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Conformationally Rigid Chelate Rings in Metal Complexes of Pyridyloxy-Substituted 2,2′-Dioxybiphenyl-Cyclotetra- and Cyclotriphosphazene Platforms

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Divalent metal halides react with pyridyloxy-substituted 2,2′-dioxybiphenyl-cyclotri- and cyclotetraphosphazene ligands to form the complexes, [MLX_2] [M = Co or Cu; L = (2,2′-dioxybiphenyl)tetrakis(2-pyridyloxy)cyclotriphosphazene (L^1) or (2,2′-dioxybiphenyl)tetrakis(4-methyl-2-pyridyloxy)cyclotriphosphazene (L^2); X = Cl or Br], [$ZnLCl_2$] [L = bis(2,2′-dioxybiphenyl)bis(2-pyridyloxy)cyclotriphosphazene (L^3) or bis(2,2′-dioxybiphenyl)bis(4-methyl-2-pyridyloxy)-cyclotriphosphazene (L^4)], [$MLCl_2$] [M = Cu or Hg; L = tris(2,2′-dioxybiphenyl)bis(2-pyridyloxy)cyclotetraphosphazene (L^5)] and [Cu_2LCl_4] (L = *trans*-bis(2,2′-dioxybiphenyl)tetrakis(2-pyridyloxy)cyclotetraphosphazene (L^6)]. Single-crystal X-ray structures show the L^2 ligand complexes to have a N_3Cl_2 five-coordinate, trigonal-bipyramidal donor set with the phosphazene ring and pendant pyridyloxy nitrogens binding to the metal ions. The coordinated L^2 ligand in the complex, [CoL^2Cl_2], slowly hydrolyses in acetonitrile with the loss of a pyridine pendant arm to form a dimetallic species, which has been characterized by crystallography as [$\{CoL^{2a}Cl\}_2$]•4MeCN (L^{2a} = [N_3P_3(biph)(OPy)$_3$(O)]$^-$, biph = 2,2′-dioxybiphenyl, OPy = 2-oxopyridine). The ligands, L^3, L^4, L^5, and L^6, bind to the metal halides via gem-substituted pyridyloxy nitrogens only. The resulting rigid eight-membered chelate rings all have distorted boat conformations, which force distorted-tetrahedral N_2Cl_2 coordination environments onto the metal ions. The spectroscopic (ESR and electronic) and magnetic properties of the complexes are reported.

Introduction

Phosphazenes are a remarkable class of inorganic molecules in which the phosphorus and nitrogen repeat units can form cyclic compounds or chains. Research output has been steadily increasing since the mid 1960s when Allcock discovered a controlled thermal route to the non-crosslinked polymer.[1] To date, polyphosphazenes have been reported covering such diverse applications as biomedical, membranes, high-performance elastomers, fire-resistant materials, electro-optical and semiconducting materials, and energy generation and storage.[2]

The inclusion of pendant donor groups for attaching metal ions to the polymer offers the chance to develop metal-rich materials with interesting magnetic, electronic, or photophysical properties. Furthermore, the facile stepwise substitution chemistry possible with the polychlorophosphazene precursor also allows physical properties of the polymer to be tailored by the choice of suitable substituents. Carriedo et al. have shown that the substitution of spirocyclic bi-oxyaryl groups as substituents on the polymer backbone yields polymers with interesting physical properties and that introducing spirocyclic groups and ligand moieties onto the polymer backbone is a good strategy for controlling the local environment of the metal ions.[3] This approach could also be used to apply greater control over the coordination chemistry of ligand-substituted polyphosphazenes.

For fundamental studies on the metal binding of ligand-substituted polyphosphazenes, it is useful to consider the cyclic analogues as model compounds.[4] Previously, we have reported the coordination chemistries of hexakis(2-pyridyloxy)cyclotriphosphazene (L) and hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene (MeL) and have shown that

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(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216−4217.

(2) (a) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; John Wiley and Sons: New Jersey, 2003. (b) *Phosphazenes: A Worldwide Insight*; Gleria, M.; De Jaeger, R., Eds.; Nova Science Publishers: New York, 2004.

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they are versatile multimodal ligands, which display a range of binding modes.[5] However, the polymodal nature of L and MeL renders their coordination chemistries somewhat unpredictable, and this is further complicated by their ability to act as bridging ligands. Hence, we considered it of interest to examine the effect of replacing sets of geminal 2-pyridyloxy groups on L and MeL with spirocyclic 2,2′-dioxybiphenyl groups. We have previously examined other ligand systems containing spirocyclic 2,2′-dioxybiphenyl groups: a bidentate (2-oxyphenyl)diphosphine[6a] and a tetradentate *bis*(2-oxy)phenanthroline system.[6b] Others have reported metal complexes of trimeric phosphazene systems containing spirocyclic 2,2′-dioxybiphenyl substituents and hydrazide,[7] (4-oxyphenyl)diphenylphosphine,[3f,8] nitrile,[9] and 4-oxypyridine[10] ligand groups. Because the flexible cyclotetraphosphazenes containing spirocyclic 2,2′-dioxybiphenyl groups are more relevant as small molecule models for the related polymeric systems,[11] we have now examined metal complexes of gem-2-pyridyloxy derivatives. Structural data on the coordination compounds of tetrameric cyclophosphazenes are prevalent for polyanionic forms such as phosphazenates or phosphimates.[12] Data also exist for protonated cationic tetramers, which can act as the ion pair for complex anions[13−15] or as cationic ligands.[16] Of the metal-ion-containing structures where the phosphazene ring is formally neutral, the reported X-ray data are for metallocene,[17−20] tungsten tetracarbonyl,[21] and platinum dichloride complexes.[15,22,23] This study adds to the available data for monometallic species and includes the first dimetallic complex.

