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Synthesis and Characterization of 6,6′-(2,4,6-Triisopropylphenyl)-2,2′-bipyridine (tripbipy) and Its Complexes of the Late First Row Transition Metals

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The synthesis of tripbipy, a new substituted bipyridine ligand (6,6′-(2,4,6-triisopropylphenyl)-2,2′-bipyridine), and the syntheses, structures, and magnetic properties of the first coordination compounds based on this ligand are described. Tripbipy was synthesized by the Suzuki coupling of 2,4,6-triisopropylphenyl boronic acid and 6,6′-dibromo-2,2′-bipyridine. Reported here are the tripbipy complexes of five late first row transition metal chlorides (MCl$_2$; M=Fe, Co, Ni, Cu, Zn). Four of the complexes MCl$_2$tripbipy (M = Fe, Co, Ni, Zn) crystallize in the space group $P2_1/c$ and are isomorphous with one solvent molecule of crystallization. The complex CuCl$_2$tripbipy crystallizes in the space group $P2_12_12_1$ with two solvent molecules of crystallization. All MCl$_2$tripbipy complexes are four coordinate and contain distorted tetrahedral metal centers. CuCl$_2$tripbipy shows a pseudo Jahn−Teller distortion, and X-band electron paramagnetic resonance (EPR) in a toluene glass gives approximate $g_{\perp,\parallel}$ values of 2.2 and 2.1. Magnetic measurements (M = Fe, Co, Ni, Cu) are consistent with high spin d^n configurations (n = 6−9, S = 2, 3/2, 1, 1/2) tetrahedral complexes and give $\chi_M T$ values at 300 K of 3.56, 2.10, 1.01, and 0.37 cm^3 M^{-1} K, respectively.

Introduction

Bipyridines are one of the most ubiquitous classes of ligands in coordination chemistry. Their ability to bind to a wide range of metal ions and stabilize different oxidation states has been extensively studied. The ability to tune both the electronics and sterics of bipyridine ligands via manipulation of substituents around the pyridyl rings has been a crucial foundation for their widespread applicability. Besides their abundant use in supramolecular,[1] nanomaterial,[2] macromolecular,[3] and photophysical chemistry,[4] bipyridine ligands have been of interest because of their potential for ligand centered redox chemistry and metal-to-ligand-charge-transfer (MLCT) interactions.[5] Herein, we report the synthesis of tripbipy (6,6′-(2,4,6-triisopropylphenyl)-2,2′-bipyridine), a new substituted bipyridine ligand, and the properties of the first coordination compounds based on this ligand.

Low coordinate metal centers are often invoked as catalytically active sites in a number of important catalytic systems, from enzymes to small molecule activation in organometallic complexes. In order to access a low coordinate active site, steric protection of the metal site is often necessary. The use of large substituents (mes = 2,4,6-trimethylphenyl, dipp = 2,6-diisopropylphenyl, trip = 2,4,6-triisopropylphenyl) in various blocking positions of carbenes,[6] arenes, and various other ligand frameworks has shown interesting structural motifs and reactivity.

Inspired by the work of Robinson,[7,8] Power,[9−12] and others using 2,4,6-triisopropylphenyl (trip) groups as large blocking groups, we have developed a synthesis of a chelating bipyridine with sterically encumbering trip groups in the 6,6′ positions. Our first foray into the coordination chemistry of tripbipy is described herein.

Results and Discussion

Syntheses. The synthesis of 6,6′-(2,4,6-triisopropylphenyl)-2,2′-bipyridine (tripbipy) is summarized in

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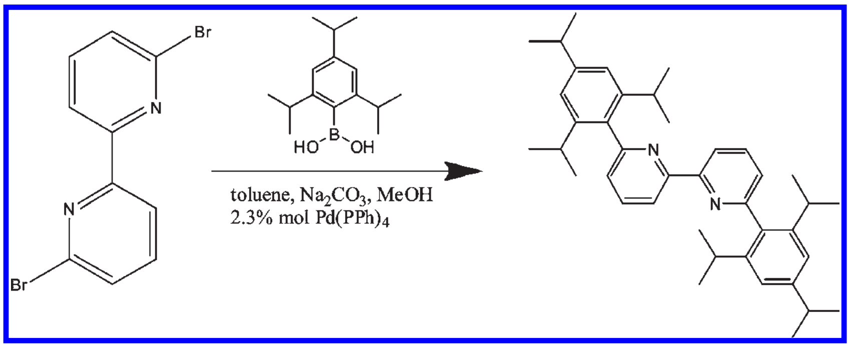
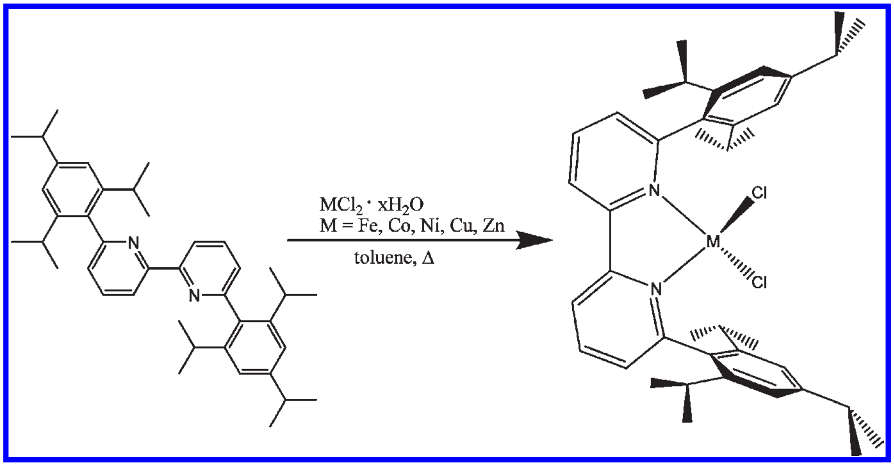
Scheme 1. Synthesis of Tripbipy



