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First Heterobimetallic Seven-Membered Macrocycle Complex with a Fe(0) → Cu(I) Donor−Acceptor Bond

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*Summary: A new ligand, 2-(N-diphenylphosphinomethyl-N-cyclohexyl)aminopyridine (NNP), was prepared by the Mannich reaction of $HPPh_2$ with 2-(N-cyclohexyl)aminopyridine and paraformaldehyde. The ligand NNP reacted with $Fe(CO)_5$ to give the monometallic complex trans-$Fe(CO)_3(NNP)_2$ (**2**). The reaction of complex **2** with $[Cu(CH_3CN)_4]^+[ClO_4]^-$ gave a novel complex **3**, $[(OC)_3Fe(\mu\text{-}NNP)_2Cu]^+ClO_4^-$, which has two seven-membered macrocycles and an Fe(0) → Cu(I) donor−acceptor bond. The molecular structure of complex **3** was determined by X-ray single-crystal analysis.*

Binuclear complexes have long been recognized to have reactivity different from that of their mononuclear analogues,[1] and their chemistry continues to be an active research area in organometallic chemistry. Studies on compounds that have two different metal centers have attracted particular interest, and there has been a great increase in the understanding of their structures and reactivities in recent years.[2] In principle, in a heterobimetallic compound each metal center could undergo the reactions observed in the mononuclear compounds; in addition, when two metal atoms are held in close proximity by bridging ligands, novel modes of reactivity can be observed. Bimetallic compounds containing a metal−metal bond are of two types: those with and those without bridging ligands. All known compounds having bridging ligands are one-, two-, or three-atom bridging three-, four-, or five-membered bimetallic cycles. We have synthesized a number of complexes containing three-atom bridging dative metal−metal bonds,[3] whereas Pomeroy et al. have prepared some unbridged complexes.[4] Until now, to our best knowledge, there are no examples of more than three-atom bridging heterobimetallic macrocycles containing metal−metal bonds in the literature. In this paper, we wish to report the design of a new ligand, 2-(*N*-diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine (NNP, **1**), and the synthesis of the novel compound containing two seven-membered macrocycles and dative Fe(0)−Cu(I) bonds, $[(OC)_3Fe(\mu\text{-}NNP)_2Cu]^+ClO_4^-$, **3**. The ligand **1**, 2-(*N*-diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine, was prepared by the Mannich reaction of 2-(*N*-cyclohexyl)aminopyridine[5] with Ph_2PH and $(HCHO)_n$. The reaction of ligand **1** with $Fe(CO)_5$ and KOH in refluxing ethanol gave the monometallic complex *trans*-$(OC)_3Fe(NNP)_2$ (**2**). Then **2** reacted with a stoichiometric amount of $[Cu(CH_3CN)_4]^+[ClO_4]^-$ in CH_2Cl_2 at room temperature conveniently to give the product $[(OC)_3Fe(\mu\text{-}NNP)_2Cu]^+ClO_4^-$ (**3**) in high yield; the latter structure has been determined by an X-ray crystal structure analysis.[6] Complex **3** comprises organometallic cation $[(OC)_3Fe(\mu\text{-}NNP)_2Cu]^+$ (Figure 1), anion ClO_4^-, and 1.5 molecules of CH_2Cl_2 packed together in the crystal lattice. As shown in Figure 1, the Fe(0) and Cu(I) centers are bridged by two ligands **1** and a metal−metal bond, such that two P atoms coordinated to Fe are *trans* to each other. The O(3), C(3), Fe(1), Cu(1), P(1), and P(2) atoms are almost in a plane; the rms deviation of fitted atoms is 0.0460. The Fe(1), Cu(1), C(1), O(1), C(2), O(2), C(3), and O(3) atoms are also almost in a plane; the rms deviation of fitted atoms is 0.0184. The two planes are nearly perpendicular, and the dihedral angle of the two planes is 88.20°. The Fe−Cu distance of 2.4572(7) Å is shorter than that of the known compound $[Fe(CO)_3(\mu\text{-}Ph_2Ppy)_2Cu(Me_2CO)]^+[ClO_4]^-$ (2.501 Å) (Ph_2Ppy = 2-(diphenylphosphino)pyridine),[7] $[Fe(CO)_3(\mu\text{-}L)_2Cu]^+[ClO_4]^-$ (2.550 Å) (L = *N*-(diphenylphosphinomethyl)morpholine),[8] and $[Fe(CO)_3(\mu\text{-}Ph_2Ppy)_2Cu(H_2O)]^+[ClO_4]^-$ (2.512 Å).[7] The Fe−Cu distance falls within the range 2.394−2.580 Å for polynuclear cluster compounds containing an Fe−Cu bond[9,11] which were first reported by G. Doyle and much shorter than the sum (2.54 Å)[10] of the atomic radii of iron and copper. The Fe atom is coordinated by the Cu atom, two phosphorus atoms in ligands **1** (the bond length of Fe−P is 2.2239(10) and 2.2324(10) Å, respectively), and three carbonyl groups with a distorted-octahedral configuration. The P−Fe−P

