

Notes

Synthesis of the New Polydentate Phosphine Ligand 1-[(Diphenylphosphino)methyl]-4-(2-pyridyl)piperazine and Structural Characterization of Its Binuclear Silver(I) and Mononuclear Iron(0) Complexes

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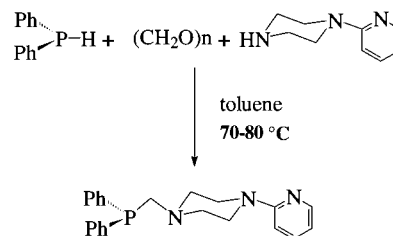
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Introduction

Polydentate phosphine ligands with $-(CH_2)_n-$ spacers between the donor atoms are useful backbones for the construction of bi- and polynuclear transition metal complexes.¹ Each additional methylene group provides a predetermined separation and flexibility between the donor centers so that metal–metal distances in such complexes can span the range involved in metal–metal bonding and metal–ligand–metal-bridged bonding.² Bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$) has been widely exploited in this fashion,³ while (diphenylarsino)(diphenylphosphino)methane ($Ph_2PCH_2AsPh_2$) has been used in the rational synthesis of heterobinuclear complexes.⁴ However, the nonrigid *PN*-phosphine ligand (diphenylphosphino)(diphenylamino)methane ($Ph_2PCH_2NPh_2$) has only been developed as a monodentate phosphine ligand to form mononuclear Rh^I ,² Au^I ,⁵ and Cu^I ⁶ complexes. The reason that it does not function as a bidentate ligand is attributed to the nearly planar configuration around the tertiary amino nitrogen atom, which precludes its coordination to a metal center, as revealed by the structures of $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$,² $Au[(Ph_2PCH_2NPh_2)_2Cl]$,⁵ $Cu[(Ph_2PCH_2NPh_2)_2(NO_3)]$, and $Cu[(Ph_2PCH_2NPh_2)_2Cl]$.⁶ Replacement of the diphenylamino group by a piperazine ring, as in the newly designed nonrigid *PN*-phosphine ligand **L**¹ (see Scheme 1), ensures that the proximal tertiary amino nitrogen atom has a pyramidal configuration, and we report here the synthesis and structure of its binuclear silver(I) complex and mononuclear iron(0) complex with a new nonrigid *PN*-phosphine ligand

Scheme 1



containing a methylene spacer in which the proximal nitrogen atom is incorporated into the six-membered ring of piperazine.

Experimental Section

General Procedure, Measurements, and Materials. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. The 1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker-300 NMR spectrometer using $Si(Me_4)$ as the external standard and $CDCl_3$ as solvent. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker-500 NMR spectrometer at 202.45 MHz using 85% H_3PO_4 as the external standard and $CDCl_3$ as solvent. $[Ag(MeCN)_4](O_3SCF_3)$ was prepared from the literature procedure.⁷

Preparation of 1-[(Diphenylphosphino)methyl]-4-(2-pyridyl)piperazine (L**¹).** Diphenylphosphine (1.86 g, 10.00 mmol) was added to a mixture of 1.63 g (10.00 mmol) of 1-(2-pyridyl)piperazine and 0.45 g (15.00 mmol) of paraformaldehyde in 20 mL of toluene at 70–80 °C. The mixture was stirred until all the solid paraformaldehyde had completely dissolved (about 5 h). This solution was cooled and then filtered through Celite. The solvent was removed in a vacuum, leaving a colorless solid which was recrystallized with dichloromethane/ethanol to give crystals of **L**¹. Yield: 2.80 g (78%). $^{31}P\{^1H\}$ NMR: δ 2.40 ppm. 1H NMR: δ 8.19 (t, $J = 0.4$ Hz, 1H), 7.47(m, 5H), 7.33 (m, 6H), 3.57 (t, $J = 1.5$ Hz, 4H), 3.28 (t, $J = 0.4$ Hz, 2H), 2.77 (t, $J = 1.1$ Hz, 4H). Anal. Calcd for $C_{22}H_{24}N_3P$: C, 73.11; H, 6.69; N, 11.62. Found: C, 73.05; H, 6.67; N, 11.63.