Scheme 2. Synthesis of MCl$_2$tripbipy



Scheme 1. Tripbipy was readily synthesized by the Suzuki coupling of 2,4,6-triisopropyphenyl (trip) boronic acid and 6, 6′-dibromo-2, 2′-bipyridine in good yields (>75%). The resulting white solid was characterized by ^{1}H and ^{13}C NMR, combustion analysis, and mass spectrometry. The coupling proceeds in high yield despite the steric bulk of the isopropyl groups flanking the boronic acid. Tripbipy is sparingly soluble in chlorinated solvents (CH$_2$CL$_2$, CHCl$_3$), toluene, and THF.

Tripbipy functions as a sterically encumbering ligand for the late transition metal chlorides, (MCl$_2$; M = Fe, Co, Ni, Cu, Zn). The syntheses of all five complexes MCl$_2$tripbipy (M = Fe, Co, Ni, Cu, Zn) are accomplished by slow addition of ethanol solutions of the metal chloride hydrates to toluene solutions of tripbipy. The overall synthetic plan is depicted in Scheme 2. The subsequent heating and removal of water from the reaction resulted in the complexes MCl$_2$tripbipy in high yields. All five MCl$_2$tripbipy complexes are stable to the atmosphere; however, in solution they are susceptible to attack from nucleophiles (H$_2$O, ACN, THF, pyridine), resulting in varying degrees of ligand dissociation from the metal as verified by ^{1}H NMR, color change, and recovery of free ligand.

X-ray Crystallography. The MCl$_2$tripbipy complexes (M = Fe, Co, Ni, Cu, Zn) were readily crystallized by vapor diffusion of pentane or diethyl ether into solutions of the complex in chloroform.

FeCl$_2$tripbipy. The molecular structure of FeCl$_2$tripbipy was determined by single crystal X-ray diffraction and crystallizes in the space group $P2_1/c$ with one solvent molecule (CHCl$_3$). The structure shows a distorted tetrahedral coordination environment around the iron center (Figure 2). Calculation of Houser's τ_4 four-coordinate geometry index[13] gives a value of 0.83 which suggests that the four coordinate geometry present is closely related to a distorted trigonal pyramidal structure (idealized trigonal pyramid = 0.85). One of the triisopropylphenyl groups is nearly orthogonal to the bipyridine plane, with a torsion angle of 86.69(4)°. The other trip group is inclined at an angle of 69.49(4)° relative to the plane of the bipy ring. This is most likely caused by crystal packing effects, and a C−H−π interaction between the solvent of crystallization and three of the carbons in the benzene ring of the trip group (C15−H41, 2.772 Å). The bite angle of the bipyridine is 77.24(6)° which is similar to the reported

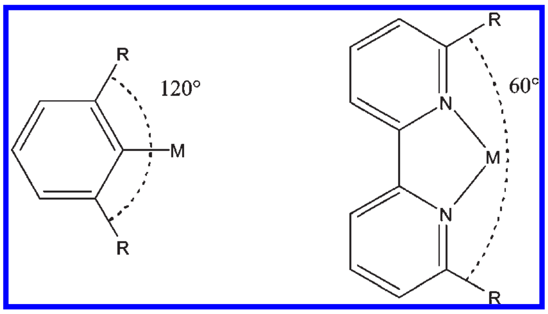


Figure 1. Idealized angles for steric protection of metal centers.

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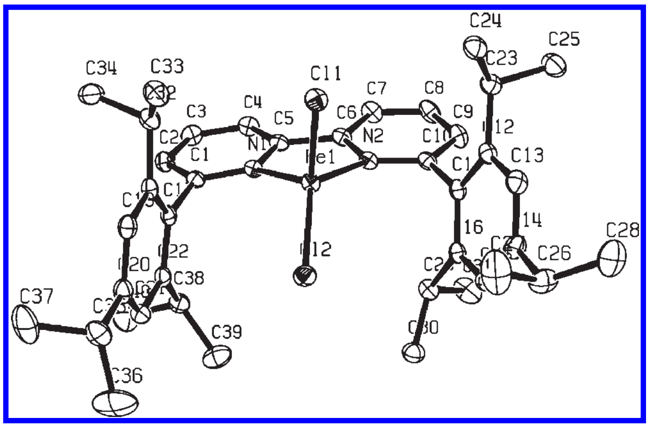

Figure 2. Molecular structure of $FeCl_2$tripbipy.

