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A Series of Dinuclear Copper Complexes Bridged by Phosphanylbipyridine Ligands: Synthesis, Structural Characterization and Electrochemistry

Alyssia M. Lilio,[a] Kyle A. Grice,[a] and Clifford P. Kubiak*[a]

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The phosphanylbipyridine ligands 6-(diphenylphosphanyl)-4,4′-dimethyl-2,2′-bipyridine (PPh_2-Me_2-bipy, **a**), 4,4′-di-*tert*-butyl-6-(diphenylphosphanyl)-2,2′-bipyridine (PPh_2-tBu_2-bipy, **b**), and 6-(diisopropylphosphanyl)-2,2′-bipyridine ($PiPr_2$bipy, **c**) and the corresponding dinuclear copper complexes $[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**1**), $[Cu_2(\mu\text{-}PPh_2\text{-}tBu_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**2**), $[Cu_2(\mu\text{-}PiPr_2\text{bipy})_2(\mu\text{-}NCCH_3)](PF_6)_2$ (**3**), and $[Cu_2(\mu\text{-}PiPr_2\text{bipy})_2\{\mu\text{-}CNCH(CH_3)_2\}](PF_6)_2$ (**4**) were synthesized. The X-ray structures of **1**–**4** show that the complexes are dinuclear with the bidentate bipyridine coordinating to one copper atom and the phosphane moiety coordinating the other copper center. Complexes **3** and **4** possess short Cu–Cu distances with bridging acetonitrile and isocyanide ligands. The cyclic voltammograms of **1**–**4** were examined under N_2 and CO_2. Under N_2, **1**–**3** show four quasi-reversible $1e^-$ reductions, and under CO_2, they show current enhancement at the second reduction. In comparison, complex **4** shows four irreversible reductions under N_2 and no current enhancement under CO_2.

Introduction

Phosphane and bipyridine ligands are ubiquitous in transition metal chemistry because of their ability to coordinate a variety of metal ions in various oxidation states. They are also widely used, because the electronic and steric properties of these ligands are easily controlled. Additionally, bipyridines are useful ligands, because they are able to act as non-innocent ligands, so they can serve as electron reservoirs for transition metal complexes.[1] The ability of bipyridine ligands to accept electrons at significantly lower potentials than the reduction of the metal centers makes them very good ligands for reduction catalysts.

Herein we report the synthesis and characterization of four new dinuclear copper complexes with substituted 6-phosphanylbipyridine ligands: $[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**1**), $[Cu_2(\mu\text{-}PPh_2\text{-}tBu_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**2**), $[Cu_2(\mu\text{-}PiPr_2\text{bipy})_2(\mu\text{-}NCCH_3)](PF_6)_2$ (**3**), and $[Cu_2(\mu\text{-}PiPr_2\text{bipy})_2\{\mu\text{-}CNCH(CH_3)_2\}](PF_6)_2$ (**4**). These complexes are similar to the dinuclear copper complex previously reported by Haines and co-workers,[2] $[Cu_2(\mu\text{-}PPh_2\text{bipy})_2(NCCH_3)_2](PF_6)_2$ (**5**), and then studied by our group for electrochemical CO_2 reduction.[3] This complex was shown to be a catalyst for the $2e^-$ reduction of CO_2 to form the reductive disproportionation products CO and CO_3^{2-}.

We were interested in modifying this dinucleating ligand framework to observe how changes to the electronics of the ligand affected the structures and electrochemistry of the corresponding dinuclear copper complexes. We examined the effects of substituting alkyl groups for the aryl groups on the phosphane as well as the effects of adding substituents to the bipyridine backbone. We also modified the structure of **3** by replacing the weakly bound bridging acetonitrile with isopropyl isocyanide. These modifications led to changes in the structures of the complexes, changes to the reduction potentials of the ligands and complexes, as well as changes in reactivity.

Results and Discussion

Syntheses

The ligands 6-(diphenylphosphanyl)-4,4′-dimethy-2,2′-bipyridine (PPh_2-Me_2-bipy, **a**) and 4,4′-di-*tert*-butyl-6-(diphenylphosphanyl)-2,2′-bipyridine (PPh_2-tBu_2-bipy, **b**) were synthesized as shown in Scheme 1. The synthesis of the ligands was performed according to modified literature procedures for similar ligands.[4] The substituted bipyridines 4,4′-dimethyl-2,2′-bipyridine and 4,4′-di-*tert*-butyl-2,2′-bipyridine were first converted into their mono-*N*-oxides by reaction with *m*-chloroperoxybenzoic acid. The *N*-oxides were then converted into the 6-chloro-substituted bipyridines by refluxing in neat $POCl_3$ under nitrogen. Ligands

[a] Department of Chemistry and Biochemistry, University of California – San Diego,
9500 Gilman Drive, Mail Code 0358, La Jolla, CA 92093-0358, USA
Fax: +1-858-534-5383
E-mail: ckubiak@ucsd.edu
Homepage: kubiak.ucsd.edu