Hence, in this article we report the first structurally characterized tetramers that contain metal ions and spirocyclic 2,2′-dioxybiphenyl groups. Forcing the 2-pyridyloxy pendant groups to be gem by blocking off the other phosphorus atoms with spirocyclic 2,2′-dioxybiphenyl groups introduces a stereochemical rigidity to the resulting 8-membered chelate rings, which influences the coordination environment of the metal atom. For comparison, we have also prepared a number of new ligand systems based on cyclotriphosphazenes that contain spirocyclic 2,2′-dioxybiphenyl groups and 2-pyridyloxy ligand moieties.

Experimental Section

General. All of the reactions were carried out under nitrogen using standard Schlenk techniques. Analytical-grade solvents were purchased from standard chemical suppliers, and with the exception of tetrahydrofuran (THF), were used without further purification or drying. The THF was distilled from sodium wire/benzophenone and stored over activated molecular sieves (4 Å). 2-Hydroxypyridine (Lancaster) and 2-hydroxy-4-methylpyridine (Aldrich) were used as received. Column chromatography was carried out on silica gel 60 (Merck) or Brockmann grade II/III alumina (Sigma). Cs_2CO_3 (Aldrich) was dried at 140 °C overnight. $[N_3P_3(biph)Cl_2]$, $[N_3P_3(biph)_2Cl_2]$, $[N_4P_4(biph)_2Cl_4]$, and $[N_4P_4(biph)_3Cl_2]$ (biph = 2,2′-dioxybiphenyl) were prepared according to literature procedures.[3j,11] $^{31}P\{^1H\}$ NMR spectra and ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer. IR spectra were run as KBr discs on a PerkinElmer FTIR Paragon 1000 spectrometer, and electronic absorption spectra were recorded using a Shimadzu UV-310-310PC scanning spectrometer. Electrospray mass spectra were collected from MeCN solutions on a Micromass ZMD spectrometer, run in positive ion mode. Magnetic susceptibility measurements were performed on a Faraday balance at room

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(3) (a) Carriedo, G. A.; García Alonso, F. J.; Presa Soto, A. *Macromolecules* **2006**, *39*, 4704−4709. (b) Carriedo, G. A.; García Alonso, F. J.; Díaz Valenzuela, C.; Valenzuela, M. L. *Polyhedron* **2006**, *25*, 105−112. (c) Carriedo, G. A.; Crochet, P.; García Alonso, F. J.; Gimeno, J.; Presa Soto, A. *Eur. J. Inorg. Chem.* **2004**, *18*, 3668−3674. (d) Carriedo, G. A.; García Alonso, F. J.; Presa Soto, A. *J. Inorg. Organomet. Polym.* **2004**, *14*, 29−37. (e) Carriedo, G. A.; García Alonso, F. J.; Luís García, A. J.; Díaz Valenzuela, C.; Yutronic, N. S. *Polyhedron* **2002**, *21*, 2587−2592. (f) Carriedo, G. A.; García Alonso, F. J.; González, P. A.; Díaz Valenzuela, C.; Yutronic, N. S. *Polyhedron* **2002**, *21*, 2579−2586. (g) Carriedo, G. A.; García, Alonso, F. J.; Presa Soto, A. *Eur. J. Inorg. Chem.* **2003**, *24*, 4341−4346. (h) Rojo, G.; Martín, G.; Agulló López, F.; Carriedo, G. A.; García Alonso, F. J.; Fidalgo Martínez, J. I. *Chem. Mater.* **2000**, *12*, 3603−3610. (i) Carriedo, G. A.; García Alonso, F. J.; Gómez Elipe, P.; García Alvarez, J. L.; Tarazona, M. P.; Rodríguez, M. T.; Saiz, E.; Vázquez, J. T.; Padrón, J. I. *Macromolecules* **2000**, *33*, 3671−3679. (j) Carriedo, G. A.; Fernández, Catuxo, L.; García, Alonso, F. J.; Gómez Elipe, P.; González, P. A. *Macromolecules* **1996**, *29*, 5320−5325.

(4) Allcock, H. R. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 661−671.

(5) (a) Ainscough, E. W.; Brodie, A. M.; Depree C. V. *J. Chem. Soc., Dalton Trans.* **1999**, 4123−4124. (b) Ainscough E. W.; Brodie A. M.; Depree C. V.; Moubaraki, B.; Murray, K. S.; Otter, C. A. *Dalton Trans.*, **2005**, 3337−3343. (c) Ainscough, E. W.; Brodie, A. M.; Depree, C. V.; Jameson, G. B.; Otter, C. A. *Inorg. Chem.* **2005**, *44*, 7325−7327. (d) Ainscough, E. W.; Brodie, A. M.; Depree, C. V.; Otter, C. A. *Polyhedron* **2006**, *25*, 2341−2352.

(6) (a) Ainscough, E. W.; Brodie, A. M.; Chaplin, A. B.; O'Connor, J. M.; Otter, C. A. *Dalton Trans.* **2006**, 1264−1266. (b) Ainscough, E. W.; Brodie, A. M.; Jameson, G. B.; Otter, C. A. *Polyhedron* **2007**, *26*, 460−471.

(7) Chandrasekhar, V.; Krishnan, V.; Steiner, A.; Bickley, J. F. *Inorg. Chem.* **2004**, *43*, 166−172.