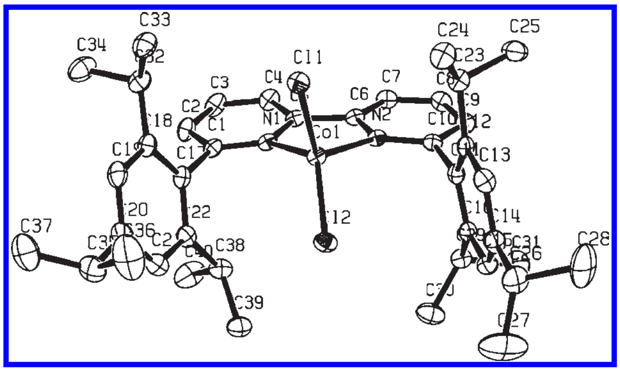

Figure 3. Molecular structure of $CoCl_2$tripbipy.

structures of $FeCl_2$(6,6'dimethyl-2,2'bipyidine) which are 77.50(10)° and 78.12(8)° for the two polymorphs.[14] The difference in Fe−Cl distances (Fe1−Cl1 = 2.2526(5) Å, Fe1−Cl2 = 2.2154(5) Å) and Fe−N (Fe1−N1 = 2.1217(15), Fe1−N2 = 2.1318(14) Å) are also believed to be indicative of crystal packing effects rather than a Jahn−Teller distortion, as comparable distortions are seen with the structurally similar diamagnetic $ZnCl_2$tripbipy complex (vide infra).

$CoCl_2$tripbipy. The cobalt complex was prepared in similar manner to $FeCl_2$tripbipy and crystallizes in the same space group $P2_1/c$ and an isomorphous unit cell with one solvent molecule of chloroform. The complex is structurally similar to $FeCl_2$tripbipy (Figure 3), in that there is one trip group close to orthogonal (87.01(7)°) to the plane of the bipyridine, and the other that is distorted (71.65(8)°) again, presumably from a C−H−π interaction from the chloroform (C15−H41 = 2.771 Å). The bite angle of the chelating pyridine is (N1−Co1−N2) 80.64(10)° and is smaller than most Co^{2+} structures reported[15] but is larger than typical Co^{3+} bipyridine complexes. Again, due to crystal packing effects, we see a slight difference in bond lengths for the Co−Cl and Co−N bonds (Table 1), similar to the trend observed for $FeCl_2$tripbipy. Using the Houser τ_4 parameter, we obtain a value of 0.86 again suggesting a distorted trigonal pyramidal geometry in the solid state.

Table 1. Selected Bond Distances (Å), Angles (deg), and τ_4 Geometry Index[13] for MCl_2tripbipy Complexes

	Fe	Co	Ni	Cu	Zn
M−N1	2.1318(14)	2.0558(25)	2.0173(21)	1.9811(23)	2.0798(26)
M−N2	2.1217(15)	2.0638(25)	2.0287(21)	2.0590(24)	2.0932(27)
M−Cl1	2.2526(5)	2.2348(9)	2.2419(11)	2.2380(9)	2.2298(9)
M−Cl2	2.2154(5)	2.1992(9)	2.1836(11)	2.1738(9)	2.1833(9)
N1−M−N2	77.24(6)	80.64(10)	81.60(9)	81.73(10)	79.72(10)
Cl1−M−N1	112.31(4)	105.55(7)	98.34(7)	96.36(7)	104.10(8)
Cl1−M−N2	103.13(4)	113.28(7)	107.17(7)	128.66(7)	111.54(8)
Cl1−M−Cl2	119.19(2)	114.55(3)	121.31(5)	100.22(4)	117.71(4)
Cl2−M−N1	114.23(4)	123.47(8)	126.76(7)	146.60(7)	122.92(8)
Cl2−M−N2	123.41(4)	114.95(7)	114.06(7)	109.02(7)	114.79(8)
τ_4	0.83	0.86	0.79	0.60	0.85

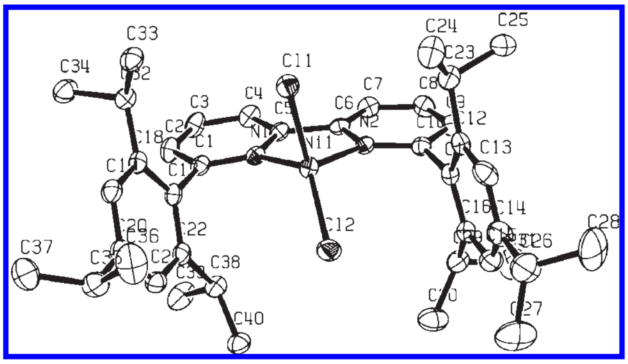

Figure 4. Molecular structure of $NiCl_2$tripbipy.

$NiCl_2$tripbipy. The nickel complex crystallizes in the same space group, $P2_1/c$, as the homologous iron(II) and cobalt(II) complexes, in an isomorphous unit cell that contains one solvent molecule ($CHCl_3$) (see Figure 4). As with the previous two compounds, one of the triispropylphenyl groups is nearly orthogonal to the bipyridine plane, and the other significantly distorted (86.96(7)° vs 71.20(7)°). The bite angle of the bipyridine is 81.60(9)°, which is smaller than most four-coordinate bipyridine structures found in the Cambridge database. This may arise from the torsion of the complex toward a square planar geometry or a pseudo Jahn−Teller distortion. The τ_4 value of 0.79 shows a stronger distortion from the tetrahedral geometry than is seen in $FeCl_2$tripbipy, $CoCl_2$tripBipy, and $ZnCl_2$tripbipy (Table 1).