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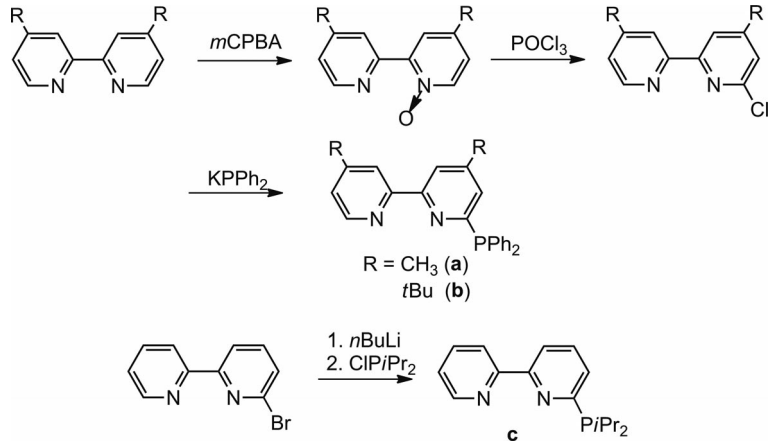
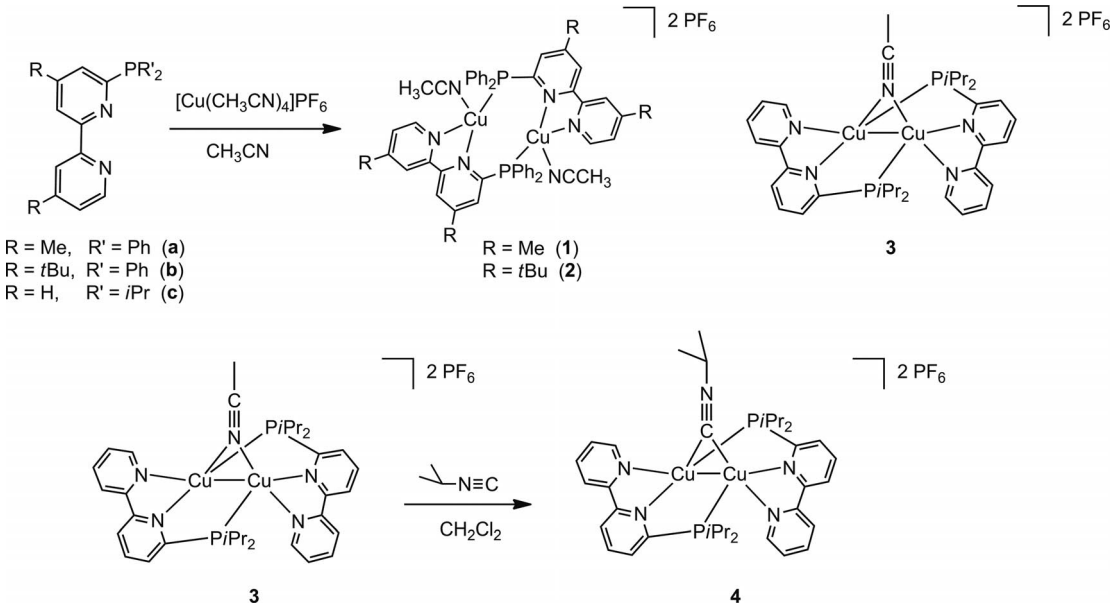


Scheme 1. Synthesis of ligands **a**, **b**, and **c**.



Scheme 2. Synthesis of complexes **1**–**4**.

6-(diphenylphosphanyl)-4,4′-dimethyl-2,2′-bipyridine (**a**) and 4,4′-di-*tert*-butyl-6-(diphenylphosphanyl)-2,2′-bipyridine (**b**) were obtained by reaction of potassium diphenylphosphide with the corresponding substituted 6-chlorobipyridines. Ligand 6-(diisopropylphosphanyl)-2,2′-bipyridine (P*i*Pr$_2$bipy, **c**) was synthesized by lithiation of 6-bromo-2,2′-bipyridine with *n*BuLi followed by addition of chlorodiisopropylphosphane. Ligands **a** and **b** were characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy as well as mass spectrometry and elemental analysis. Ligand **c** was a viscous oil, and we were unable to obtain a satisfactory elemental analysis. Ligand **c** was ultimately characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and mass spectrometry.

Complexes **1**–**4** were synthesized as shown is Scheme 2. Dinuclear copper complexes [Cu$_2$(μ-PPh$_2$-Me$_2$-bipy)$_2$-(NCCH$_3$)$_2$](PF$_6$)$_2$ (**1**), [Cu$_2$(μ-PPh$_2$-*t*Bu$_2$-bipy)$_2$(NCCH$_3$)$_2$]-(PF$_6$)$_2$ (**2**), and [Cu$_2$(μ-P*i*Pr$_2$bipy)$_2$(μ-NCCH$_3$)](PF$_6$)$_2$ (**3**) were synthesized by adding 1 equiv. of the ligand to an acetonitrile solution of the Cu$^{\mathrm{I}}$ salt [Cu(NCCH$_3$)$_4$]PF$_6$. After stirring the solutions overnight, the solvent volume was reduced, and yellow powders were precipitated by addition of diethyl ether. Complex **4** was synthesized by adding 1 equiv. of isopropyl isocyanide to a solution of [Cu$_2$(μ-P*i*Pr$_2$bipy)$_2$-(μ-NCCH$_3$)](PF$_6$)$_2$ in CH$_2$Cl$_2$. After stirring the solution overnight, the solvent volume was reduced, and the product was precipitated by addition of tetrahydrofuran. Complexes **1**–**4** were characterized by elemental analysis, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and X-ray crystallography.

Structural Characterization

In order to verify that complexes **1**–**4** were dinuclear and similar to complex **5**, they were characterized by X-ray crystallography. Suitable crystals for X-ray diffraction of **1** and **4** were obtained by layering hexanes over dichloromethane solutions. Crystals of **2** and **3** were obtained through the

slow diffusion of diethyl ether into acetonitrile solutions. Molecular structures of the cations are shown in Figures 1, 2, 3, and 4, and more selected bond lengths and angles are displayed in Table S1 in the Supporting Information.