(8) (a) Carriedo, G. A.; García, Alonso, F. J.; González, P. A.; Gómez Elipe, P. *Polyhedron* **1999**, *18*, 2853−2859. (b) Carriedo, G. A.; García Alonso, F. J.; García, J. L.; Carbajo Rodrigo, J.; López Ortiz, F. *Eur. J. Inorg. Chem.* **1999**, *6*, 1015−1020.

(9) (a) Díaz, C.; Izquierdo, I.; Mendizábal, F.; Yutronic, N. *Inorg. Chim. Acta* **1999**, *294*, 20−27. (b) Díaz, C.; Castillo, P. *J. Inorg. Organomet. Polymers* **2002**, *11*, 183−192.

(10) Harmjanz, M.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, *13*, 1386−1387.

(11) Ainscough, E. W.; Brodie, A. M.; Chaplin, A. B.; Derwahl, A.; Harrison, J. A.; Otter, C. A. *Inorg. Chem.* **2007**, *46*, 2575−2583.

(12) For some examples see (a) Roemer, R. S.; Schnick, W. *Z. Anorg. Allg. Chem.* **2006**, *632*, 59−63. (b) Roemer, R. S.; Schnick, W. *Z. Anorg. Allg. Chem.* **2005**, *631*, 31−37. (c) Lawson, G. T.; Jacob, C.; Steiner, A. *Eur. J. Inorg. Chem.* **1999**, *11*, 1881−1887. (d) Steiner, A.; Wright, D. S. *Chem. Commun.* **1997**, 283−284. (e) Berking, B.; Mootz, D. *Acta Crystallogr. B* **1971**, *27*, 740−747.

(13) Calhoun, H. P.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1974**, 377−381

(14) Trotter, J.; Whitlow, S. H. *J. Chem. Soc. A* **1970**, 460−464.

(15) O'Brien, J. P.; Allen, R. W.; Allcock, H. R. *Inorg. Chem.* **1979**, *18*, 2230−2235.

(16) Trotter, J.; Whitlow, S. H. *J. Chem. Soc. A* **1970**, 455−459.

(17) Herberhold, M.; Hofmann, A.; Milius, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1599−1608.

(18) Herberhold, M.; Hoffmann, A.; Milius, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 545−553.

(19) Allcock, H. R.; Lavin, K. D.; Riding, G. R.; Whittle, R. R. *Organometallics* **1984**, *3*, 663−669.

(20) Allcock, H. R.; Lavin, K. D.; Riding, G. R.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337−2347.

(21) Calhoun, H. P.; Paddock, N. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1973** 2708−2712.

(22) O'Brien, J. P.; Allen, R. W.; Allcock, H. R. *J. Am. Chem. Soc.* **1977**, *99*, 3987−3991.

(23) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *Chem. Commun.* **1976**, 717−718.

temperature. X-band EPR spectra were recorded at 113 K on a Varian E-104A spectrometer equipped with an E-257 variable-temperature controller and operating at about 9.0 GHz. The spectral g values were calibrated with (diphenylpicryl)hydrazyl (DPPH) as a standard. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

Syntheses. (2,2′-Dioxybiphenyl)tetrakis(2-pyridyloxy)cyclotriphosphazene (L^1). To a stirred suspension of [N_3P_3(biph)Cl_4] (0.26 g, 0.57 mmol) in acetone (80 mL) was added 2-hydroxypyridine (0.22 g, 2.30 mmol) and Cs_2CO_3 (0.86 g, 2.64 mmol). After stirring under N_2 for 2 days, the solution was filtered through Celite, washed with CH_2Cl_2 and dried under vacuum. White crystals were obtained by slow diffusion from CH_2Cl_2/hexane at 4 °C. Yield: 0.63 g (81%). Anal. Calcd for $C_{32}H_{24}N_7O_6P_3$: C, 55.26; H, 3.48; N, 14.10. Found: C, 55.09; H, 3.87; N, 13.46. ESMS: *m*/*z* 696 $[M+H]^+$, 828 *m*/*z* $[M+Cs]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.8 ppm (t, $J_{PP} = 94$ Hz), 8.0 ppm (d, $J_{PP} = 95$ Hz). ^1H NMR ($CDCl_3$): δ 8.22 (m, 4H), 7.63 (m, 4H), 7.38 (m, 2H), 7.22 (m, 4H), 7.11 (m, 4H), 7.04 (m, 4H), 6.77 (m, 2H). ν/cm^{-1} (PN): 1225, 1172.

(2,2′-Dioxybiphenyl)tetrakis(4-methyl-2-pyridyloxy)cyclotriphosphazene (L^2). To a stirred suspension of [N_3P_3(biph)Cl_4] (1.31 g, 2.85 mmol) in acetone (100 mL) was added 2-hydroxy-4-methylpyridine (1.25 g, 11.45 mmol) and Cs_2CO_3 (4.25 g, 13.04 mmol). After stirring at reflux under N_2 for 8 days, the reaction mixture was filtered through a Celite pad, which was washed with acetone. The combined filtrates were added slowly to a small quantity of distilled water (5 mL) to form a milky solution, which on continued addition yielded the product as a white precipitate. The precipitate was collected by filtration and dried under vacuum. Yield: 1.28 g (50%). Anal. Calcd for $C_{36}H_{32}N_7O_6P_3$: C, 57.53; H, 4.29; N, 13.05. Found: C, 57.25; H, 4.42; N, 12.98. ESMS: *m*/*z* 752 $[M+H]^+$. ^{31}P NMR ($CDCl_3$): δ 26.5 ppm (t, $J = 96$ Hz), 7.9 ppm (d, $J = 97$ Hz). ^1H NMR ($CDCl_3$): δ 8.09 (m, 4H), 7.51 (m, 2H), 7.31 (m, 4H), 6.94 (m, 8H) 6.81 (m, 2H), 2.31 (s, 12H). ν/cm^{-1} (PN): 1195, 1142.