$CuCl_2$tripbipy. The copper complex is the only compound in this series that did not crystallize in the space group $P2_1/c$. Rather it crystallized in the space group $P2_12_12_1$ with two independent solvent molecules ($CHCl_3$). The geometry around the metal center is severely distorted, $\tau_4 = 0.60$. We attribute this distortion away from tetrahedral geometry to a strong pseudo Jahn−Teller distortion which is not uncommon with Cu^{2+} d^9 complexes.[16] We still see the orthogonal and canted dispositions of the two trip groups that are seen in the structures of the iron, cobalt, and nickel complexes; however, there is no solvent molecule within close contact of the trip group to be the sole cause of the distortion. This can be attributed to crystal packing effects, and the steric repulsion of the chloride due to an elongation of the Cu−Cl bond arising from the pseudo Jahn−Teller distortion. A Houser

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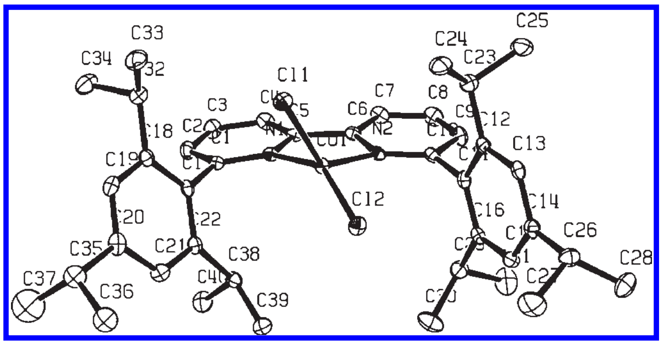

Figure 5. Molecular structure of $CuCl_2$tripbipy.

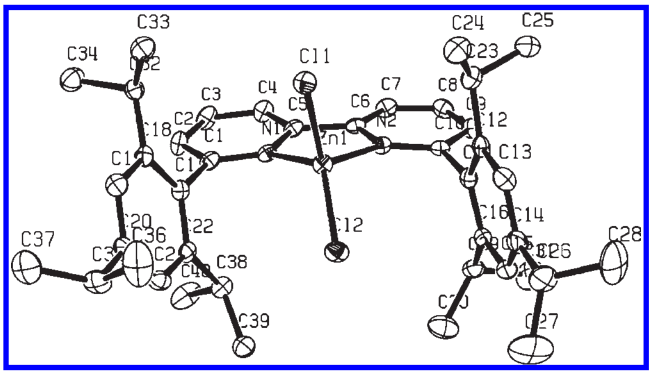

Figure 6. Molecular structure of $ZnCl_2$tripbipy.

τ_4 value of 0.60 is severely distorted from the traditional four-coordinate geometries, and its value lies closer to that of a seesaw (0.65). However, close inspection of the geometry suggests that the structure most closely resembles an intermediate geometry between tetrahedral and square planar, where the steric bulk of the trip groups impedes the transition to square planar (Figure 5).

$ZnCl_2$tripbipy. The zinc complex crystallizes in same space group $P2_1/c$ and isomorphous unit cell with one solvent of crystallization as the iron, cobalt, and nickel complexes (Figure 6). As with the previous metals, we see a distortion in one of the trip groups while the other is nearly normal to the bipyridine ligand plane (70.96(8)° vs 86.94(7)°). As in the related complexes, this is attributed to the solvent C−H bond being within 2.777 Å (C15−H41) of the π system of the distorted trip group, which is within the range for a C−H−π interaction.[17] However, in solution, the molecule shows C_{2v} symmetry from the ^{13}C and ^{1}H NMR, suggesting that the distortion from tetrahedral geometry arises from crystal packing effects rather than an intrinsic electronic or steric property.

Summary of Structures. The tripbipy complexes of iron, cobalt, nickel, and zinc all crystallize in the same space group ($P2_1/c$) and in an almost identical unit cell (a = 8.96(5), b = 28.14(7), c = 16.78(8), α = 90, β = 99.8(3), γ = 90), where the standard deviations are those for the mean cell constants for the four structures. These four complexes are nearly isostructural, with only minimal changes around the metal core. The $CuCl_2$tripbipy complex, on the other hand, crystallized in the space group ($P2_12_12_1$) with two solvent molecules of crystallization, and its structure is quite different from the iron, cobalt, nickel, and zinc members of the series. The bulk of the trip groups has effectively controlled the coordination environment around the metal center in both coordination number, and geometry. This is in contrast to the more prevalent metal halide complexes in which there is coordination of two or three bipyridines to the metal center. Previously the MCl_2bipy (M = Fe, Co, Ni) complexes have been obtained through thermal decomposition of the parent tris-bipyridine complex and have been shown to consist of polymeric chains containing six-coordinate metal centers.[18,19]

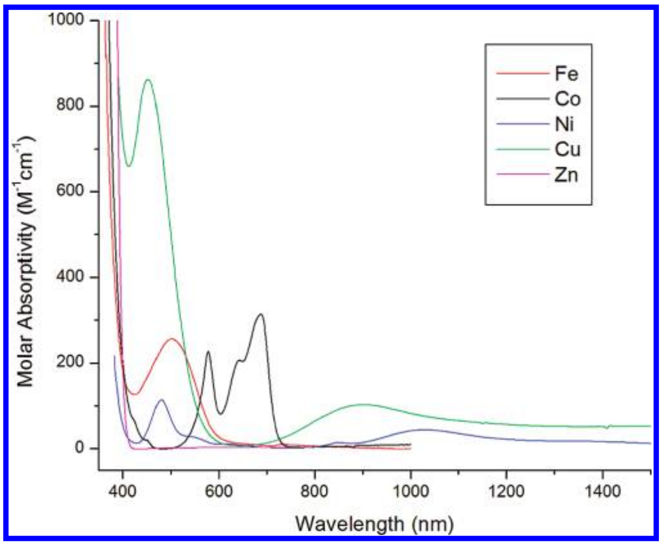

Figure 7. Near-infrared visible spectra of MCl_2tripbipy complexes.