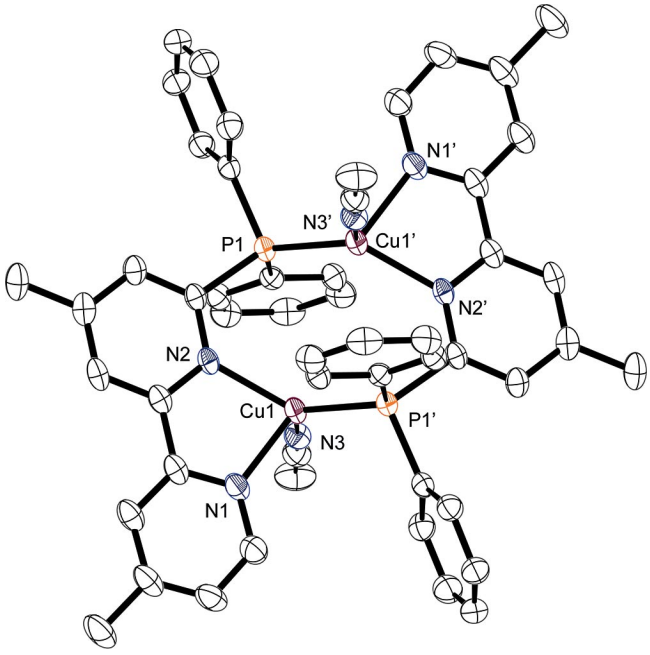


Figure 1. Molecular structure of **1**. The counterions, hydrogen atoms, and co-crystallized solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Cu1–Cu1′ 3.7244(6), Cu1–N1 2.091(2), Cu1–N2 2.087(2), Cu1–P1 2.1991(7), Cu1–N3 2.003(2); N1–Cu1–N2 79.10(1), N3–Cu1–N2 108.95(8), N3–Cu1–P1 119.67(7), N3–Cu1–N1 98.81(1), P1–Cu1–N1 110.89(6). P1–Cu1–N2 127.09(6).

Similar to the compound **5** reported by Haines and coworkers, the solid-state structure of $[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-}bipy)_2(NCCH_3)_2](PF_6)_2$ (**1**) reveals that the cation is dinuclear with the ligands coordinating the two copper centers in a head-to-tail manner so that each copper atom is coordinated to the phosphorus atom of one bridging ligand and the chelating bipyridine of the other. An acetonitrile ligand occupies the fourth coordination site on each copper atom. The coordination geometry of each copper atom is considerably distorted from the expected tetrahedral geometry, as reflected by the P–Cu–N angles and N–Cu–N angles of 127.09(6)° and 79.10(1)°, respectively. Calculation of Houser's τ_4 four-coordinate geometry index gives a value of 0.80,[5] which is closer to the value expected for an ideal trigonal-pyramidal geometry (τ_4 = 0.85) than it is to the value expected for a perfect tetrahedral geometry (τ_4 = 1.0). The distance between the two copper atoms is 3.7244(6) Å, which is slightly contracted compared to the Cu–Cu distance in the original complex **5** (3.941 Å).

The solid-state structure of $[Cu_2(\mu\text{-}PPh_2\text{-}t\text{Bu}_2\text{-}bipy)_2(NCCH_3)_2](PF_6)_2$ (**2**) is also dinuclear, and the ligand coordinates the copper centers in the same manner as in **1**. Complex **2** has also an acetonitrile ligand occupying the

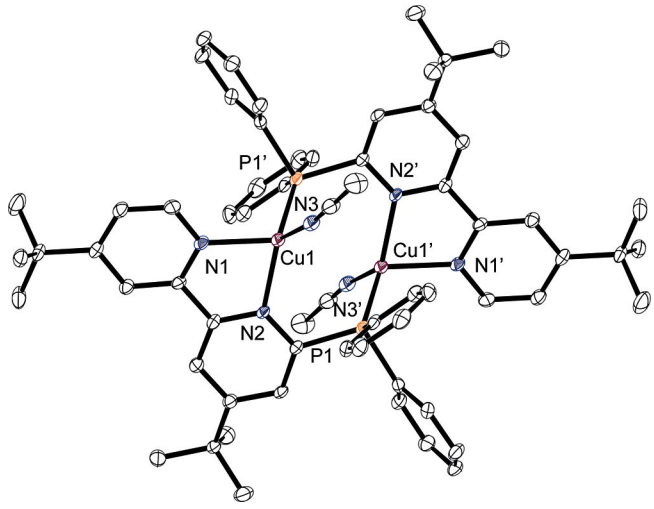


Figure 2. Molecular structure of **2**. The counterions, hydrogen atoms, and co-crystallized solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Cu1–Cu1′ 3.6809(7), Cu1–N1 2.062(2), Cu1–N2 2.054(2), Cu1–N3 1.977(3), Cu1–P1 2.2074(10); P1–Cu1–N2 121.74(7), N3–Cu1–P1 106.62(8), N1–Cu1–N2 79.8(1), N2–Cu1–N3 124.49(11), N1–Cu1–N3 108.87(11), N1–Cu1–P1 106.62(8).

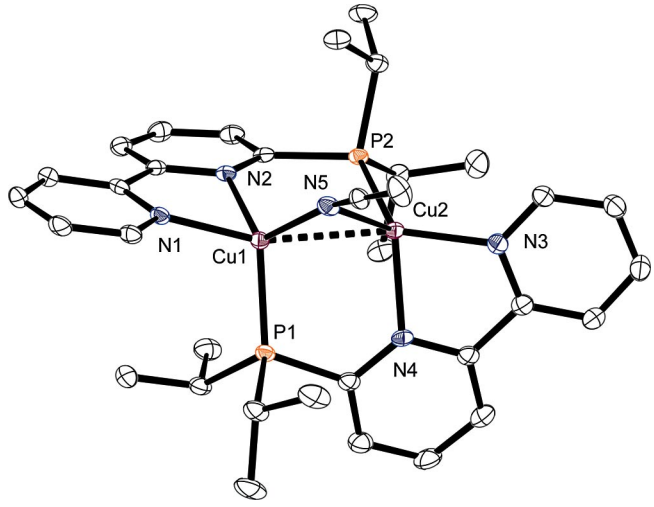


Figure 3. Molecular structure of **3**. The counterions, hydrogen atoms, and co-crystallized solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.7067(4), Cu1–N1 2.0421(19), Cu1–N2 2.0665(18), Cu1–N5 2.533(2), Cu1–P1 2.1848(6), Cu2–N5 2.008(2); N1–Cu1–N2 79.85(8), N1–Cu1–N5 108.89(7), N1–Cu1–P1 122.40(6), N2–Cu1–N5 106.91(7), N2–Cu1–P1 127.44(6)°.

fourth coordination site on each copper atom and displays a distorted trigonal-pyramidal coordination environment as reflected by the Houser τ_4 index value of 0.81. The distance between the two copper atoms is 3.6809(7) Å.