Preparation of Binuclear Silver(I) Complex $[Ag(\mu-L^1)(O_3SCF_3)]_2$. **1.** To a solution containing 0.36 g (1.00 mmol) of **L**¹ in 30 mL of CH_3CN was added solid $[Ag(MeCN)_4](O_3SCF_3)$ (0.42 g, 1.00 mmol). The resulting solution was stirred at room temperature for 1 h. Subsequent diffusion of diethyl ether into the concentrated solution gave $[Ag(\mu-L^1)(O_3SCF_3)]_2$ as colorless crystals. Yield: 0.52 g (85%). $^{31}P\{^1H\}$ NMR: δ 21.40 ppm. Anal. Calcd for $C_{46}H_{48}Ag_2F_6N_6O_6P_2S_2$: C, 44.67; H, 3.91; N, 6.80. Found: C, 44.57; H, 3.90; N, 6.75. Crystals of $[Ag(\mu-L^1)(O_3SCF_3)]_2 \cdot MeCN \cdot \frac{1}{2}H_2O$ suitable for X-ray analysis were obtained by vapor diffusion of diisopropyl ether into its acetonitrile solution.

Preparation of Mononuclear Iron(0) Complex *trans*- $Fe(CO)_3(L^1)_2$. **2.** To a solution of NaOH (0.10 g, 2.50 mmol) in *n*-butanol (20 mL) was added $Fe(CO)_5$ (0.15 mL, 1.2 mmol), and the mixture was stirred for 30 min at room temperature. Then **L**¹ (0.90 g, 2.50 mmol) was added, and the mixture was refluxed for 2 h. After the solution was cooled to room temperature, a yellow precipitate appeared. The precipitate was filtered out and recrystallized from $CH_2Cl_2/MeOH$ to give yellow crystals of **2**. Yield: 0.63 g (61%). $^{31}P\{^1H\}$: δ 70.60 ppm. Anal. Calcd for $C_{47}H_{48}FeN_6O_3P_2$: C, 65.43; H, 5.61; N, 9.24. Found: C, 64.83; H, 5.58; N, 9.62.

X-ray Crystallography. Intensity data for $1 \cdot MeCN \cdot \frac{1}{2}H_2O$ were collected in the variable ω -scan mode on a four-circle diffractometer

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Table 1. Crystal Data for 1·MeCN·1/2H₂O and 2

formula	C ₄₆ H ₄₈ Ag ₂ F ₆ N ₆ O ₆ P ₂ S ₂ · MeCN·1/2H ₂ O (1·MeCN· 1/2H ₂ O)	C ₄₇ H ₄₈ FeN ₆ O ₃ P ₂ (2)
fw	1286.77	862.76
T, K	294	294
cryst syst	monoclinic	monoclinic
space group	C2/c (No. 15)	P2 ₁ /c (No. 14)
unit-cell dimens		
a (Å)	21.444(3)	11.644(2)
b (Å)	15.615(3)	11.945(5)
c (Å)	17.370(6)	31.875(5)
β (deg)	103.39(1)	91.47(1)
V (Å ³)	5658(3)	4432(2)
Z	4	4
F(000)	2604	1808
D _c (g cm ⁻³)	1.555	1.254
λ, Å (Mo Kα)	0.710 73	0.710 73
μ, cm ⁻¹	0.899	0.458
collcn range (2θ, deg)	3–52	4–52
goodness-of-fit index	0.93	1.39
no. of unique reflctns	5576	7571
no. of obsd reflctns	2846	7132
(F ≥ 4σ(F))		
no. of variables, p	348	532
R _F ^a	0.069	0.059
R _{wF} ^{2 b}	0.136	0.063

$${}^a R_F \equiv \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}, {}^b R_{wF^2} \equiv \frac{[\sum w(|F_o| - |F_c|)^2]}{[\sum w|F_o|^2]}^{1/2}$$