In our case, the tripbipy ligand appears to be an enforcer of tetrahedral coordination geometries, precluding six-coordination in the cases of iron(II) and cobalt(II), and a square planar geometry in the cases of nickel(II) and copper(II). By far, the majority of nickel(II) bipy four-coordinate complexes are square planar.[20] By using bipyridine as a backbone to rigidly hold the trip groups near the metal center, we are able to narrow the open space between the trip groups. This can be quantified as the angle defined between the two trip groups and the metal center. In the $ZnCl_2$tripbipy complex, this angle is 42.72(12)°. In comparison, substituted 2,6-bisphenylbenzene (*m*-terphenyl) complexes present an angle between the two flanking phenyl group planes of nearly 120°.[7,9−12] A comparison of the angles between the substituents of a 2,6-phenyl type ligand vs a 6,6′-bipy ligand is presented in Figure 1. This protection of the metal center by tripbipy may allow for the stabilization of geometries and coordination environments unseen with substituted terphenyl groups.

Electronic Spectra. The electronic spectra of the title compounds in dichloromethane are shown in Figure 7. All compounds show a ligand based $\pi \rightarrow \pi^*$ transition centered near 310 nm (ε = 11000−17000 M^{-1} cm^{-1}). The Fe complex shows a single d−d transition at 505 nm (ε = 260 M^{-1} cm^{-1})

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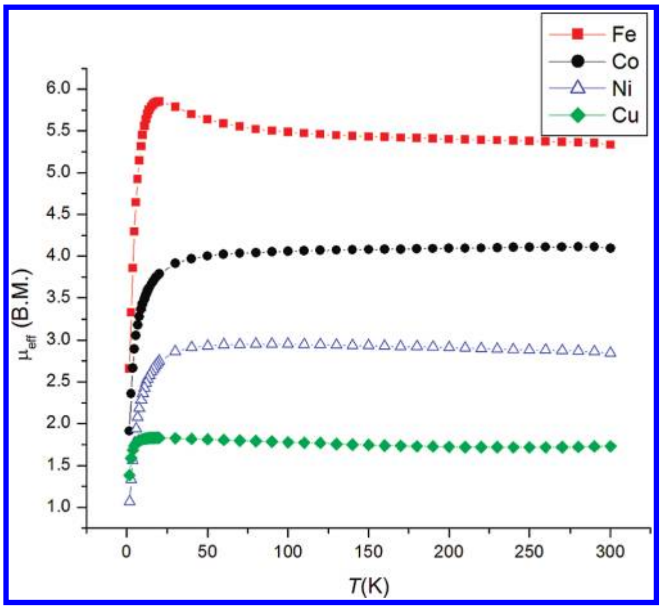

Figure 8. Plot of μ_{eff} vs T for MCl_2tripbipy, M = Fe, Co, Ni, Cu.

which we assign to the $^5E_2 \rightarrow {}^5T_2$ transition, consistent with a monomeric tetrahedral iron center. Here, the irreducible representations and states are referred to Td symmetry, not the structurally more precise C_{2v} symmetry for comparison to related tetrahedral complexes. The electronic spectrum of $FeCl_2$tripbipy is quite different from that of $FeCl_2$bipy which shows transitions corresponding to polymeric chains in C_{2v} symmetry.[18]

The $CoCl_2$tripbipy complex shows three distinct bands at 690, 640, 580 nm (ε = 310, 210, 230 M^{-1} cm^{-1}), and these are assigned to the nominally $^4A_2 \rightarrow {}^4T_1$ transition. The fine structure of this transition is attributed to reduced symmetry of the T_1 state. $NiCl_2$tripbipy shows a number of peaks in the regions of 480−610 nm and 845−1280 nm (Figure 7). These are attributed to the various components of the $^3T_1 \rightarrow {}^3A_2$ and $^3T_1 \rightarrow {}^3T_2$ transitions, respectively. Again these are the transitions are referred to *Td* symmetry and compare favorably to the spectra of tetrahedral $NiCl_4^{2-}$.[21]

The copper complex shows a MLCT band at 450 nm (ε = 860 M^{-1} cm^{-1}) and a broad d−d transition centered at 890 nm (ε = 100 M^{-1} cm^{-1}) and contains the transitions expected for $^2E_2 \rightarrow {}^2T_2$. This matches well with the literature for monomeric Cu^{II} complexes.[22−24] As expected $ZnCl_2$tripbipy shows no d−d transitions, only a ligand based $\pi - \pi^*$ transition at 310 nm (ε = 17000 M^{-1} cm^{-1})

Magnetic Studies. To further characterize the properties of the new tripbipy complexes, magnetic data were used to confirm the number of unpaired spins within each complex. Magnetic data of the MCl_2tripbipy complexes at 4 T is shown in Figure 8. For $FeCl_2$tripbipy, the $\chi_M T$ at 300 K (3.56 cm^3 mol^{-1} K) is consistent with a tetrahedral Fe^{2+} center with an S = 2 ground state. This value is nearly constant through the range of 300−100 K and increases upon cooling to reach a maximum value of 4.27 cm^3 mol^{-1} K, and then decreases below 18 K. This behavior suggests weak intermolecular coupling at lower temperatures, with the decrease of $\chi_M T$ below 18 K being attributed to zero-field splitting.

