87.0(1)
Fe(1)−Ag(1)−Fe(2)	170.98(9)	P(2)−Fe(2)−C(8)	176.8(7)
P(1)−Fe(1)−Ag(1)	88.6(1)		
Complex **4**·2THF[a]			
Fe(1)−P(1)	2.211(1)	Fe(2)−P(2)	2.219(2)
Fe(1)−Hg(1)	2.5886(9)	Fe(2)−Hg(1)	2.5760(9)
Fe(1)−Hg(2)	2.555(1)	Fe(2)−Hg(2A)	2.565(1)
Hg(1)−Hg(2)	3.4083(5)	Hg(1)−N(1)	2.650(5)
P(1)−Fe(1)−Hg(1)	95.60(5)	P(2)−Fe(2)−Hg(1)	91.66(5)
P(1)−Fe(1)−Hg(2)	175.07(7)	P(2)−Fe(2)−Hg(2A)	177.11(7)
Hg(1)−Fe(1)−Hg(2)	83.00(3)	Hg(1)−Fe(2)−Hg(2A)	86.43(3)
Fe(1)−Hg(1)−N(1)	85.9(1)	Fe(2)−Hg(1)−N(1)	88.5(1)
Fe(1)−Hg(1)−Fe(2)	170.80(4)	Fe(1)−Hg(2)−Fe(2A)	172.80(3)
Complex **5**·2THF[b]			
Fe(1)−P(1)	2.225(1)	Fe(2)−P(2)	2.243(1)
Fe(2)−P(2A)	2.243(1)	Fe(1)−Hg(1)	2.6560(7)
Fe(1)−Hg(2)	2.4839(7)	Fe(2)−Hg(1)	2.5491(6)
Fe(2)−Hg(1A)	2.5491(6)	Hg(1)−N(1)	2.571(3)
Hg(1)−Hg(1A)	3.3348(4)	Hg(2)−O(5)	2.339(4)
Hg(2)−O(6)	2.487(5)		
P(1)−Fe(1)−Hg(1)	93.40(4)	P(2)−Fe(2)−P(2A)	166.74(7)
P(1)−Fe(1)−Hg(2)	173.80(4)	P(2)−Fe(2)−Hg(1)	91.66(5)
Hg(1)−Fe(1)−Hg(2)	89.45(2)	P(2)−Fe(2)−Hg(1A)	81.60(3)
Fe(1)−Hg(1)−N(1)	87.36(8)	Hg(1)−Fe(2)−Hg(1A)	81.71(3)
Fe(2)−Hg(1)−N(1)	88.5(1)	Fe(1)−Hg(1)−Fe(2)	93.82(8)

[a] Symmetry code: A $1 - x, -y, 1 - z$. [b] Symmetry code: A $-x, y, 1/2 - z$.

Scheme 2



1000 diffractometer system using Mo Kα radiation ($\lambda = 0.71073$ Å; frames of oscillation range 0.3°; 50 kV, 30 mA; $2\theta_{max} = 45°$ for **2**; $2\theta_{max} = 56°$ for all others). An empirical absorption correction (SADABS) was applied to the raw intensities. The crystal structures were determined by direct methods and refined by full-matrix least squares using the SHELXTL-PC program package.[6] Non-hydrogen atoms were subjected to anisotropic refinement. The phenyl groups in **2** were refined as hexagons (C−C bond length and C−C−C angle fixed at 1.39 Å and 120°, respectively) due to the low data−to−parameter ratio. All hydrogen atoms were generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement. A summary of crystal data is given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Further details are given in the Supporting Information.

Spectroscopic Measurements. Infrared spectra were recorded on a Shimadzu 435 spectrometer as KBr disks. $^{31}P\{^1H\}$ NMR spectra were recorded on an AC−P200 spectrometer at 81.03 MHz using H_3PO_4 as the external standard and $CDCl_3$ as solvent.

Result and Discussion

The ligand 2,6-bis(diphenylphosphino)pyridine, $(Ph_2P)_2py$ (L), is closely related to diphenylphosphinopyridine, Ph_2Ppy, which has been used extensively in constructing many binuclear complexes (Scheme 1). To date, four modes of coordination for ligand L have been established by means of X-ray crystallography, all are bridging modes, as illustrated in Scheme 2.