(Siemens R3m/V) using Mo Kα radiation (λ = 0.710 73 Å, 50 kV, 25 mA, 2θ_{min} = 3°, 2θ_{max} = 52°) at 294 K. The intensity data of 2 were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA (2θ_{min} = 4°, 2θ_{max} = 52°, 36 5° oscillation frames in the range of 0–180°, exposure 8 min/frame).⁸ A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABCOR program.⁹ The crystal structures were determined by direct methods, and non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement on the F² data.

All computation were performed on an IBM-compatible 486 PC with the SHELXL-PC program package.¹⁰ Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.¹¹

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1.

Results and Discussion

Heating a mixture of diphenylphosphine, 1-(2-pyridyl)-piperazine, and paraformaldehyde in toluene in a manner similar

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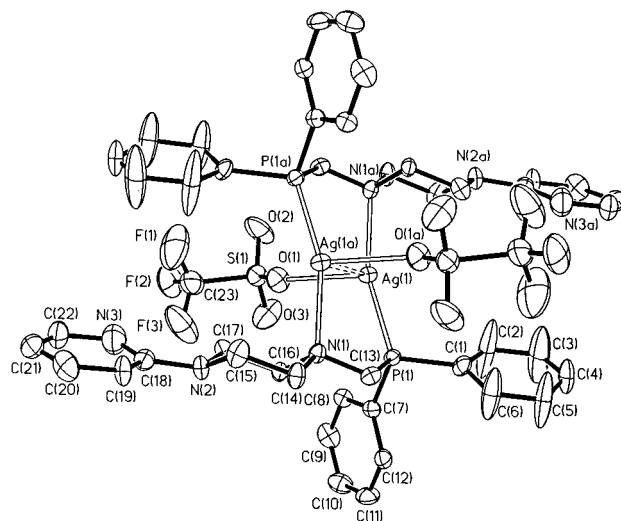
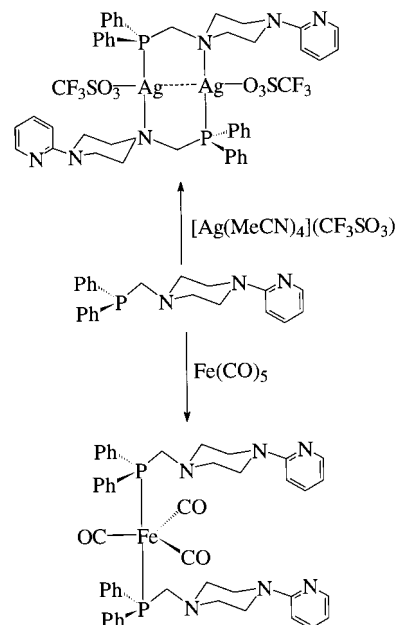


Figure 1. ORTEP drawing (35% thermal ellipsoids) showing the molecular structure of [Ag(μ-L)(O₃SCF₃)₂]₂, **1**, in 1·MeCN·1/2H₂O. Pertinent bond lengths (Å) and angles (deg): Ag(1)–Ag(1a) 3.033(1), Ag(1)–P(1) 2.383(1), Ag(1)–O(1) 2.557(2), Ag(1)–N(1a) 2.279(2); P(1)–Ag(1)–O(1) 108.2(1), P(1)–Ag(1)–Ag(1a) 84.9(1), P(1)–Ag(1)–N(1a) 153.2(1), O(1)–Ag(1)–Ag(1a) 84.9(1), O(1)–Ag(1)–N(1a) 95.3(1), N(1a)–Ag(1)–Ag(1a) 84.6(1). Symmetry code: (a) –x + 1/2, –y + 1/2, –z.