The $\chi_M T$ of $CoCl_2$tripbipy at 300 K (2.10 cm^3 mol^{-1} K) supports the assignment of a high spin tetrahedral Co^{2+} center (S = 3/2). Unlike the $FeCl_2$tripbipy complex, we do not see any long-range coupling at lower temperatures. The $\chi_M T$ stays nearly constant from 300 to 40 K and then below 40 K starts decreasing presumably from the zero-field splitting. The $\chi_M T$ at 300 K for $NiCl_2$tripbipy at 4 T is 1.01 cm^3 mol^{-1} K and is consistent with a Ni^{2+} center with 2 unpaired electrons giving a S = 1 ground state. As with the $CoCl_2$tripbipy system, we do not see magnetic coupling at lower temperatures, and similarly, we see $\chi_M T$ staying relatively constant until the temperature is below 40 K. The magnetic response of $CuCl_2$tripbipy gives a $\chi_M T$ at 300 K of 0.37 cm^3 mol^{-1} K and stays relatively constant over the entire temperature range; it is not until below 5 K that we begin to see the value decrease.

The observed μ_{eff} values of the MCl_2tripbipy complexes compare favorably with the spin only values. The C_{2v} symmetry of the complexes sufficiently lifts orbital degeneracies to quench spin−orbit coupling. The magnetic behavior of MCl_2tripbipy differs from reported MCl_2bipy complexes. $FeCl_2$bipy has been shown to be a ferromagnet with a Curie temperature of ~4 K,[18] while in the case of $FeCl_2$tripbipy, the metal centers are magnetically dilute from the large separation in the lattice (d(Fe−Fe) 8.6 Å) imposed by the bulky tripbipy ligand. With the nickel and cobalt MCl_2bipy analogs, a high μ_{eff} value has been reported (α-$CoCl_2$bipy 5.10 μ_B, $NiCl_2$bipy 3.38 μ_B), consistent with octahedral chloro-bridged chains.[19] In a similar system $NiI_2(PPh_3)$ shows values close to the spin only value (2.9 μ_B) arising from distortion of the molecule away from tetrahedral symmetry.[25]

Electrochemistry. The electrochemistry of $FeCl_2$tripbipy in CH_2Cl_2 shows a reversible $1e^-$ oxidation at 0.48 V vs Fc/Fc^+ corresponding to the Fe^{II}/Fe^{III} couple and an irreversible $2e^-$ reduction at −1.87 V vs Fc/Fc^+ that is tentatively assigned to the Fe^{II}/Fe^0 couple. The number of electrons transferred was determined by differential pulse voltametry with a known concentration of an internal standard (Fc). Controlled potential electrolysis experiments were inconclusive due to fouling of the electrode presumably from decomposition of the complex. Sample voltamograms can be found in the Supporting Information. $CoCl_2$tripbipy shows an irreversible $2e^-$ reduction at −1.68 V vs Fc/Fc^+. No oxidation to Co^{III} was observed out to +1.2 V vs Fc/Fc^+ in CH_2CL_2. As with $FeCl_2$tripbipy, we assign this as a metal-based reduction. Similarly, $NiCl_2$tripbipy shows an irreversible reduction at −1.43 vs Fc/Fc^+. This is tentatively assigned to the Ni^{II}/Ni^0 couple.

The electrochemistry of $CuCl_2$tripbipy in CH_2Cl_2 at slow scan rates (0.025 V/s) shows a single reversible reduction at 0.05 V vs Fc/Fc^+. At faster scan rates (> 0.05 V/s), the voltamograms become more convoluted, which may be due to a coupled chemical reaction with the solvent and or electrolyte. $CuCl_2$tripbipy will

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Table 2. Crystallographic Data and Refinement Information