In the solid-state structure of $[Cu_2(\mu\text{-}P\textit{i}Pr_2bipy)_2(\mu\text{-}NCCH_3)](PF_6)_2$ (**3**), the asymmetric unit contains two independent dinuclear complexes with slightly different bond lengths and angles as well as two free acetonitrile molecules. These small differences in the two dimers are likely due to

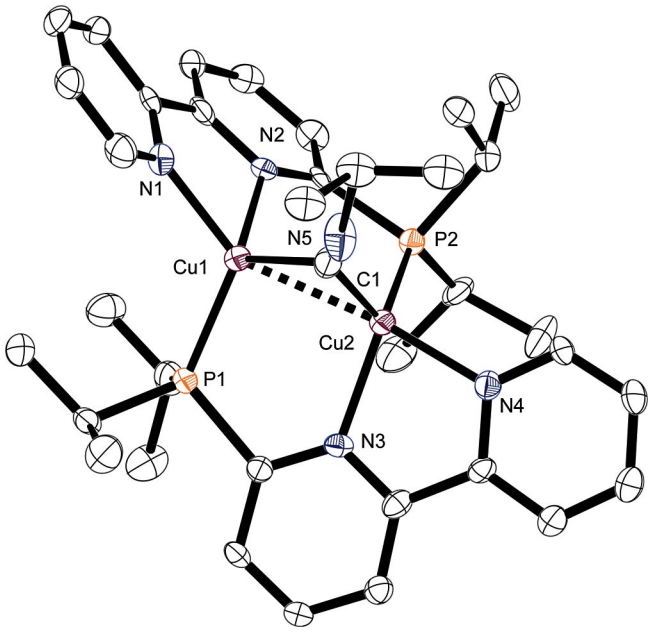


Figure 4. Molecular structure of **4**. The counterions, hydrogen atoms, and co-crystallized solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.5124(9), Cu1–N1 2.053(4), Cu1–C1 2.054(6), Cu1–N2 2.089(4); N1–Cu1–C1 103.8(2), N1–Cu1–N2 78.73(17), C1–Cu1–N2 113.05(19), N1–Cu1–P1 122.02(13), C1–Cu1–P1 118.69(16), N2–Cu1–P1 113.95(13).

crystal packing effects. Similar to **1** and **2**, the structure of **3** displays coordination of the phosphanylbipyridine ligand in a head-to-tail fashion, but the copper ions are considerably closer to each other [2.6969(5) Å in one of the independent dinuclear molecules and 2.7067(4) Å in the other]. These distances are slightly shorter than twice the van der Waals radius of Cu (1.40 Å).[6] Another significant difference between complex **3** and complexes **1** and **2** is that there is only one acetonitrile ligand that is asymmetrically interacting with both of the copper centers of **3**. This is similar to a recently reported complex where the tridentate ligand 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine was shown to form a μ-η^1:η^1-acetonitrile-bridged dicopper complex described as having a three-center two-electron bonding interaction.[7] In **3**, the copper centers are four-coordinate with the bridging acetonitrile occupying the fourth coordination site. The dimers exhibit distorted trigonal-pyramidal geometry, possessing τ_4 values of 0.78 and 0.87 in one dimer and 0.78 and 0.88 in the other. The average distance between the copper atoms and the asymmetrically bridging acetonitrile molecules are 2.5135(1) Å and 2.0115(1) Å for the cations of **3**. The acetonitrile tilts towards the copper center with the longer Cu–$NCCH_3$ bond as shown by the inequivalent Cu–N–C angles, suggesting that there is possibly a weak interaction between one copper center and the nitrile π system.[7,8] Despite the solid-state structural differences between the open structures of **1**, **2** and **5**, and the closed structure of **3** with its short Cu–Cu separation and semibridging acetonitrile, the spectroscopic and electrochemical features of all four complexes are very similar in solution (vide infra).

Short separations between Cu^I centers have been explained in terms of mixing of the Cu s and p orbitals with the 3d orbitals.[9] Mixing of s and p orbitals of the appropriate symmetry with d-orbital-based σ and σ^* orbitals effectively leads to linear combinations that increase the bonding character of the σ orbital and decrease the antibonding character of σ^*.[9a,9b] The overall structure of complex **3**, with its semibridging acetonitrile, is also reminiscent of the d^{10}–d^{10} dinuclear Ni^0 "cradle" complexes bridged by single π-acceptor ligands.[10] In these dinuclear Ni^0 complexes, the short Ni–Ni separations were rationalized in terms of dπ^* to bridging ligand π^* backbonding, effectively depopulating a metal–metal antibonding interaction to leave a net metal–metal bonding interaction. The ability of π-accepting bridging ligands in Cu^I–Cu^I dimers to reduce the antibonding nature to the d^{10}–d^{10} core has also been previously reported.[11] In order to understand whether the semibridging acetonitrile could be helping to promote d^{10}–d^{10} dinuclear interactions in a similar way in this copper dimer, we attempted to replace the acetonitrile with a stronger π-accepting ligand to see if this would result in a shorter Cu^I–Cu^I separation.

Complex **4** is structurally very similar to **3**, except that the bridging acetonitrile ligand has been replaced with isopropyl isocyanide. Complex **4** is one of few Cu^I dimers bridged by isocyanides.[7,12] Analogously to **3**, the asymmetric unit of **4** also contains two independent dinuclear complexes that have slightly different bond lengths and angles. The bridging isocyanide is also slightly tilted towards one of the copper centers, suggesting the possibility of an interaction between one of the Cu atoms and the nitrile π system. The separation of the Cu^I–Cu^I centers in complex **4** is decreased by approximately 0.18 Å in comparison to **3**. We believe that the increased π-acceptor ability of isopropyl isocyanide compared to acetonitrile results in more donation from the copper dπ^* electron density to the π-acceptor bridging ligand, thus reducing the antibonding between d^{10} copper centers and allowing the copper atoms to be closer.