Bis(2,2′-dioxybiphenyl)bis(2-pyridyloxy)cyclotriphosphazene (L^3). A mixture of [P_3N_3(biph)$_2Cl_2$] (1.48 g, 2.58 mmol), 2-hydroxypyridine (0.65 g 6.88 mmol), and Cs_2CO_3 (4.48 g, 13.83 mmol) in acetone (100 mL) was stirred at room temperature over 2 h. The acetone was removed on a rotary evaporator, and the solid was extracted with CH_2Cl_2 (5 × 100 mL). Filtration and removal of the CH_2Cl_2 on a rotary evaporator gave a white solid, which was further purified by column chromatography with CH_2Cl_2 as eluent. Yield: 1.44 g (81%). Anal. Calcd for $C_{34}H_{24}N_5O_6P_3$: C, 59.05; H, 3.50; N, 10.13. Found C, 59.18; H, 3.59; N, 9.90. ESMS: *m*/*z* 692, $[MH^+]$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.6 ppm (d, 2P, $J = 95$ Hz), 10.1 ppm (t, P, $J = 94$ Hz). ^1H NMR ($CDCl_3$): δ 8.47 (m, 2H), 7.77 (m, 2H), 7.49 (m, 4H), 7.34 (m, 4H), 7.27 (m, 4H), 7.21 to 7.13 (m, 4H), 7.07 (m, 4H). ν/cm^{-1} (PN): 1229, 1176.

Bis(2,2′-dioxybiphenyl)bis(4-methyl-2-pyridyloxy)cyclotriphosphazene (L^4). A mixture of [P_3N_3(biph)$_2Cl_2$] (2.00 g, 3.48 mmol), 4-methyl-2-hydroxypyridine (0.95 g, 8.71 mmol), and Cs_2CO_3 (5.10 g, 15.64 mmol) in THF (130 mL) was stirred over 2 h. The solvent was removed on a rotary evaporator, and the residue was extracted with CH_2Cl_2 (5 × 100 mL), filtered, and taken to dryness. Colorless rectangular crystals were obtained by diffusing diethylether into a solution of the crude product in CH_2Cl_2 (50 mL) overnight. Yield: 1.65 g (70%). Anal. Calcd for $C_{36}H_{28}N_5O_6P_3$: C, 60.09; H, 3.92; N, 9.73%. Found C, 60.09; H, 3.75; N, 9.75. ESMS: *m*/*z* 720, $[MH^+]$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.1 ppm (d, 2P, $J = 95$ Hz), 10.6 ppm (t, P, $J = 94$ Hz). ^1H NMR ($CDCl_3$): δ 8.31 (m, 2H), 7.49 (m, 4H), 7.34 (m, 4H), 7.27 (m, 4H), 7.09 (m, 4H), 7.00 (m, 4H), 2.39 (s, 6H). ν/cm^{-1} (PN): 1230, 1200, 1181.

Tris(2,2′-dioxybiphenyl)bis(2-pyridyloxy)cyclotetraphosphazene (L^5). To a solution containing 2-hydroxypyridine (0.73 g, 7.67 mmol) in THF (70 mL), NaH (0.16 g, 6.67 mmol) was added, and the mixture was heated at reflux over 30 min. [P_4N_4(biph)$_3Cl_2$] (2.00 g, 2.49 mmol) in THF (30 mL) was added and the mixture was heated at reflux over a further 16 h. The THF was removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 (100 mL). This solution was washed with water (250 mL), and the aqueous phase was separated and washed with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed on a rotary evaporator to give a white-yellow solid. This residue was taken up in CH_2Cl_2/hexane (1:1) and loaded onto a short column. Initial elution with CH_2Cl_2/hexane (1:1) removed some impurities, and a pure fraction of the product was eluted with CH_2Cl_2, which was removed to give a white solid. Yield 1.85 g (80%). Anal. Calcd for $C_{46}H_{32}N_6O_8P_4$: 60.01; H, 3.50; N, 9.13. Found:C, 60.30; H, 3.43; N, 8.87. ESMS *m*/*z* 921, $[MH^+]$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.3 to 4.5 ppm (m, 3P), −14.0 to −15.2 ppm (m, P). ^1H NMR ($CDCl_3$): δ 8.37 (m, 2H), 7.61 (m, 2H), 7.47 (m, 2H), 7.41 (m, 8H), 7.25 − 7.16 (m, 16H), 7.08 (m, 2H), 6.94 (m, 4H). ν/cm^{-1} (PN): 1238, 1190.

***trans*-Bis(2,2′-dioxybiphenyl)tetrakis(2-pyridyloxy)cyclotetraphosphazene (L^6).** To a solution of 2-hydroxypyridine (0.55 g, 5.80 mmol) in THF (50 mL), NaH (0.23 g of a 60% dispersion in oil, 5.80 mmol NaH) was added, and the mixture was stirred over 30 min. A cis/trans mixture of [N_4P_4(biph)$_2Cl_4$] (1.00 g, 1.45 mmol) was added, and the mixture was heated at reflux overnight. The cooled reaction mixture was taken to dryness and extracted with CH_2Cl_2. The extract was filtered through Celite and taken to dryness on a rotary evaporator to give a cis/trans mixture of [N_4P_4(biph)$_2$(OPy)$_4$]. Column chromatography of a sample of the crude material (approximately 0.5 g) on alumina using CH_2Cl_2 as eluent yielded a pure fraction of *trans*-[N_4P_4(biph)$_2$(OPy)$_4$] (0.23 g) that was dried under vacuum. Anal. Calcd for $C_{44}H_{32}N_8O_8P_4$: C, 57.15; H, 3.49; N, 12.12. Found: C, 57.27; H, 3.53; N, 12.12. ESMS: *m*/*z* 925 $[MH^+]$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.27 (t, 2P, $J_{PP} = 94$ Hz), −16.46 (t, 2P, 95 Hz). ^1H NMR ($CDCl_3$): δ 8.34 (m, 4H), 7.55 (m, 4H), 7.35 (m, 4H), 7.22 to 7.11 (m, 8H), 7.06 (m, 4H), 6.69 (m, 4H). ν/cm^{-1} (PN): 1238, 1213, 1188. Cis (in mixture); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 4.46 (m, 2P), −15.32 (m, 2P).