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Scheme 1

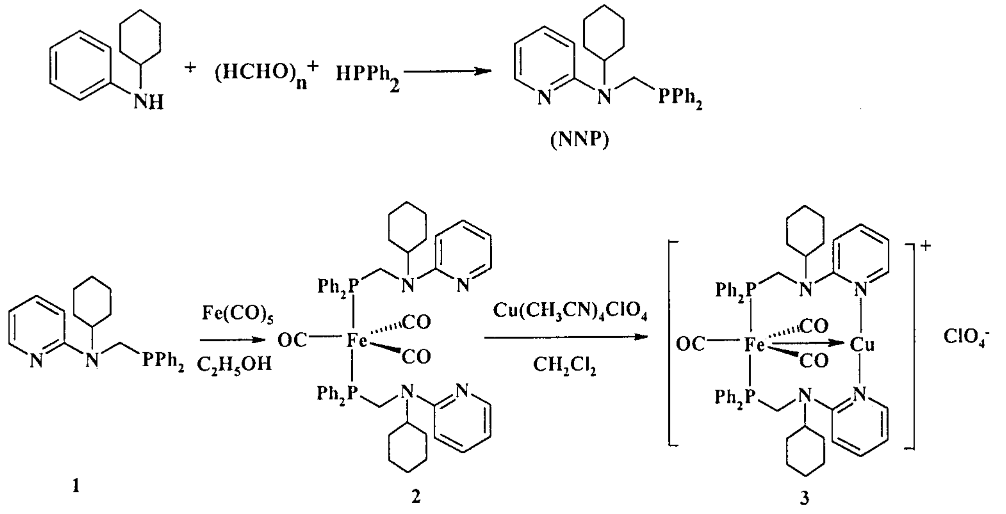

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Cu(1)−N(1)	2.027(3)	Cu(1)−N(3)	2.053(4)
Cu(1)−C(1)	2.399(4)	Cu(1)−C(2)	2.448(4)
Cu(1)−Fe(1)	2.4572(7)	Fe(1)−C(3)	1.765(4)
Fe(1)−C(2)	1.786(4)	Fe(1)−C(1)	1.799(4)
Fe(1)−P(1)	2.2239(10)	Fe(1)−P(2)	2.2324(10)
P(2)−C(39)q	1.868(4)	P(1)−C(22)	1.828(4)
C(8)−N(2)	1.382(5)	N(2)−C(15)	1.456(5)
N(2)−C(9)	1.481(5)	C(32)−N(4)	1.432(5)
N(4)−C(39)	1.480(5)	N(4)−C(33)	1.506(5)
N(1)−Cu(1)−N(3)	113.53(15)	N(1)−Cu(1)−Fe(1)	128.80(10)
N(3)−Cu(1)−Fe(1)	117.53(11)	C(1)−Cu(1)−Fe(1)	43.48(10)
C(2)−Cu(1)−Fe(1)	42.70(10)	C(3)−Fe(1)−C(2)	115.59(19)
C(3)−Fe(1)−C(1)	109.49(19)	C(2)−Fe(1)−C(1)	134.92(19)
C(3)−Fe(1)−P(1)	90.95(12)	C(2)−Fe(1)−P(1)	90.53(12)
C(1)−Fe(1)−P(1)	89.10(12)	C(3)−Fe(1)−P(2)	91.50(13)
C(2)−Fe(1)−P(2)	88.01(12)	C(1)−Fe(1)−P(2)	90.51(13)
P(1)−Fe(1)−P(2)	177.51(4)	P(1)−Fe(1)−Cu(1)	90.12(3)
P(2)−Fe(1)−Cu(1)	87.47(3)	C(40)−P(2)−C(46)	101.26(18)
C(40)−P(2)−C(39)	108.69(19)	C(46)−P(2)−C(39)	94.60(17)
C(15)−P(1)−Fe(1)	116.93(13)	O(1)−C(1)−Fe(1)	173.8(4)
O(2)−C(2)−Fe(1)	173.4(4)	O(3)−C(3)−Fe(1)	179.7(5)
C(8)−N(2)−C(15)	116.3(3)	N(2)−C(15)−P(1)	116.8(2)
N(3)−C(32)−N(4)	113.7(3)	C(31)−C(32)−N(4)	125.4(4)
C(32)−N(4)−C(39)	111.7(3)	C(39)−N(4)−C(33)	111.9(3)
N(4)−C(39)−P(2)	119.9(3)		