Electrochemistry

The electrochemistry of the free ligands was examined in order to compare the reduction potentials to those of the metal complexes. Ligands **a**–**c** show a quasi-reversible $1e^-$ reduction and a further irreversible reduction. These potentials were measured in dry acetonitrile under N_2 and referenced to SCE by using an internal Fc/Fc^+ standard. The electrochemistry of the phosphanylbipyridine ligand originally reported by Haines, PPh_2bipy (**d**), was also examined, and it similarly had a reversible $1e^-$ reduction followed by an irreversible reduction. As expected, the reduction potentials of **d** are more positive than the potentials for ligands **a**, **b**, and **c**, which have electron-donating substituents on the bipyridine or the phosphane. The two reductions of the

ligands are attributed to the formation of the bipyridine radical anion and dianion species.[13] Upon complexation to copper, these reduction potentials are shifted anodically by ca. 700 mV because of the reduced electron density on the ligands. The reduction potentials of ligands **a**–**d** are summarized in Table 1.

Table 1. Reduction potentials of ligands and copper complexes.

Compound	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$
PPh_2-Me_2-bipy (**a**)	–2.20	–	–2.69[a]	–
PPh_2-tBu$_2$-bipy (**b**)	–2.23	–	–2.75[a]	–
PiPr$_2$bipy (**c**)	–2.00	–	–2.60[a]	–
PPh_2bipy (**d**)	–2.02	–	–2.51[a]	–
1	–1.47	–1.65	–1.98	–2.21
2	–1.46	–1.66	–1.97	–2.11
3	–1.41	–1.65	–1.99	–2.35
4	–1.43	–1.64	–2.04[a]	–2.27[a]
5	–1.38[b]	–1.56[b]	–1.88[b]	–2.03[b]

[a] Potentials reported in V vs. SCE. Peaks are irreversible and reported as $E_{cathodic}$. [b] Potentials for the four reductions in the original complex **5** were determined in this work. All scans were carried out at 100 mV/s in acetonitrile with 0.1 M TBAH as the supporting electrolyte.

Complexes **1**–**3** exhibit four quasi-reversible 1e$^-$ reductions in dry acetonitrile under an inert gas (see Figure 5 for a typical voltammogram). The CVs of the remaining complexes under N_2 can be found in the Supporting Information (Figures S1–S3). This electrochemistry is different from that of the reported electrochemistry for the parent compound **5**,[3] where only two quasi-reversible 1e$^-$ reductions were described. Our re-examination of the electrochemistry of **5** revealed that it also had two more reductions in the cathodic region. In the three acetonitrile-coordinated complexes reported in this paper (**1**–**3**), the reductions occur at potentials that are slightly more negative compared to that of the original complex **5** due to the increased donor strength of the ligands. The electrochemistry of complex **4** in acetonitrile shows two well-resolved irreversible reductions followed by two overlapping irreversible peaks. On the return scan, a significant oxidative peak is noted, which could be indicative of a stripping wave due to the oxidation of Cu^0 that had been deposited on the surface. When scanning out only to the first two reductions, upon the return scan, they become quasi-reversible, similar to the first two reductions in compounds **1**–**3**. The cyclic voltammogram showing the first two reductions of complex **4** and showing the further negative scan can be found in the Supporting Information (Figures S7 and S8). The reduction potentials for complexes **1**–**5** are tabulated in Table 1.

When scanning positively after reaching the four reductions in **1**–**3**, no significant stripping wave was observed, indicating that the complexes remain intact as they are being reduced. Full scans of the complexes can be found in the Supporting Information (Figures S4–S7). It is our understanding that the four reductions seen in **1**–**3** and the first two reductions in **5** are predominantly ligand-based bipyridine reductions rather than reductions of the copper centers. In the free ligand electrochemistry, the peak separation between the first (bipyridine radical anion) and the second (bipyridine dianion) reduction is ca. 500 mV. The approximate peak separation between the first two reductions in the electrochemistry of **1**, **2**, **3**, and **5** is ca. 200 mV, and the separation between the first peaks and third reductions are ca. 500 mV. We conclude from these data that one electron sequentially goes into each bipyridine ring before the third and fourth electrons produce the bipyridine dianions. In **4**, the first two reductions are also likely bipyridine-based, with one electron sequentially going into each bipyridine ring. The other two reductions could be due to the reduction of Cu^I to Cu^0 or to the reduction of the isocyanide ligand.[14]

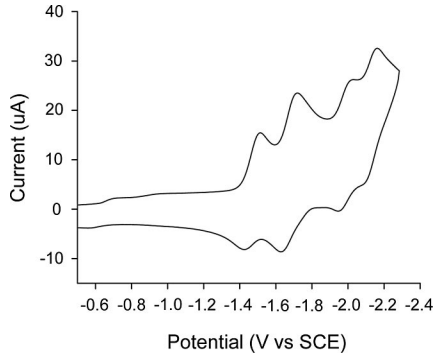


Figure 5. Cyclic voltammogram of $[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**1**) under N_2 in acetonitrile with 0.1 M TBAH.

Under CO_2, complexes **1**–**3** exhibit significant increases in current at the second reduction and the disappearance of the returning oxidation waves [see Figure 6 for a typical voltammogram (CVs of the remaining complexes under CO_2 can be found in the Supporting Information, Figures S9 and S10)]. After re-sparging with nitrogen, the original CV responses are restored. This behavior is indicative of CO_2 reduction. The amount of current enhancement is similar for complexes **1**, **2**, and **3** as well as for the original complex **5**, which has previously been well studied as a CO_2 reduction catalyst.[3]

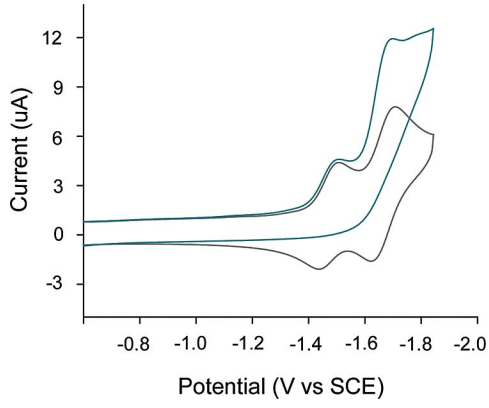


Figure 6. Cyclic voltammogram of $[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-bipy})_2(NCCH_3)_2](PF_6)_2$ (**1**) under N_2 and under CO_2 in acetonitrile with 0.1 M TBAH.