[CoL^1Cl_2]. L^1 (0.13 g, 0.18 mmol) and $CoCl_2$ (0.024 g, 0.183 mmol) were added to CH_2Cl_2 (40 mL), and the mixture was stirred overnight. A blue precipitate formed that was collected by filtration and heated to reflux in MeCN. Blue crystals were formed on cooling. Yield: 0.08 g (51%). Anal. Calcd for $C_{32}H_{24}Cl_2CoN_7O_6P_3$: C, 46.57; H, 2.93; N, 11.88. Found: C, 46.36; H, 2.98; N, 12.08. ESMS: *m*/*z* 789 $[CoL^1Cl]^+$. ν/cm^{-1} (PN): 1234, 1217, 1184.

[CoL^1Br_2]. L^1 (0.068 g, 0.098 mmol) and $CoBr_2$ (0.021 g, 0.096 mmol) were added to CH_2Cl_2 (10 mL), and the mixture was stirred overnight. The resulting dark-blue solution and precipitate were taken to dryness on a rotary evaporator, and the residue was heated at reflux in MeCN, from which dark-blue crystals formed on cooling. Yield: 0.04 g (50%). ESMS: *m*/*z* 832.95 $[CoL^1Br]^+$. Anal. Calcd for $C_{32}H_{24}Br_2CoN_7O_6P_3$: C, 42.04; H, 2.65; N, 10.72. Found: C, 41.89, H, 2.80, N, 10.68. ν/cm^{-1} (PN): 1233, 1216, 1202, 1183.

[CuL^1Cl_2]·MeCN·0.66C_6H_{12}. L^1 (0.101 g, 0.145 mmol) and $CuCl_2$ (0.019 g, 0.146 mmol) were added to CH_2Cl_2 (25 mL), and the mixture was stirred overnight. The resulting yellow/gold solution was filtered through a Celite pad, which was washed with CH_2Cl_2.

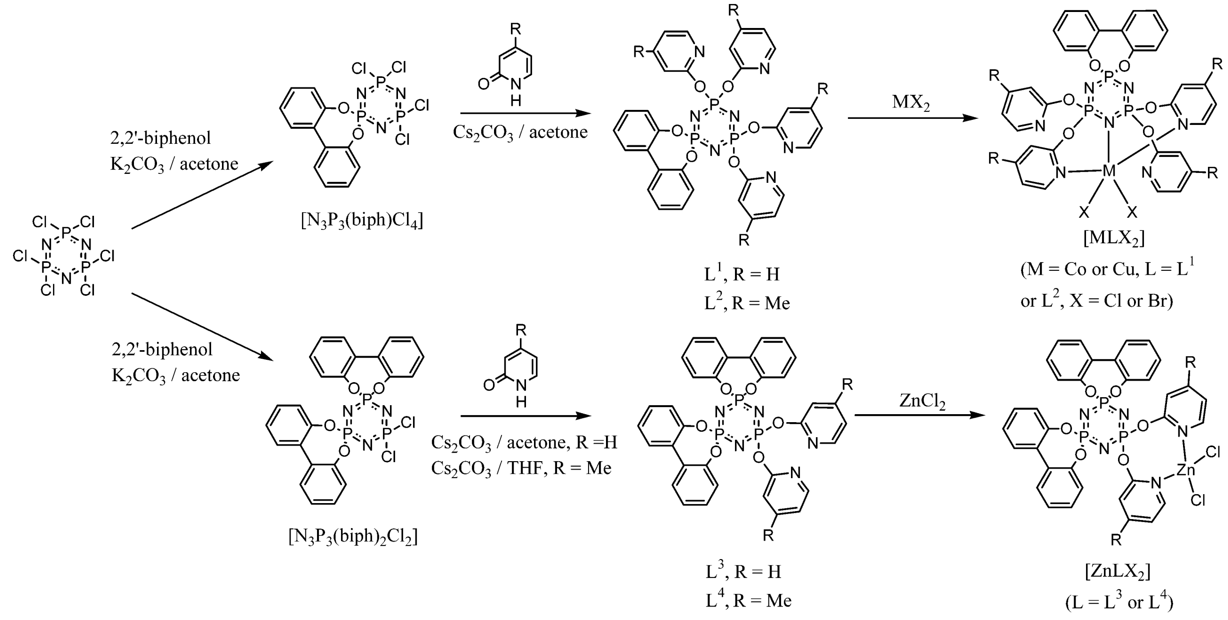
Table 1. Crystal and Refinement Data for the Complexes