There are a number of structurally characterized complexes that contain the L ligand bonded in mode **A**, including $Pd_3Cl_6(\mu\text{-L})_3$,[5a] $Pt_2Cl_4(\mu\text{-L})_2\cdot 6CH_2Cl_2$,[5b] $Pt_2I_4(\mu\text{-L})_2\cdot 2CH_2Cl_2$,[5b] $[Rh_2(\mu\text{-L})_2(CO)_2(CH_3OH)Cl](PF_6)\cdot 2CH_2Cl_2$,[5c] $[Au_2(\mu\text{-L})_3](ClO_4)_2$,[5d] $[Au_2(C\equiv CPh)(\mu\text{-L})]_\infty$,[5e] $[Cu_2(\mu\text{-L})_3](PF_6)_2$,[5f] $[Ag_2(\mu\text{-L})_3](ClO_4)_2\cdot 2CH_2Cl_2$,[5g] and $[Ag(MeCN)_2(\mu\text{-L})]_\infty$.[5h] There exists only one example of a complex that contains the ligand coordinated in mode **B**, namely $[Rh_2(\mu\text{-I})(\mu\text{-L})_2(\mu\text{-CO})](PF_6)\cdot 2CH_2Cl_2$.[5i] There exist three examples that contain the ligand coordinated in mode **C**, namely $[Mo_2Cl_4(\mu\text{-L})_2]\cdot 2CH_2Cl_2$, $[Re_2Cl_4(\mu\text{-L})_2]$, and $[(n\text{-Bu})_4N]\cdot[Re_2Cl_7(\mu\text{-L})]\cdot CH_2Cl_2$;[5j] in all these cases, the metal−metal separations (2.15−2.28 Å) are shorter than those found in mode **A**, **B**, and **D**. The complex $[Rh_4(\mu\text{-Cl})_2Cl_2(\mu\text{-L})_2(\mu\text{-CO})(CO)_2]\cdot 2CH_2Cl_2$ has a molecular symmetry of C_2, with each L ligand coordinated in mode **D** to three metal centers from either end of an approximately linear array of four rhodium atoms.[5a] The only two structurally characterized species that contains the L ligand bonded to different metal types are $[Rh_2Sn(SnCl_3)Cl_3(CO)_2(\mu\text{-L})_2]\cdot 2CH_2Cl_2$[5k] and $[Ir_2Cu(CO)_2Cl_2(MeCN)(\mu\text{-L})_2](ClO_4)\cdot 2MeCN$[5l] in which the ligands adopt coordination mode **D** with their outer P atoms coordinated to the same metals and the middle N atoms bonded to the other metal.

In view of the insolubility of L in ethanol, a mixed solvent of dichloromethane and ethanol was used to synthesize $[Fe(CO)_4]_2(\mu\text{-L})$ by analogy to the synthesis of $Fe(CO)_4(\mu\text{-Ph}_2py)$.[3a] However, when equal stoichiometric amounts of $Fe(CO)_5$ and L were used, the yield of the product was low (<10%). Therefore a large excess of $Fe(CO)_5$ (5 equiv of $Fe(CO)_5$ and 1 equiv of L) was employed, and a higher yield of the product