It is notable that complexes **1**–**3** and **5** effect the reduction of CO_2 with similar current enhancements (1.5–1.7× increase at the peak current) and at similar potentials

(–1.56 to –1.66 V vs. SCE, at the second reduction). Under CO_2, **4** shows no current enhancement at the second reduction. This is attributed to the fact that the loss of the labile acetonitrile ligand is necessary for CO_2 to bind to the copper center. With the more strongly coordinated isocyanide ligand, CO_2 is unable to coordinate to the copper centers, which is a necessary step in electrocatalytic reduction.

Conclusions

Four dinuclear copper complexes bridged by tridentate 6-phosphanyl-2,2′-bipyridine ligands have been synthesized. These complexes have been structurally characterized by X-ray crystallography, and the Cu^I–Cu^I distances in the crystal structures can be controlled by modification of the phosphanylbipyridine ligand and substitution of acetonitrile for an isocyanide. Complexes **1**–**3** are capable of performing the electrochemical reduction of CO_2, whereas complex **4**, with a bridging isocyanide, showed no CO_2 reduction activity.

Although the three new copper complexes **1**–**3** display only modest current enhancements under CO_2, they are notable in that they are rare examples of homogeneous copper-based systems that affect CO_2 reduction. There are only a few homogeneous copper-based systems able to reduce CO_2.[15] Copper is a relatively cheap and abundant metal and has very unique properties as a metallic electrode material, being one of the few metals capable of catalyzing electrochemical reduction of CO_2 to hydrocarbon fuels, including CH_4 and C_2H_4.[16] These properties make it an interesting metal to study in homogeneous molecular catalysts.

Ongoing work in our laboratory is focused on understanding the electronic nature of the reduced species that reacts with CO_2 and elucidating the mechanism of CO_2 reduction with complexes **1**–**3**.

Experimental Section

General Methods: Unless otherwise noted, all reactions were carried out under N_2 by using standard Schlenk and glovebox techniques. Acetonitrile and thf were dried with activated molecular sieves and alumina and degassed prior to use. 6-Bromo-2,2′-bipyridine,[17] 4,4′-dimethyl-2,2′-bipyridine *N*-oxide,[18] 6-diphenylphosphanyl-2,2′-bipyridine (**d**),[4] and $[Cu_2(\mu\text{-}PPh_2bipy)_2(NCCH_3)_2](PF)_2$ (**5**)[2] were synthesized as previously reported. All other chemicals were obtained from commercial suppliers and used without further purification. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded by using a 300 MHz or 400 MHz Varian spectrometer. ^1H chemical shifts were referenced against the residual solvent signal and are reported in ppm downfield of tetramethylsilane (δ = 0 ppm). $^{31}P\{^1H\}$ NMR chemical shifts were referenced by using a phosphoric acid capillary insert as an internal standard (δ = 0 ppm). Mass spectrometry data was collected with a Finnagan LCQDECA in ESI positive ion mode. Elemental analyses were performed by NuMega Resonance Labs, San Diego, CA.

Syntheses

6-Chloro-4,4′-dimethyl-2,2′-bipyridine: 4,4′-Dimethyl-2,2′-bipyridine *N*-oxide (1.86 g, 10.8 mmol) was added slowly to $POCl_3$ (10 mL, 16.5 g, 107 mmol) at 0 °C. The mixture was stirred at reflux at 100 °C overnight. The excess $POCl_3$ was removed under vacuum leaving a black residue. A small amount of ice-cold water was added, and the reaction mixture was basified with 5 M NaOH (25 mL). The solution was extracted with CH_2Cl_2 (3 × 20 mL), and the organic fractions were collected and dried with Na_2SO_4. The solvent was evaporated leaving a brown residue. The residue was purified by column chromatography on silica (20% EtOAc/hexanes) to afford a white powder (0.907 g, 45%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 7.17 (s, 1 H, Ar*H*) 7.20 (d, *J* = 5.1 Hz, 1 H, Ar*H*), 8.26 (s, 1 H, Ar*H*), 8.28 (s, 1 H, Ar*H*), 8.51 (d, *J* = 5.1 Hz, 1 H, Ar*H*) ppm. ESI-MS: calcd. for $[M + H]^+$ 219.6; found 219.0. $C_{12}H_{11}ClN_2$ (218.69): calcd. C 65.91, H 5.07, N 12.81; found C 65.51, H 5.43, N 13.06.

6-(Diphenylphosphanyl)-4,4′-dimethyl-2,2′-bipyridine (a): 6-Chloro-4,4′-dimethyl-2,2′-bipyridine (0.382 g, 1.75 mmol) was dissolved in thf (10 mL), and the solution was cooled to –78 °C. Potassium diphenylphosphide (0.5 M in thf, 4.2 mL, 2.1 mmol) was added slowly by cannula. The dark red mixture was warmed to room temperature and stirred overnight. HCl (6 M) was then added to the reaction mixture followed by a solution of 10% ammonium hydroxide until the mixture was basic. This was extracted with diethyl ether (3 × 20 mL), and the organic fractions were dried with Na_2SO_4. The solvent was removed under vacuum to yield an oily yellow solid. The product was precipitated from acetonitrile to render 0.305 g of a white powder (47%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 2.33 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 7.01 (s, 1 H, Ar*H*), 7.11 (d, *J* = 5.0 Hz, 1 H, Ar*H*), 7.33–7.48 (10 H, Ar*H*), 8.09 (s, 1 H, Ar*H*), 8.17 (s, 1 H, Ar*H*), 8.47 (d, *J* = 4.9 Hz, 1 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = –3.70 ppm. ESI-MS: calcd. for $[M + H]^+$ 369.1; found 369.1. $C_{24}H_{21}N_2P$ (368.42): calcd. C 78.24, H 5.75, N 7.60; found C 78.11, H 6.23, N 8.00.