compound	[Co$L^2$$Cl_2$]·1.27MeCN	[Co$L^2$$Br_2$]·1.21MeCN	[Cu$L^2$$Br_2$]·$CH_2Cl_2$	[{CoL^{2a}Cl}$_2$]·4MeCN
molecular formula	$C_{38.5}H_{35.75}Cl_2CoN_{8.25}O_6P_3$	$C_{38.5}H_{35.75}Br_2CoN_{8.25}O_6P_3$	$C_{37}H_{34}Br_2Cl_2CuN_7O_6P_3$	$C_{34}H_{32}ClCoN_8O_6P_3$
fw	932.74	1021.66	1059.88	835.97
T (K)	84(2)	84(2)	84(2)	273(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$
a (Å)	13.0331(1)	12.9529(2)	12.9284(2)	10.8684(15)
b (Å)	10.4670(1)	10.5835(2)	10.4443(2)	13.1852(19)
c (Å)	31.1040(1)	31.5286(1)	31.9761(4)	13.3977(19)
α (deg)				90.424(9)
β (deg)	95.424(1)	94.630(1)	94.128(1)	91.364(9)
γ (deg)				91.055(9)
V (Å^3)	4224.14(5)	4308.08(8)	4306.47(12)	1919.0(5)
Z	4	4	4	2
μ(Mo Kα) (mm^{-1})	0.702	2.420	2.651	0.696
ρ_{calcd} (g cm^{-3})	1.467	1.575	1.635	1.447
2θ max (deg)	50.70	50.70	50.70	50.70
no. of unique reflns	7705	7874	7872	7010
data/restraints/params	7705/0/557	7874/0/558	7872/0/527	7010/0/483
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0301$, $wR_2 = 0.0705$	$R_1 = 0.0312$, $wR_2 = 0.0620$	$R_1 = 0.0516$, $wR_2 = 0.1014$	$R_1 = 0.0677$, $wR_2 = 0.1451$
R indices (all data)	$R_1 = 0.0370$, $wR_2 = 0.0743$	$R_1 = 0.0419$, $wR_2 = 0.0657$	$R_1 = 0.0892$, $wR_2 = 0.1144$	$R_1 = 0.1577$, $wR_2 = 0.1776$
GOF on F^2	1.070	1.069	1.044	0.953
compound	[Zn$L^3$$Cl_2$]·MeCN·0.5$Et_2O$	[Zn$L^4$$Cl_2$]·2MeCN	[Hg$L^5$$Cl_2$]·$CH_2Cl_2$	[Cu$L^5$$Cl_2$]·MeCN·2.3$Et_2O$
molecular formula	$C_{38}H_{32}Cl_2N_6O_{6.5}P_3Zn$	$C_{40}H_{34}Cl_2N_7O_6P_3Zn$	$C_{47}H_{34}Cl_4HgN_6O_8P_4$	$C_{56.28}H_{58.2}Cl_2CuN_7O_{10.32}P_4$
fw	905.92	937.92	1277.07	1256.15
T (K)	150(2)	198(2)	150(2)	150(2)
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$	$Pca2(1)$
a (Å)	11.7837(2)	12.0491(4)	12.2715(1)	17.6846(8)
b (Å)	14.1371(3)	26.9266(9)	19.470(2)	13.7662(8)
c (Å)	14.4231(3)	13.3655(4)	20.5278(1)	22.0391(13)
α (deg)	109.944(1)			
β (deg)	95.733(1)	97.951(2)	90.194(1)	
γ (deg)	112.589(1)			
V (Å^3)	2010.34(7)	4294.6(2)	4924.00(7)	5365.4(5)
Z	2	4	4	4
μ(Mo Kα) (mm^{-1})	0.926	0.862	3.533	0.696
ρ_{calcd} (g cm^{-3})	1.496	1.451	1.723	1.555
2θ max (deg)	52.26	51.36	51.42	50.70
no. of unique reflns	7924	8152	9293	9818
data/restraints/params	7924/6/ 499	8152/18/547	9293/0/631	9818/49/643
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0276$, $wR_2 = 0.0731$	$R_1 = 0.0332$, $wR_2 = 0.0639$	$R_1 = 0.0244$, $wR_2 = 0.0610$	$R_1 = 0.0684$, $wR_2 = 0.1546$
R indices (all data)	$R_1 = 0.0333$, $wR_2 = 0.0759$	$R_1 = 0.0557$, $wR_2 = 0.0711$	$R = 0.0277$, $wR_2 = 0.0630$	$R_1 = 0.1011$, $wR_2 = 0.1689$
GOF on F^2	1.034	1.011	1.095	0.958
compound	[$Cu_2$$L^6$$Cl_2$]·$H_2O$·3.26$Et_2O$			
molecular formula	$C_{62}H_{74.6}Cl_4Cu_2N_8O_{12.26}P_4$			
molecular weight	1520.88			
T (K)	150(2)			
cryst syst	tetragonal			
space group	$I4(1)/a$			
a (Å)	23.6564(3)			
b (Å)	23.6564(3)			
c (Å)	24.3070(7)			
α (deg)				
β (deg)				
γ (deg)				
V (Å^3)	13 602.8(5)			
Z	10			
μ(Mo Kα) (mm^{-1})	1.178			
ρ_{calcd} (g cm^{-3})	1.856			
2θ max (deg)	50.70			
no. of unique reflns	6214			
data/restraints/params	6214/26/388			
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0510$, $wR_2 = 0.1608$			
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1655$			
GOF on F^2	1.116			