angle is 177.51(4)°, nearly in a line. The three-coordinated environment around the Cu(I) consisted of the Fe atom and two pyridyl nitrogen atoms of ligand **1** (Cu−N bond lengths are 2.027(3) and 2.053(4) Å, respectively). An interesting feature of this compound is the semibridging interaction between the copper atom and the carbonyl ligands, C(1)O(1) and C(2)O(2). The distances Cu(1)−C(1) (2.399 Å) and Cu(1)−C(2) (2.448 Å) fall well within the copper−carbonyl group distance range of 2.25−2.46 Å, which is considered as a semibridging interaction in mixed iron−copper carbonyl clusters.[11] In addition, the angles Fe(1)−C(1)−O(1) of 173.8(4)° and Fe(1)−C(2)−O(2) of 173.4(4)°, deviating significantly from linearity, are also consistent with the semibridging interaction between the Cu(I) and carbonyl groups C(1)O(1) and C(2)O(2).

As mentioned above, the new type of complex differs from one-, two-, or three-atom bridging binuclear complexes with metal−metal bonds. In this complex, the metal−metal bond is on a nontensile stress state, and it is more similar to Pomeroy's complexes containing unbridged dative metal−metal bonds. If this type of complex undergoes homolysis or heterolysis of the metal−metal bond, two active species stabilized by polyatom bridging ligands would be formed. Therefore, it is anticipated that they will exhibit some new reactivities toward small molecules and novel catalytic activities, such as the hydroformylation of olefins[12] and the carbonylation of alcohol.[13] Further studies are being carried out.

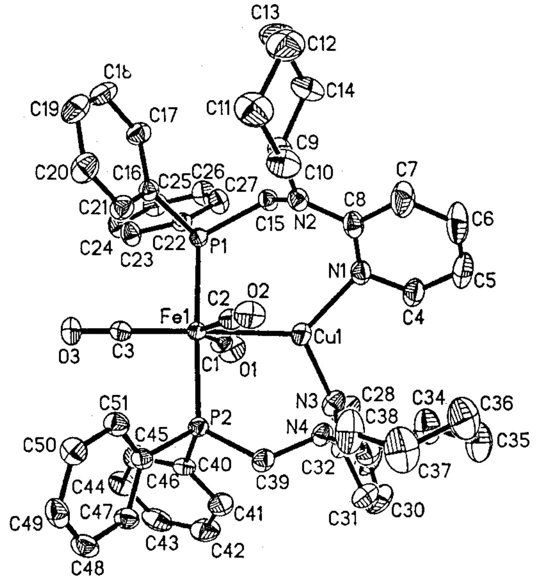

Figure 1. Molecular structure of complex 3 (cation part) with atom-labeling scheme.

Experimental Section

General Procedures. All reactions were carried out under a prepurified nitrogen atmosphere using standard Schlenk or vacuum line techniques. All solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Column chromatography was carried out using silica gel of 300−400 mesh. [2-(*N*-Cyclohexyl)amino]-pyridine was prepared according to the literature methods.[5] IR spectra were recorded on a Bruker FT-IR Equinox-55

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infrared spectrophotometer; ^{1}H NMR spectra and ^{31}P NMR spectra were recorded on a Bruker AC-200 NMR spectrometer. Elemental analyses were performed by a Yanaco MT-3 analyzer. Melting points were determined on a Yanaco micromelting point apparatus MP-500.