compound	$FeCl_2$tripBipy	$CoCl_2$tripBipy	$NiCl_2$tripBipy	$CuCl_2$tripBipy	$ZnCl_2$tripBipy
empirical formula	$FeCl_2C_{40}H_{52}\cdot CHCl_3$	$CoCl_2C_{40}H_{52}\cdot CHCl_3$	$NiCl_2C_{40}H_{52}\cdot CHCl_3$	$CuCl_2C_{40}H_{52}\cdot 2CHCl_3$	$ZnCl_2C_{40}H_{52}\cdot CHCl_3$
formula weight	806.98	810.07	809.83	934.06	816.55
crystal system lattice parameters	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
a (Å)	8.9257(5)	8.9196(7)	9.036(6)	13.785(5)	8.9639(8)
b (Å)	28.1409(17)	28.052(2)	28.218(18)	16.968(6)	28.157(2)
c (Å)	16.8549(10)	16.8310(14)	16.666(11)	19.525(7)	16.7861(14)
α (deg)	90	90	90	90	90
β (deg)	100.1670(10)	100.069(2)	99.386(9)	90	99.866(1)
γ (deg)	90	90	90	90	90
V (Å^3)	4167.1(4)	4146.4(6)	4192(5)	4567.17(27)	4174.0(6)
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
Z value	4	4	4	4	4
ρ_{calc} (g cm^{-3})	1.286	1.298	1.283	1.360	1.300
μ (Mo Kα) (mm^{-1})	0.71073	0.71073	0.71073	0.71073	0.71073
temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
2θ max (deg)	50.9	50.82	51.42	50.98	50.78
no. obs ($I > 2\alpha(I)$)	7713	7645	7858	8485	7721
no. parameters	454	454	454	490	454
goodness of fit	1.041	1.064	1.064	0.955	1.013
max shift in cycle	0.002	0.002	0.002	0.001	0.001
residuals: $R1$; $wR2$	0.0309; 0.0751	0.0497; 0.1371	0.0423; 0.1020	0.0317; 0.0753	0.0491; 0.1135
largest peak	0.435	0.595	1.016	0.303	0.732
deepest hole	−0.456	−0.893	−0.672	−0.345	−0.467

oxidize Fc to Fc$^+$ as evident in the CV's and the color change of the solution upon addition of ferrocene.

Electrochemistry of $ZnCl_2$tripbipy in CH_2CL_2 shows a reversible ligand based reduction at −1.94 V vs Fc/Fc$^+$. Due to the filled d orbitals of zinc and the reversibility of the reduction, this reduction is assigned as ligand-based. This also lends credence to the assignment of the reductions seen in the previous Fe, Co, and Ni complexes as metal, not ligand based.

EPR. In order to further probe the electronic structure of $CuCl_2$tripbipy, EPR was performed in a toluene solution at room temperature and in a frozen glass at X band frequencies. The isotropic g value in fluid solution is 2.044 with an apparent A value of 222 MHz, which is consistent with coupling to ^{65,63}Cu nuclei with I = 3/2. In a frozen glass at 110 K, the spectrum becomes more convoluted and gives apparent $g_{\perp}$ and $g_{\parallel}$ values near 2.2 and 2.1, respectively. The EPR data suggest a tetrahedral compression toward square planar resulting in the free electron residing in a d_{xy} orbital. This is consistent with the shorter than average Cu−Cl bonds and strongly distorted tetrahedral molecular geometry seen in the X-ray diffraction study. The hyperfine coupling to the Cu nucleus was unresolved due to overlap of the $g_{\perp}$ and $g_{\parallel}$ transitions. EPR spectra and simulations can be found in the Supporting Information.

Conclusions

Tripbipy has been shown to be an effective ligand for control of the coordination number and geometry of five late first row transition metals. Coordination to metal chlorides (M = Fe, Co, Ni, Cu, Zn) gives pseudotetrahedral coordination environments. Tripbipy can be regarded as an "enforcer" of tetrahedral geometries when alternate octahedral or square planar geometries are available. Tripbipy, through its large flanking arms and narrow coordination region between them, is able to protect the metal centers to which it is attached. Tripbipy does show a tendency to be labilized in the presence of other nucleophilic ligands. We anticipate that tripbipy will find important applications in stabilizing coordinativly unsaturated species in low oxidation states.

Experimental Section

General Considerations. 6,6′-Dibromo-2,2′-bipyridine was synthesized according to literature procedures;[26] all other chemicals were purchased from commercial sources and used as received. Toluene and methylene chloride were sparged with argon and dried over basic alumina with a custom dry solvent system. $CHCl_3$ was filtered through activated basic alumina and distilled over P_2O_5. Magnetic measurements were collected on a Quantum Design MPMS 5 SQUID magnetometer. The susceptibility measurements were performed in the 1.8−300 K temperature range with an applied field of 4 T. Data were corrected for diamagnetic contributions from both the sample holder and the tripbipy ligand using Pascal's constants. Electrochemistry was carried out using a BAS epsilon workstation using a glassy carbon working electrode, Pt wire counter, and Ag/AgCl pseudoreference electrode using tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. All solutions were referenced to Fc/Fc$^+$ using an internal standard. ^{1}H NMR were obtained using a Jeol ECA-500 spectrometer. ^{13}C NMR were obtained using Varian Mercury 400 and 500 spectrometers. All NMR spectra were referenced to internal solvent peaks. UV/vis/NIR spectra were collected on a Shimadzu UV-3600 in dichloromethane. Combustion analysis was performed by Midwest MicroLab, LLC, Indianapolis, IN.

Crystallographic Structure Determinations. Single-crystal X-ray structure determinations were carried out at 150(2) K on either a Bruker P4 or platform diffractometer using Mo Kα radiation (λ = 0.71073 Å) in conjunction with a Bruker APEX detector. All structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares procedures using SHELXL-97.[27] Crystallographic data collection and refinement information can be found in Table 2.

Synthesis of Trip$_2$Bipy (1). To a toluene (250 mL) solution of 6,6′-dibromo-2,2′-bipyridine (2 g, 6.37 mmol) an excess of

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(26) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53.

(27) Sheldrick, G. *Acta Cryst. A* **2008**, *64*, 112.