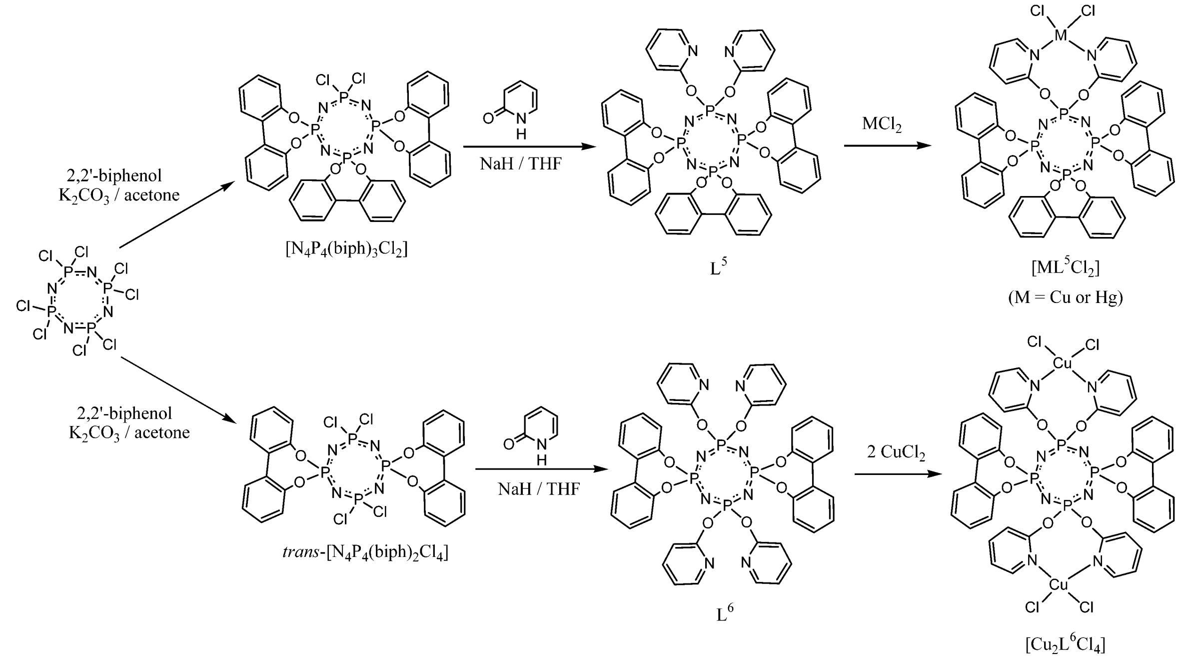
The combined filtrate was taken to dryness on a rotary evaporator to give a green solid. The solid was heated at reflux in MeCN, and on cooling, nucleation was initiated to give a green powder that was washed with hexane and dried under vacuum. Yield: 0.06 g (48%). Anal. Calcd for $C_{32}H_{24}Cl_2CuN_7O_6P_3$·0.66 C_6H_{14}·MeCN: C, 49.12; H, 4.01; N, 12.06. Found: C, 49.27; H, 3.17; N, 12.42. ESMS: m/z 793 [CuL^1Cl]$^+$, 758 [CuL^1]$^+$. ν/cm^{-1} (PN): 1238, 1217, 1190.

[Cu$L^1$$Br_2$]. L^1 (0.067 g, 0.095 mmol) and $CuBr_2$ (0.021 g, 0.094 mmol) were added to CH_2Cl_2 (10 mL), and the mixture was stirred

Scheme 1



Scheme 2



overnight. The resulting dark-green opaque solution was filtered through a Celite pad, which was washed with CH_2Cl_2. The volume of the combined filtrates was reduced to approximately 10 mL and layered with hexane. Small yellow crystals formed on standing at room temperature. Yield: 0.05 g (56%). Anal. Calcd for $C_{32}H_{24}Br_2CuN_7O_6P_3$: C, 41.83; H, 2.63; N, 10.67. Found: C, 41.71, H, 2.81, N, 10.57. ESMS: *m/z* 758 $[CuL^1]^+$. ν/cm^{-1} (PN): 1232, 1217, 1182.

$[CoL^2Cl_2]$. L^2 (0.066 g, 0.088 mmol) and $CoCl_2$ (0.013 g, 0.100 mmol) were added to 30 mL of CH_2Cl_2 and stirred overnight. The resulting pale-blue liquid remained clear throughout the reaction. A layer of hexane was added to the solution, and dark-blue crystals were obtained on standing. Yield: 0.04 g (46%). ESMS: *m/z* 845 $[CoL^2Cl]^+$. Anal. Calcd for $C_{36}H_{32}Cl_2CoN_7O_6P_3 \cdot CH_2Cl_2$: C, 45.99; H, 3.55; N, 10.15. Found: C, 46.43; H, 3.79; N, 10.08. ν/cm^{-1} (PN): 1233, 1218, 1195. When the decanted supernatant solution was allowed to stand over several months, a crop of X-ray-quality crystals formed from the hydrolyzed dimeric complex $[\{CoL^{2a}Cl\}_2] \cdot 4MeCN$ ($L^{2a} = [N_3P_3(biph)(OPy)_3(O)]^-$, OPy = 2-oxopyridine).

$[CoL^2Br_2]$. L^2 (0.103 g, 0.137 mmol) and $CoBr_2$ (0.030 g, 0.137 mmol) were added to CH_2Cl_2 (20 mL), and the mixture was stirred overnight. The resulting dark-blue solution was taken to dryness on a rotary evaporator, and the residue was heated at reflux in MeCN, from which X-ray-quality blue crystals formed on cooling. Yield: 0.05 g (42%). Anal. Calcd for $C_{36}H_{32}Br_2CoN_7O_6P_3 \cdot MeCN$: C, 45.13; H, 3.49; N, 11.08. Found: C, 45.08; H, 3.71; N, 10.76. ESMS: *m/z* 889 $[CoL^2Br]^+$. ν/cm^{-1} (PN): 1235, 1223, 1194.