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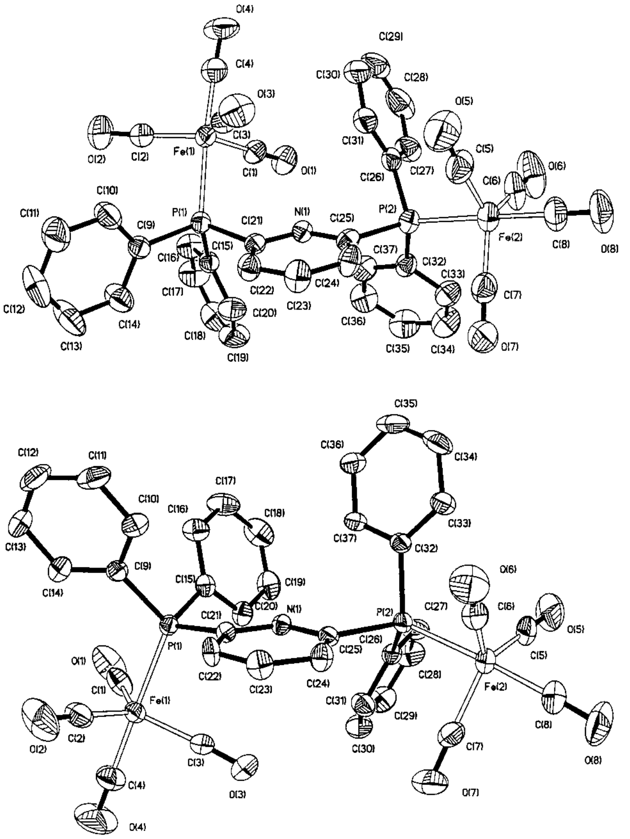

Figure 1. Perspective view (35% thermal ellipsoids) of $\{Fe(CO)_4\}_2(\mu\text{-}L)$ **1** in crystalline form **1a** (top) and **1b** (bottom). L = 2,6-bis(diphenylphosphino)pyridine, $(Ph_2P)_2py$.

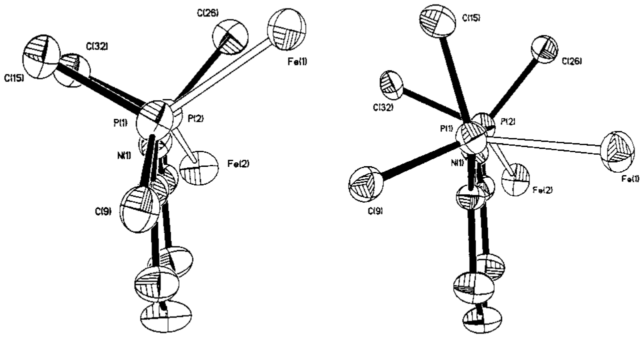

Figure 2. Perspective view (35% thermal ellipsoids) of the two conformations of **1** in form **1a** (eclipsed, left) and **1b** (staggered, right). For clarity the carbonyl groups and ipso carbon atoms of the phenyl rings have been omitted.

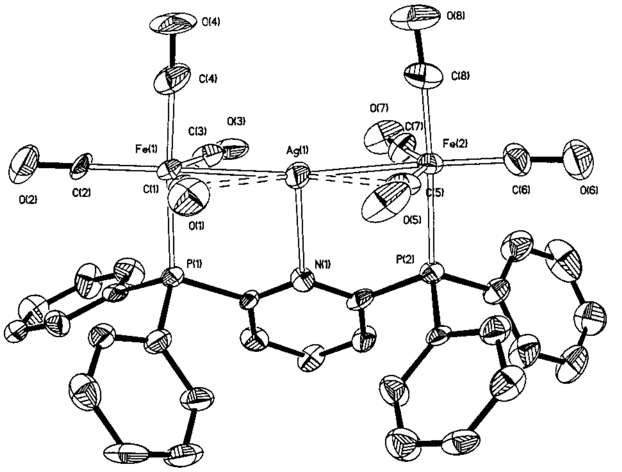

Figure 3. Perspective view (35% thermal ellipsoids) of the $[\{Fe(CO)_4\}_2Ag(\mu\text{-}L]^+$ cation in **2**.

was obtained (about 50%). The IR spectrum of **1** shows four peaks in the range of 1900−2050 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a singlet at δ 75.6 ppm, which indicates the two phosphorus atoms are in the same chemical environment.

When different solvents (EtOH and hexane) were used to diffuse into a solution of $\{Fe(CO)_4\}_2(\mu\text{-}L)$ **1** in CH_2Cl_2, two crystalline solvates that display allomorphism were obtained. Different conformations of the molecule exist in the two allomorphic forms **1a** and **b**, as shown in Figure 1. Selected bond lengths and angles are listed in Table 2. In both conformations, the ligand L coordinates to the metal centers in mode **A**. The coordination environment about each iron atom may be described as a trigonal bipyramid, with three carbonyl groups lying in the equatorial plane (the sum of the three C−Fe−C angles is nearly 360°) and a phosphorus atom and the remaining carbonyl group occupying the axial positions (the P−Fe−C angle is nearly 180°). Figure 2 clearly shows that the conformation of **1**, when viewed as a Newman projection along the line P(1)···P(2), is eclipsed in **1a** and staggered in **1b**.