4,4′-Di-*tert*-butyl-2,2′-bipyridine *N*-Oxide: 4,4′-Di-*tert*-butyl-2,2′-bipyridine (3.00 g, 1.12 mmol) was dissolved in $CHCl_3$ (10 mL) The solution was cooled to 0 °C, and 3-chloroperoxybenzoic acid (3.19 g of 77% max.) in $CHCl_3$ (20 mL) was added dropwise over a period of 2 h. The mixture was allowed to come to room temperature and was stirred overnight. The solvent was removed under vacuum leaving a yellow oily residue. This was purified by column chromatography on basic alumina (20% EtOAc/hexanes) to afford an off-white powder (1.95 g, 61%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, CH_3), 1.35 (s, 9 H, CH_3), 7.22 (d, *J* = 2.9 Hz, 1 H, Ar*H*), 7.31 (d, *J* = 5.2 Hz, 1 H, Ar*H*), 8.05 (s, 1 H, Ar*H*), 8.21 (d, *J* = 6.9 Hz, 1 H, Ar*H*), 8.61 (d, *J* = 5.2 Hz, 1 H, Ar*H*), 8.87 (s, 1 H, Ar*H*) ppm. ESI-MS: calcd. for $[M + H]^+$ 285.4; found 285.3. $C_{18}H_{24}N_2O$ (284.40): calcd. C 76.02, H 8.51, N 9.85; found C 75.68, H 8.79, N 10.12.

4,4′-Di-*tert*-butyl-6-chloro-2,2′-bipyridine: 4,4′-Di-*tert*-butyl-6-chloro-2,2′-bipyridine was synthesized analogously to 6-chloro-4,4′-dimethyl-2,2′-bipyridine. The crude product was purified by column chromatography on silica (30% EtOAc/hexane). The major fraction was collected and concentrated to yield a white solid (35%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 9 H, CH_3), 1.37 (s, 9 H, CH_3), 7.27–7.37 (m, 2 H, Ar*H*), 8.32 (s, 2 H, 2 Ar*H*), 8.57 (d, *J* = 5.3 Hz, 1 H, Ar*H*) ppm. ESI-MS: calcd. for $[M + H]^+$ 303.8; found 303.3. $C_{18}H_{23}ClN_2$ (302.85): calcd. C 71.39, H 7.66, N 9.25; found C 71.00, H 7.36, N 9.25.

4,4′-Di-*tert*-butyl-6-(diphenylphosphanyl)-2,2′-bipyridine (b): 4,4′-Di-*tert*-butyl-6-(diphenylphosphanyl)-2,2′-bipyridine was synthesized according to the same procedure used to synthesize 6-(diphenylphosphanyl)-4,4′-dimethyl-2,2′-bipyridine (62%). ^1H NMR (400 Hz, CD_2Cl_2): δ = 1.32 (s, 9 H, CCH_3), 1.33 (s, 9 H, CCH_3),

7.29 (m, 2 H, Ar*H*), 7.40 (m, 9 H, Ar*H*), 7.55 (m, 5 H, Ar*H*),8.26 (s, *J* = 1.9 Hz, 1 H, Ar*H*), 8.35 (s, 1 H, Ar*H*), 8.59 (d, *J* = 5.22 Hz, 1 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CHCl_3$): δ = –1.62 ppm. ESI-MS: calcd. for $[M + H]^+$ 453.6; found 453.3. $C_{30}H_{33}N_2P$ (452.58): calcd. C 79.62, H 7.35, N 6.19; found C 78.88, H 7.67, N 6.94.

6-(Diisopropylphosphanyl)-2,2′-bipyridine (c): 6-Bromo-2,2′-bipyridine (1.00 g, 4.25 mmol) was dissolved in Et_2O (20 mL) and cooled to –78 °C with an acetone/dry ice bath. *n*BuLi (1.6 M in hexanes, 2.67 mL, 4.27 mmol) was added dropwise, producing a dark-orange solution. The solution was stirred at –78 °C for 2 h, after which a solution of chlorodiisopropylphosphane (0.68 mL, 4.27 mmol) in Et_2O (10 mL) was added slowly to the reaction mixture. The mixture was allowed to come slowly to room temperature and was stirred at room temperature overnight. The resulting yellow solution was filtered, and the filtrate was concentrated under vacuum to afford a bright orange oil. This was dissolved in hexanes and filtered. The filtrate was concentrated to yield 1.12 g (96%) of a viscous orange oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 (dd, $^3J_{P,H}$ = 11.8, $^3J_{H,H}$ = 7.0 Hz, 6 H, CHCH_3), 1.15 (dd, $^3J_{P,H}$ = 14.5, $^3J_{H,H}$ = 7.0 Hz, 6 H, CHCH_3), 2.36–2.28 (septd, $^3J_{P,H}$ = 2.5, $^3J_{H,H}$ = 7.0 Hz, 2 H, C*H*CH$_3$), 7.23 (m, 1 H, Ar*H*), 7.46 (m, 1 H, Ar*H*), 7.69 (m, 1 H, Ar*H*), 7.78 (m, 1 H, Ar*H*), 8.30 (m, 1 H, Ar*H*), 8.46 (m, 1 H, Ar*H*), 8.64 (m, 1 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 15.15 ppm. ESI-MS: calcd. for $[M + H]^+$ 273.3; found 273.1.

$[Cu_2(\mu\text{-}PPh_2\text{-}Me_2\text{-}bipy)_2(NCCH_3)_2](PF_6)_2$ (1): A solution of 6-(diphenylphosphanyl)-2,2′-bypyridine (0.301 g, 0.860 mmol) in acetonitrile (20 mL) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (0.320 mg, 0.860 mol) in acetonitrile (50 mL), producing a yellow solution, which was stirred overnight. The solvent was reduced under vacuum, and Et_2O was added to precipitate the product. The solution was filtered to afford 0.296 g (58%) of **1** as a yellow solid. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.91 (s, 6 H, CH_3CN), 2.53 (s, 6 H, CH_3), 2.56 (s, 6 H, CH_3), 7.00–7.10 (m, 8 H, Ar*H*), 7.16 (s, 2 H, Ar*H*), 7.26 (d, *J* = 5.1 Hz, 2 H, Ar*H*), 7.35 (t, *J* = 7.6 Hz, 8 H, Ar*H*), 7.49 (7, *J* = 7.5 Hz, 4 H, Ar*H*), 7.91 (d, *J* = 5.3 Hz, 2 H, Ar*H*),8.19 (s, 2 H, Ar*H*), 8.29 (s, 2 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 10.04 ppm. $C_{52}H_{48}Cu_2F_{12}N_6P_4$ (1235.95): calcd. C 50.53, H 3.91, N 6.80; found C 50.59, H 3.98, N 6.64.