2,4,6-triisopropylbenzene boronic acid (4 g, 16.1 mmol) suspended in 30 mL of methanol was added. A 30 mL portion of 2 M sodium carbonate and 175 mg of $Pd(PPh_3)_4$ (2.3% mol cat) were added and refluxed for 72 h in air. After cooling, the layers were separated, the organic layer was washed with brine (2 × 100 mL), and the aqueous layer was washed with chloroform (2 × 100 mL). The organic fractions were combined and dried under rotary evaporation. The crude solid was then dissolved in minimal amount of hot chloroform, filtered, and crashed out with methanol. The white precipitate was filtered and dried in vacuo at 80 °C. Yield: 2.78 g, 4.97 mmol, 78.0%. ^{1}H NMR (500 MHz, CH_2Cl_2, 20 °C): $\delta = 8.41$ (d, 2H, J = 8 Hz), 7.81 (t, 2H, J = 8 Hz), 7.27 (d, 2H, J = 8 Hz), 7.13 (s, 4H), 2.97 (sep., 2H, J = 7 Hz), 2.60 (sep., 4H, J = 7 Hz), 1.32 (d, 12H, J = 7 Hz), 1.14 (d, 12H, J = 6 Hz), 1.12 (d, 12H, J = 6 Hz). ^{13}C NMR (125.1 MHz, $CHCl_3$, 20 °C): $\delta = 159.3$, 156.0, 148.7, 146.5, 136.9, 136.4, 125.1, 120.9, 119.2, 34.6, 30.5, 24.5, 24.3, 24.2 ppm. Anal. calcd for $C_{40}H_{52}N_2$: C, 85.66; H, 9.35; N, 4.99. Found: C, 85.41; H, 9.44; N, 5.04.

Synthesis of MCl_2tripbipy. To a solution of tripbipy in toluene (200 mg, 0.357 mmol, 25 mL), 1 equiv of the corresponding metal chloride or chloride hydrate in 3 mL EtOH was added slowly and refluxed for 3 h. The condenser was then removed, and the solution was reduced to 10 mL under heat and N_2. After cooling, 50 mL of pentane was added to the solution and cooled to −20 °C overnight. Crystals were filtered and washed with pentane and dried in vacuo.

$FeCl_2$tripbipy. 70.9 mg $FeCl_2 \cdot 4H_2O$, 0.357 mmol. Yield 218 mg, 0.318 mmol, 89.1%. Anal. calcd for $C_{40}H_{52}N_2Cl_2Fe$: C, 69.87; H, 7.62; N, 4.07. Found: C, 68.68; H, 7.75; N, 3.82. Crystals suitable for X-ray diffraction were grown from vapor diffusion of pentane into chloroform.

$CoCl_2$tripbipy. 46.3 mg $CoCl_2$, 0.357 mmol. Yield 202 mg, 0.292 mmol, 82.0%. Anal. calcd for $C_{40}H_{52}N_2Cl_2Co$: C, 69.56; H, 7.59; N, 4.06. Found: C, 68.73; H, 7.53; N, 4.04. Crystals suitable for X-ray diffraction were grown from the vapor diffusion of Et_2O into chloroform.

$NiCl_2$tripbipy. 84.8 mg $NiCl_2 \cdot 6H_2O$, 0.357 mmol. Yield 198 mg, 0.287 mmol, 80.4%. Recrystallized from $CHCl_3$/pentane as the chloroform solvate. Anal. calcd for $C_{40}H_{52}N_2Cl_2Ni \cdot CHCl_3$: C, 60.81; H, 6.60; N, 3.46. Found: C, 61.23; H, 6.76; N, 3.48. Crystals suitable for X-ray diffraction were grown from the vapor diffusion of pentane into chloroform.

$CuCl_2$tripbipy. 60.8 mg $CuCl_2 \cdot 2H_2O$, 0.357 mmol. Yield 247 mg, 0.348 mmol, 97.5%. Orange-red crystals, Anal. calcd for $C_{40}H_{52}N_2Cl_2Cu$: C, 69.10; H, 7.54; N, 4.03. Found: C, 68.19; H, 7.52; N, 3.99. Crystals suitable for X-ray diffraction were grown from the vapor diffusion of Et_2O into chloroform.

$ZnCl_2$tripbipy. 48.6 mg $ZnCl_2$, 0.357 mmol. Yield 235 mg, 0.337 mmol, 94.5%. ^{1}H NMR (500.2 MHz, CH_2Cl_2, 20 °C): $\delta = 8.31$ (d, 2H, J = 7 Hz), 8.16 (t, 2H, J = 8 Hz), 7.66 (d, 2H, J = 7 Hz), 7.03 (s, 4H), 2.86 (sep., 2H, J = 7 Hz), 2.39 (sep., 4H, J = 7 Hz), 1.29 (d, 12H, J = 7 Hz), 1.22 (d, 12H, J = 7 Hz), 0.95 (d, 12H, J = 7 Hz). ^{13}C NMR (100.6 MHz, $CHCl_3$, 20 °C): $\delta = 162.0$, 150.7, 149.6, 146.7, 139.8, 131.6, 129.7, 121.0, 120.5, 34.5, 26.1, 24.1, 22.7 ppm. Anal. calcd for $C_{40}H_{52}N_2Cl_2Zn$: C, 68.91; H, 7.52; N, 4.02. Found: C, 68.80; H, 7.49; N, 4.07. Crystals suitable for X-ray diffraction were grown from the vapor diffusion of Et_2O into chloroform.

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Supporting Information Available: Figures S1−S7 and a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.