The reaction of **1** with $AgClO_4$ and $HgCl_2$ in molar ratio of 1:1 and 1:2 in benzene and dichloromethane gave compound $[\{Fe(CO)_4\}_2Ag(\mu\text{-}L)](ClO_4)$ **2** and **3**, respectively, which were fully characterized by IR and $^{31}P\{^1H\}$ NMR. The $^{31}P\{^1H\}$ NMR spectrum of complex **2** consists of a doublet, which is attributed to the sum of $^2J(P-Ag)$ and $^3J(P-Ag)$ coupling via the Fe atom and via pyridine group, respectively. The silver atom bridges two iron centers, so the two phosphorus atoms are in equivalent chemical environments. On the other hand, the abundance ratio of ^{107}Ag and ^{109}Ag is close to 50%, and $^2J(P-Ag)$ and $^3J(P-Ag)$ coupling via the Fe atom and pyridine group generates a doublet with $J(P-Ag)$ = 12 Hz. Compared to **1**, the IR ν(CO) spectrum of polynuclear complex **2** shifts to higher frequencies, which is consistent with both a change in stereochemistry and a decrease in electron density on the iron(0) atom.

An ORTEP drawing with atom numbering for the cation in $[\{Fe(CO)_4\}_2Ag(\mu\text{-}L)](ClO_4)$ **2** is shown in Figure 3. Selected bond lengths and angles are listed in Table 2. The iron and silver centers are linked by the bridging ligand L. A distorted octahedral geometry is adopted by each of the two Fe atoms, in which the angles P(1)−Fe(1)−C(4) and P(2)−Fe(2)−C(8) are 175.9(6) and 176.8(7)°, respectively, and the other three CO moieties of the each iron and the silver metal lie in a plane perpendicular to the P−Fe−C axis. In this complex, the silver atom is only three coordinated, with two Fe−Ag distances of 2.627(3) and 2.652(3) Å, which are comparable to those of the Fe−Ag clusters containing the $Fe(CO)_4^{2-}$ fragment in $[Fe_8(CO)_{32}Ag_{13}]^{4-}$ (2.695−2.762 Å),[7a] $[Fe_4(CO)_{16}Ag_4]^{4-}$ (2.570−2.600 Å), $[Fe_4(CO)_{16}Ag_5]^{3-}$ (2.585−2.727 Å),[7b] $Fe_4(CO)_{16}Ag_8(dppm)_2$ (2.608−2.666 Å), and $Fe_4(CO)_{16}Ag_4Au_4(dppe)_2$ (2.643−2.711 Å),[7c] but shorter than that (2.760(1) Å) in $Fe(CO)_3(\mu\text{-}Ph_2Ppy)_2Ag(Ph_2Ppy)ClO_4$.[3b] The three metal atoms in complex **2** are approximately colinear with an Fe−Ag−Fe angle of 170.98(9)°, and the Fe−Ag−N angles are close to 90°. The weak interactions of the $(CO)_1$ and $(CO)_5$ ligands with the Ag^+ center (Ag(1)−C(1) 2.63(2) Å and Ag(1)−C(5) 2.65(2) Å) are

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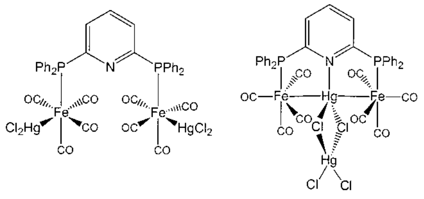

Figure 4. Possible structures of $\{Fe(CO)_4\}_2Hg_2Cl_4(\mu\text{-L})$, **3**.

presumably responsible for the nonlinearity of the edge Fe−Ag−Fe. It has been found that the silver ion can act as a single-electron transfer reagent that oxidizes $Fe(CO)_3(R_3P)_2$ to form $[Fe(CO)_3(R_3P)_2]^+$,[8a] which is more reactive and easily decomposed. On the other hand, compared with Collman's reagent $Fe(CO)_4^{2-}$, the coordination ability of a neutral iron carbonyl is weak, and examples of its complexes with silver(I) are rare.[3b] It has been reported that a silver salt becomes less exoergic in THF than in CH_2Cl_2,[8b] so THF was used to recrystallize compound **2**. In this complex, the bridging ligand L plays an important role in stabilizing the Fe→Ag dative bond.