$[Cu_2(\mu\text{-}PPh_2\text{-}t\text{Bu}_2\text{-}bipy)_2(NCCH_3)_2](PF_6)_2$ (2): Complex **2** was synthesized analogously to **1** (79%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18 H, CH_3), 1.39 (s, 18 H, CH_3), 1.88 (s, 6 H, CH_3CN), 7.00–7.05 (m, 8 H, Ar*H*), 7.19 (s, 2 H, Ar*H*), 7.30–7.49 (m, 14 H, Ar*H*), 8.02 (d, *J* = 5.5 Hz, 2 H, Ar*H*), 8.21 (s, 2 H, Ar*H*), 8.28 (s, 2 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 10.11 ppm. $C_{64}H_{72}Cu_2F_{12}N_6P_4$ (1404.28): calcd. C 54.70, H 5.17, N 5.98; found C 54.36, H 5.30, N 5.60.

$[Cu_2(\mu\text{-}P\textit{i}Pr_2bipy)_2(\mu\text{-}NCCH_3)](PF_6)_2$ (3): Complex **3** was synthesized analogously to **1** (77%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.96–1.02 (m, 24 H, CHCH_3), 2.09 (s, 3 H, NCCH_3), 2.51 (m, 4 H, C*H*CH$_3$), 7.80–7.80 (m, 4 H, Ar*H*), 8.24 (t, *J* = 8.1 Hz, 2 H, Ar*H*), 8.33 (t, *J* = 8.1 Hz, 2 H, Ar*H*), 8.40 (d, *J* = 8.1 Hz, 2 H, Ar*H*), 8.45 (d, *J* = 8.3 Hz, 2 H, Ar*H*), 8.85 (d, *J* = 5.2 Hz, 2 H, Ar*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 34.11 ppm. $C_{36}H_{48}Cu_2F_{12}N_6P_4$ (1043.78): calcd. C 41.43, H 4.64, N 5.83; found C 39.97, H 4.76, N 6.20.

$[Cu_2(\mu\text{-}P\textit{i}Pr_2bipy)_2\{\mu\text{-}CNCH(CH_3)_2\}](PF_6)_2$ (4): Complex **3** (0.130g; 0.128 mmol) was dissolved in CH_2Cl_2 (10 mL). Isopropyl isocyanide (8.8 mg, 0.127 mmol) dissolved in CH_2Cl_2 (1 mL) was added by syringe. The yellow solution was stirred overnight. The solvent was reduced, and a yellow powder was precipitated by the addition of thf. The product was collected by filtration and dried to yield 0.079 g (62%) of a yellow powder. ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.54 (dd, $^3J_{P,H}$ = 17.6, $^3J_{H,H}$ = 7.0 Hz, 6 H, CHCH_3), 0.69 (dd, $^3J_{P,H}$ = 16.0, $^3J_{H,H}$ = 6.8 Hz, 6 H, CHCH_3), 1.00–1.27 (m, 18 H, CHCH_3), 2.38 (m, 2 H,C*H*CH$_3$), 2.53 (m, 2 H, C*H*CH$_3$), 3.99 (sept, *J* = 6.6 Hz, 1 H, C*H*CH$_3$), 7.84–7.88 (m, 4 H, Ar*H*), 8.23–8.38 (m, 4 H, Ar*H*), 8.43–8.60 (m, 4 H, Ar*H*), 8.89 (d, 2 *H*, ArH) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 35.18 ppm. $C_{37}H_{50}Cu_2F_{12}N_5P_4$ (1043.80): calcd. C 41.95, H 4.79, N 6.79; found C 41.95, H 5.20, N 6.52.

Electrochemistry: Electrochemical experiments were performed by using a BAS Epsilon potentiostat. Cyclic voltammetry experiments were performed under N_2 or CO_2 in a one-compartment cell with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode with ferrocene as an internal reference. All experiments were performed by using 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte, acetonitrile as the solvent, and with copper complex concentrations ranging from 0.25 to 1.0 mM.

Crystallography: Single-crystal X-ray structural data was collected at 100 K with either a Bruker P4 or Platform, or a Kappa diffractometer equipped with a Bruker Apex detector. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures using SHELXL-97.[19] Crystallographic data collection and refinement information can be found in Table S2. In complex **2**, one of the hexafluorophosphate anions showed disorder, which was modeled and refined. In **4**, one of the isopropyl groups in the bridging isocyanides showed disorder, which was modeled and refined. CCDC-904679 (**1**), -904680 (**2**), -904681 (**3**), and -904682 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Additional electrochemical data and crystallographic information for complexes **1**–**4**.

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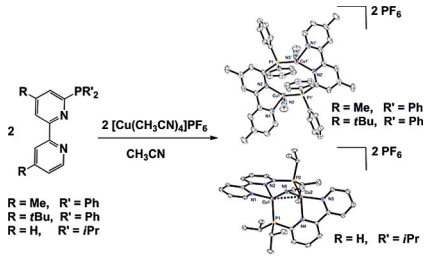
Dimeric Copper Complexes

Three phosphanylbipyridine ligands that react with Cu^{I} to form dimeric complexes have been synthesized and structurally characterized. The Cu–Cu distance can be controlled by ligand substitution, and electrochemical studies of the dimers suggest that four sequential 1e⁻ reductions of the bipyridine ligands occur. Catalytic behavior is observed under CO_2.



Keywords: Dinuclear complexes / Copper / Bridging ligands / Cyclic voltammetry / Electrochemistry