Scheme 2



to that devised by Maier¹² yielded a colorless solution, from which 1-[(diphenylphosphino)methyl]-4-(2-pyridyl)piperazine (L¹) was obtained as colorless crystals after evaporation and crystallization from dichloromethane/ethanol (Scheme 1). The ³¹P{¹H} NMR spectrum gave a singlet at 2.4 ppm. The ¹H NMR spectrum showed characteristic resonances of phenyl and pyridyl protons as well as three groups of methylene protons. Compared to (diphenylphosphino)(diphenylamino)methane, this PN-phosphine ligand has a pyramidal nitrogen atom seated at the bridgehead of the piperazine ring, which can readily coordinate to a metal center with its lone-pair electrons.

Reaction of L¹ with an equimolar amount of [Ag(CH₃CN)₄](O₃SCF₃) in acetonitrile at room temperature leads to rapid

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formation of $[\text{Ag}(\mu\text{-L}^1)(\text{O}_3\text{SCF}_3)_2]$ (Scheme 2). Slow diffusion of diisopropyl ether into an acetonitrile solution afforded colorless crystals of $[\text{Ag}(\mu\text{-L}^1)(\text{O}_3\text{SCF}_3)_2] \cdot \text{MeCN} \cdot \frac{1}{2}\text{H}_2\text{O}$, the structure of which was determined by single-crystal X-ray analysis.

A perspective view of the binuclear complex **1**, $[\text{Ag}(\mu\text{-L}^1)(\text{O}_3\text{SCF}_3)_2]$, which has molecular symmetry $\bar{1}$, is displayed in Figure 1 with atom numbering. The silver atoms are bridged by a pair of polydentate phosphine ligands in the head-to-tail configuration. The coordination geometry at each silver atom is highly distorted tetrahedral with the largest bond angle $\text{P}(1)\text{-Ag}(1)\text{-N}(1a) = 153.2(1)^\circ$, and further stabilization was accomplished by the coordination of an anionic trifluoromethanesulfonate ligand. The $\text{Ag}\cdots\text{Ag}$ separation of $3.033(1)$ Å is in agreement with those $(2.943(2)\text{--}3.014(2)$ Å) in $[\text{Ag}_3(\text{dppp})_2(\text{MeCN})_2(\text{ClO}_4)_2](\text{ClO}_4)$ [dppp = bis(diphenylphosphino)phenylphosphine],¹³ those $(3.005(2), 3.184(2)$ Å) in $\{[\text{Ag}_2(\text{MeCN})_2(\mu\text{-L}^2)]\}_n(\text{ClO}_4)_{2n}$ ($\text{L}^2 = 3,6\text{-bis(diphenylphosphino)pyridazine}$),¹⁴ $(3.162(1)\text{--}3.223(1)$ Å) in $[\text{Ag}\{\text{HC}(\text{PPh}_2)_3\}_2\text{Cl}](\text{ClO}_4)_2 \cdot 2\text{MeCN}$,¹⁵ and that those (3.085) Å) in $[\text{Ag}_2(\text{dppm})_2(\text{NO}_3)_2]$,¹⁶ indicating the possibility of weak metal–metal interaction in this binuclear complex. The $\text{Ag}\text{-N}$ bond length of $2.274(7)$ Å is much shorter than those $(2.456(5), 2.478(6)$ Å) in $[(\text{OC})_3\text{Fe}(\mu\text{-dppy})_2\text{Ag}(\text{dppy})](\text{ClO}_4) \cdot \text{MeOH}$ (dppy = 2-(diphenylphosphino)pyridine).¹⁷

Reactions of L^1 with $\text{Fe}(\text{CO})_5$ and NaOH in refluxing *n*-butanol afforded a yellow precipitate formulated as *trans*- $\text{Fe}(\text{CO})_3(\text{L}^1)_2$. The IR spectrum showed an intense carbonyl absorption at 1874 cm^{-1} , which implies that the local symmetry about the Fe atom is near D_{3h} .