When compound **1** was reacted with $HgCl_2$ in an equimolar ratio, the IR and $^{31}P\{^1H\}$ NMR spectra showed that the reaction did not proceed to completion, and half of the starting materials remained. However, when the molar ratio of compound **1** and $HgCl_2$ reached 1:2, all starting materials were consumed, and compound **3** was obtained. Unfortunately, single crystals of compound **3** could not be obtained using a variety of solvents. Compared to compound **1**, the IR ν(CO) spectrum of compound **3** exhibits splitting and a shift to higher wavenumber. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet shifted from δ 75.6 to 69.0 ppm, which indicates that the two phosphorus atoms in **3** have the same chemical environment and the electron density on the iron(0) atoms decreases. The spectral data suggest that Fe→Hg dative bonds are formed in **3**, whose two possible structures are shown in Figure 4.

The reaction of $Hg(MeCO_2)_2$ with $[Fe(CO)_4]_2(\mu\text{-L})$ in a 2:1 molar ratio in THF, for two weeks at room temperature, yielded $[\{Fe(CO)_3Hg\}_2(\mu\text{-L})]_2$ **4**, whose octanuclear structure is similar to those of $[Fe(CO)_4Cd]_4$, $[Fe(CO)_4Ag]_4^{4-}$, and $[Fe(CO)_4Au]_4^{4-}$.[7b,9] The IR ν(CO) spectrum of complex **4** shows two peaks, which indicates that the three CO group are in two distinct environments.

An ORTEP drawing with atom numbering for complex **4** is shown in Figure 5. Selected bond lengths and angles are listed in Table 2. The eight metals are alternately arranged in a square with iron atoms at its corners and a mercury atom located at the center of each edge. Although this configuration was assumed for $[Fe(CO)_4Hg]_4$, no direct evidence was provided.[9a] Each iron atom is in a distorted octahedral environment, being coordinated by three CO ligands, two cis positioned mercury atoms (Hg−Fe−Hg angle: 83.00(3)° and 86.43(3)°), which are comparable with those in $[Fe(CO)_4(HgCl)_2]$ and $[\{Fe(CO)_4\}_5Hg_7(SBu^t)_3Cl]$,[10] and one phosphorus atom of ligand L. The angles P(1)−Fe(1)−Hg(2) and P(2)−Fe(2)−Hg(2a) are 175.07(7) and 177.11(7)°, respectively, and the other three CO moieties of the each iron and the Hg(1) metal lie in a plane perpendicular to the P−Fe−Hg(2) axis. The Fe−Hg distances fall in the range of 2.555(1)−2.589(1) Å, which are similar to those in iron−mercury clusters containing an $Fe(CO)_4^{2-}$ fragment and a linear Fe−Hg−Fe free system,[10] but shorter than those in the binuclear complexes $Fe(CO)_3(R_3P)_2HgX_2$ (X = Cl, Br, I, SCN).[3c,3d,11] On the other hand, the long Hg(1)···Hg(2) distance of 3.4083(5) Å can be taken to be a weak interaction when compared with the Hg−Hg covalent bond length of 2.89 Å in $[\{(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg\}_4]$.[12a] Similar weak bonding interactions are found in $[HgPBu^t]_4$ (Hg···Hg 3.330(1)−3.564(1) Å)[12b] and $[\{Fe(CO)_4\}_5Hg_7(SBu^t)_3Cl]$ (Hg···Hg 3.294(2)−3.731(2) Å).[10a] This weak interaction also decreases the Hg−Fe−Hg angle. Comparing the square metallic cores in the series of complexes $[Fe(CO)_4Cd]_4$, $[Fe(CO)_4Ag]_4^{4-}$, $[Fe(CO)_4Au]_4^{4-}$, and **4**, the M−Fe−M and Fe−M−Fe angles in the silver (72−80° and 161−169°) and gold (65−70° and 156−158°) complexes are much smaller than the corresponding values in the mercury (83−86° and 171−173°) and cadmium (88−89° and 170−171°) complexes, which is attributed to argentophilic and aurophilic interactions. The average Ag−Ag and Au−Au distances of about 3.0 Å, though weak, cause an inward bending of the Fe−M−Fe linear sequences.