Preparation of 2-(*N*-Diphenylphosphinomethyl-*N*-cyclohexyl)aminopyridine (1). Ph_2PH (1.86 g, 10 mmol) was added with stirring to a solution of [2-(*N*-cyclohexyl)amino]-pyridine (1.76 g, 10 mmol) and paraformaldehyde (0.45 g, 15 mmol) in toluene (20 mL) at 70−80 °C. The mixture was stirred at 70−80 °C until all of paraformaldehyde had completely disappeared (about 5 h). The solution was cooled and then filtered through Celite. The solvent was removed under vacuum, and the residue was recrystallized with CH_2Cl_2/CH_3OH to give 3.01 g (81%) of **1** as a white solid powder, mp 86−86.5 °C. The sample for analysis was further purified by recrystallization from CH_2Cl_2/*n*-hexane. Anal. Calcd for $C_{24}H_{27}N_2P$: C, 76.98; H, 7.27; N, 7.48. Found: C, 76.80; H, 7.17, N, 7.50. ^{31}P NMR ($CDCl_3$): −13.57(s) ppm.

Preparation of Monometallic Complex *trans*-$(OC)_3Fe(NNP)_2$ (2). $Fe(CO)_5$ (0.6 mL, 4.6 mmol) was added to a solution of KOH (0.52 g, 9.2 mmol) in C_2H_5OH (60 mL) and stirred for 10 min, then ligand **1** (3.21 g, 8.6 mmol) was added to the solution. The mixture was refluxed for 5 h and cooled, and the solvent was removed. The residue was recrystallized from CH_2Cl_2/CH_3OH to give the yellow solid of complex **2** (3.13 g, 82%). Anal. Calcd for $C_{51}H_{54}FeN_4O_3P_2$: C, 68.92; H, 6.12; N, 6.30. Found: C, 68.72; H, 6.21; N, 6.18. IR (KBr, disk): $\nu_{(C\equiv O)}$ 1865(s), 1887(s), 1967(w) cm^{-1}. ^{31}P NMR ($CDCl_3$): 77.54(s) ppm.

Preparation of Heterometallic Complex $[(OC)_3Fe(\mu\text{-}NNP)_2Cu]^+ClO_4^-$ (3). The solid of $[Cu(CH_3CN)_4]^+[ClO_4]^-$ (0.10 g, 0.25 mmol) was added to the solution of complex **2** (0.23 g, 0.25 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 20 min at room temperature. After the solid disappeared completely, the mixture was filtered and the solvent was removed properly to give 0.21 g (80%) of **3** as pale yellow solid. The sample for analysis was further purified by recrystallization from CH_2Cl_2/*n*-hexane. Anal. Calcd for $C_{51}H_{54}ClCuFeN_4O_7P_2\cdot 0.5CH_2Cl_2$: C, 56.59; H, 5.08; N, 5.12. Found: C, 56.30; H, 4.82; N, 4.91. IR (KBr, disk): $\nu_{(C\equiv O)}$ 1868(vs), 1901(s), 1972(m) cm^{-1}; $\nu_{(perchloride)}$ 1091(vs) cm^{-1}. ^{31}P NMR ($CDCl_3$): 80.82(s) ppm.

X-ray Diffraction Single-Crystal Structural Determination of Complex 3. The X-ray quality crystal of complex **3** was grown by slow evaporation of its solution in CH_2Cl_2/hexane and was in the form of a pale yellow plate. The single crystal of **3** was mounted on a glass fiber in an arbitrary orientation and determined on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Details of the crystal, data collection, and structure refinement are included in the Supporting Information. The structure was solved by a direct phase determination method (Multan 82). Of all the data, 11 545 were unique and 8061 ($>2\sigma(I)$) were used to refine the structure employing 672 parameters. The atom positions were determined using direct methods, employing SHELXTL-97 and successive difference Fourier map calculations. The final refinement was accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Most hydrogen atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C−H bond length of 0.95 Å. All calculations were performed on a Bruker Smart computer using the SHELXL-97 program system.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for compound **3**. This material is available free of charge via the Internet at http://pubs.asc.org.

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