The molecular structure of **2**, *trans*- $\text{Fe}(\text{CO})_3(\text{L}^1)_2$, is depicted in Figure 2 with atom numbering. The coordination environment about the iron atom may be best described as an FeP_2C_3 trigonal bipyramid with two phosphine ligands occupying axial positions and three carbonyl groups lying on the equatorial plane. The $\text{P}\text{-Fe}\text{-P}$ angle of $175.7(1)^\circ$ is comparable to that $(174.2(1)^\circ)$ in *trans*- $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{Ppy})_2$ ¹⁸ and that $(177.1(1)^\circ)$

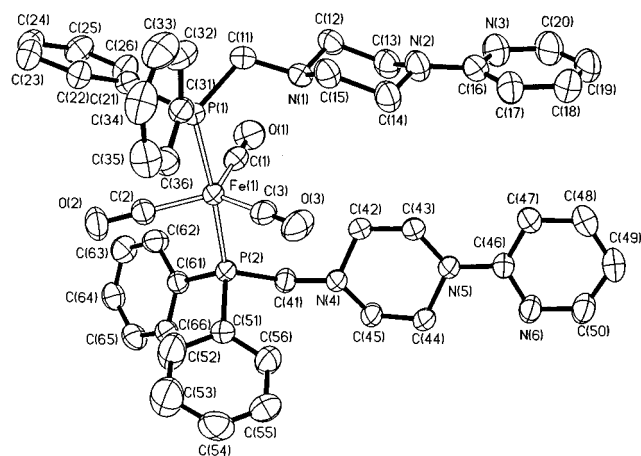


Figure 2. ORTEP drawing (35% thermal ellipsoids) showing the molecular structure of **2**, *trans*- $\text{Fe}(\text{CO})_3(\text{L}^1)_2$. Pertinent bond lengths (Å) and angles (deg): $\text{Fe}(1)\text{-P}(1)$ 2.209(1), $\text{Fe}(1)\text{-P}(2)$ 2.215(1), $\text{Fe}(1)\text{-C}(1)$ 1.753(3), $\text{Fe}(1)\text{-C}(2)$ 1.758(3), $\text{Fe}(1)\text{-C}(3)$ 1.767(3); $\text{P}(1)\text{-Fe}(1)\text{-P}(2)$ 175.7(1), $\text{C}(1)\text{-Fe}(1)\text{-C}(2)$ 120.2(2), $\text{C}(1)\text{-Fe}(1)\text{-C}(3)$ 117.6(1), $\text{C}(2)\text{-Fe}(1)\text{-C}(3)$ 122.2(2).

in *trans*- $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{Ppy})_2$.¹⁹ The three $\text{C}\text{-Fe}\text{-C}$ angles ($120.2(2)$, $117.6(1)$, and $122.2(2)^\circ$) are not far from the ideal value of 120° . One noteworthy feature of this structure is that the mean planes of the outstretched (pyridyl)piperazine groups are virtually orthogonal to each other (Figure 2).

In summary, we have taken advantage of the coordination ability of the pyramidal nitrogen atom of the piperazine ring in the new nonrigid *PV* ligand to generate the binuclear silver(I) complex $[\text{Ag}(\mu\text{-L}^1)(\text{O}_3\text{SCF}_3)_2]$, in which weak metal–metal interaction is imposed by simultaneous tight binding of the P and N ligand atoms to two metal centers. Ligand L^1 was also shown to function as a monodentate ligand in forming the mononuclear iron(0) complex *trans*- $\text{Fe}(\text{CO})_3(\text{L}^1)_2$.

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Supporting Information Available: Tables of atomic parameters and bond lengths and angles for $\mathbf{1} \cdot \text{MeCN} \cdot \frac{1}{2}\text{H}_2\text{O}$ and **2** (12 pages). Ordering information is given on any current masthead page.

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