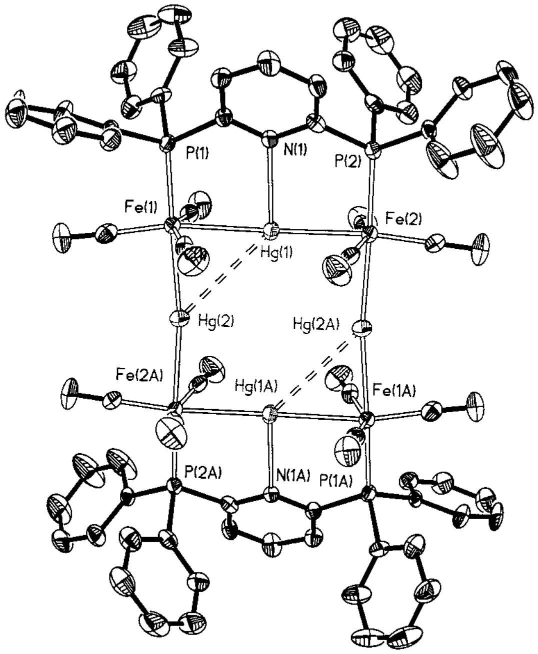

Figure 5. Perspective view (35% thermal ellipsoids) of $[\{Fe(CO)_3Hg\}_2(\mu\text{-L})]_2$, **4**.

Since the size of the Fe_4Hg_4 square in complex **4** is about 5.2 × 5.2 Å, we attempted to insert a silver(I) atom into the central cavity. It is known that a silver ion can be positioned at the center of $[Fe(CO)_4Ag]_4^{4-}$ to form $[Fe_4(CO)_{16}Ag_5]^{3-}$,[7b] and

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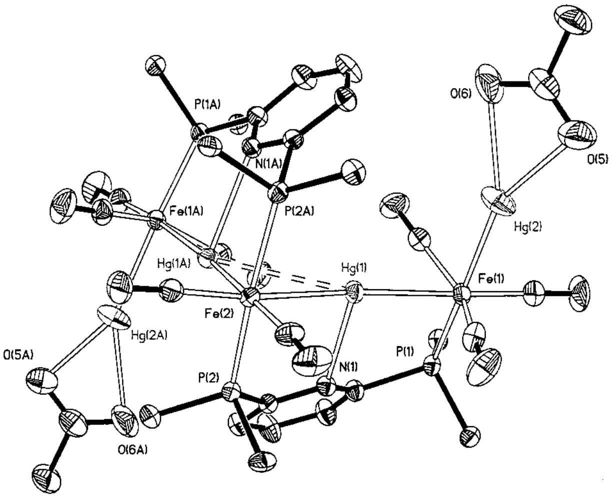
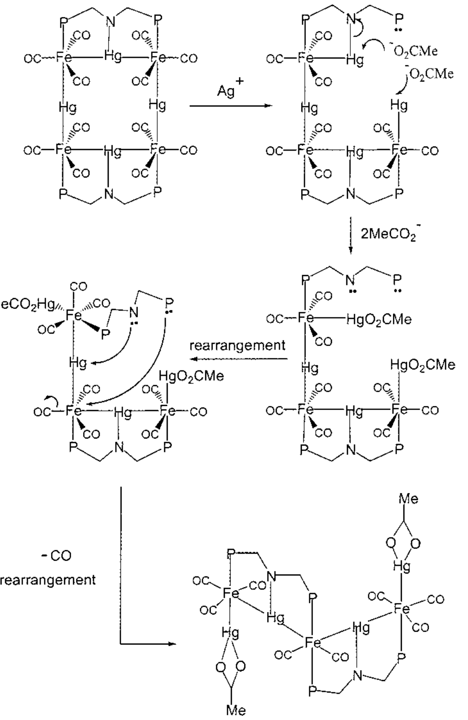


Figure 6. Perspective view (35% thermal ellipsoids) of $Fe_3(CO)_8Hg_4(\mu\text{-}L)_2(MeCO_2)_2$, **5**. For each phenyl ring in a Ph_2P group, only the ipso carbon atom is shown.

some complexes containing a Hg−Ag bond have been reported.[13] We also took note of the fact that in the synthesis of complex **4**, acetic acid is formed. Therefore, a reaction was carried out by mixing Ag_2CO_3, $Hg(MeCO_2)_2$ and compound **1** in molar ratio 1:4:2 in THF, with a view to effect a gradual release of silver ions, but the product obtained, namely compound **5**, was not the intended one that would feature a nine atom Fe_4Hg_4Ag square grid.

An ORTEP drawing with atom numbering for $Fe_3(CO)_8Hg_4(\mu\text{-}L)_2(MeCO_2)_2$ **5** is shown in Figure 6. Selected bond lengths and angles are listed in Table 2. The complex lies on a crystallographic two-fold axis; the middle iron atom is coordinated by two trans phosphine ligands, two cis CO ligands, and two cis Hg atoms. In the proposed mechanism shown in Scheme 3, one $Fe(CO)_3$ group in **4** is oxidized and cleaved by a silver(I) ion, generating an empty phosphine site on one L ligand. Next, a pair of acetate ligands each chelates an exposed Hg atom, freeing a pyridyl site on the same L ligand. A Berry pseudorotation about the proximal Fe atom then positions the η^1-L ligand and the HgO_2CMe group trans to each other. Finally, nucleophilic attachment of the dangling pyridyl and phosphine sites to the adjacent Hg and $Fe(CO)_3$ centers, respectively, dislodges a CO ligand and causes another Berry rearrangement at the middle Fe atom, such that the bulky PPh_2 groups occupy trans positions around it. In the resulting molecular structure of **5**, the seven metal atoms form a kinky wire with bends at the three iron centers, and the CO groups are approximately coplanar. Both independent iron atoms are in distorted octahedral environments, the P(1)−Fe(1)−Hg(2) and P(2)−Fe(2)−P(2A) angles are 173.80(4) and 166.74(7)°, respectively. The Hg(1)···Hg(1A) contact of 3.3348(4) Å is suggestive of a weak interaction between the two metal centers. The angle Hg(1)−Fe(2)−Hg(1A) (81.60(3)°) is significantly smaller than Hg(1)−Fe(1)−Hg(2) (89.45(2)°), which is not affected by the Hg···Hg interaction. On the other hand, the Hg−N bond distance of 2.571(3) Å in **5** is slightly shorter than that of 2.650(5) Å in **4**, and both are comparable to those in $Fe(CO)_3(\mu\text{-}Ph_2Ppy)_2HgX_2$ (X = Cl, Br, I, SCN).[3c,3d] The Fe−Hg distances in **5** fall in the range of 2.4839(7)−2.6560(7) Å, which is similar to those in **4** and other iron−mercury clusters.[10]

Scheme 3



Conclusion

In summary, we have taken advantage of the coordination ability of the rigid P,N,P-tridentate ligand 2,6-bis(diphenylphosphino)pyridine (L) to synthesize a new organometallic Fe,N,Fe-tridentate ligand $\{Fe(CO)_4\}_2(\mu\text{-}L)$, which proved to be quite versatile for the generation of hetero-polynuclear complexes consolidated by Fe→M (M = Ag, Hg) dative bonding.

Acknowledgment. This work is supported by Hong Kong Research Grants Council Earmarked Grant Ref. No. CUHK 4022/98P.

Supporting Information Available: An X-ray crystallographic file in CIF format for compounds **1a**, **1b**, **2**, **4**·2THF, and **5**·2THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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