$[CuL^2Cl_2]$. L^2 (0.048 g, 0.064 mmol) and $CuCl_2$ (0.009 g, 0.067 mmol) were added to CH_2Cl_2 (30 mL), and the mixture was stirred under N_2 overnight. A hexane layer was added to the yellow solution that formed. After 10 days of storage at room temperature, the solution had turned pale-green with the formation of microc-

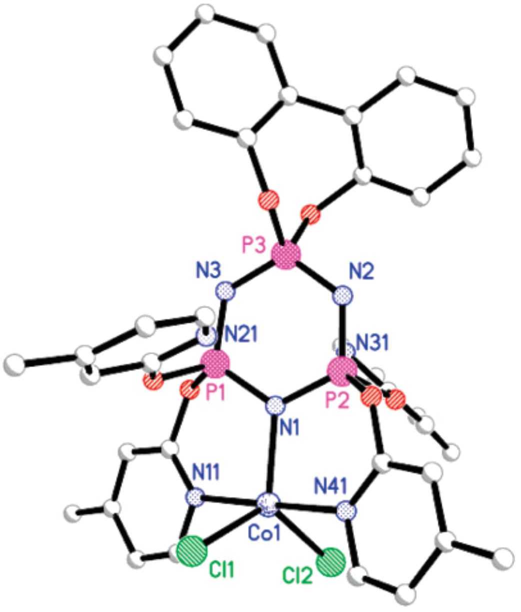


Figure 1. [CoL^{2}Cl$_2$] with hydrogen atoms removed.

rystals. The crystals were collected by filtration and washed with distilled water to remove any residual CuCl$_2$. Yield: 0.02 g (44%). Anal. Calcd for $C_{36}H_{32}Cl_2CuN_7O_6P_3 \cdot H_2O \cdot 0.33C_6H_{14}$: C, 48.86; H, 4.32; N, 10.50. Found: C, 48.90; H, 3.99; N, 10.57. ESMS: *m*/*z* 814 [CuL^2]$^+$, 849 [CuL^{2}Cl]$^+$. υ/cm^{-1} (PN): 1232, 1217, 1190, 1165.

[CuL^{2}Br$_2$]. L^2 (0.076 g, 0.102 mmol) and CuBr$_2$ (0.023 g, 0.103 mmol) were added to CH$_2$Cl$_2$ (30 mL), and the mixture was stirred overnight. The initial pale-yellow coloration developed into a clear yellow/green solution as the reaction progressed. The solution was reduced under vacuum to approximately 15 mL, and a layer of hexane was added. After 4 weeks of standing at 4 °C, fine yellow crystals of X-ray quality were formed (0.06 g, 58%). Anal. Calcd for $C_{36}H_{32}Br_2CuN_7O_6P_3 \cdot CH_2Cl_2$: C, 41.93; H, 3.23; N, 9.25. Found: C, 41.50; H, 3.43; N, 8.98. ESMS: *m*/*z* 814 [CuL^2]$^+$. υ/cm^{-1} (PN): 1233, 1218, 1191.

[ZnL^{3}Cl$_2$]·MeCN·0.5Et$_2$O. To a solution containing L^3 (0.1 g, 1.5 mmol) in CH$_2$Cl$_2$ (10 mL) was added ZnCl$_2$ (0.012 g, 1.5 mmol), and the mixture was stirred at room temperature. The CH$_2$Cl$_2$ was removed on a rotary evaporator, and vapor diffusion of Et$_2$O into a MeCN solution of the residue afforded a crystalline crop of the complex. Yield: 0.08 g (67%). Anal. Calcd for $C_{38}H_{32}Cl_2N_6O_{6.5}P_3Zn$:C, 50.38; H, 3.56; N, 9.28. Found: C, 50.45; H, 3.37: N, 9.47. ESMS: *m*/*z* 790, [ZnL^{3}Cl]$^+$. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 24.8 ppm (br d, 2P, $J_{PP} = 93$ Hz), 10.5 ppm (br t, P, $J_{PP} = 93$ Hz). ^{1}H NMR (CDCl$_3$): δ 8.61 (br m, 2H), 7.95 (br, m 2H), 7.53 (br m, 4H), 7.44−7.28 (br, m, 12H), 7.16 (br, m, 4H).

[ZnL^{4}Cl$_2$]·0.5MeCN. To a solution containing L^4 (0.408 g, 0.57 mmol) in CH$_2$Cl$_2$ (40 mL) was added ZnCl$_2$ (0.096 g, 0.70 mmol), and the mixture was stirred at room temperature. The mixture was filtered through Celite, and the filtrate was taken to dryness on a rotary evaporator. The residue was dissolved in hot MeCN, and a crystalline crop of the complex formed after standing over 2 weeks. Yield: 0.297 g (59%). Anal. Calcd for: $C_{37}H_{29.5}Cl_2N_{5.5}O_6P_3Zn$: C, 50.66; H, 3.37; N, 8.79. Found: C, 50.68; H, 3.56; N, 9.08. ESMS: not obtainable. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 24.1 ppm (br d, 2P, $J_{PP} = 93$ Hz), 11.0 ppm (br t, P, $J_{PP} = 94$ Hz). ^{1}H NMR (CDCl$_3$): δ 8.56 (br m, 2H), 7.54 (br, m 4H), 7.42 (br m, 4H), 7.35 (br, m, 4H), 7.25 (br, m, 8H) 7.20 (br, m, 2H), 2.49 (br, s, 6H). υ/cm^{-1} (PN): 1232, 1200, 1179.

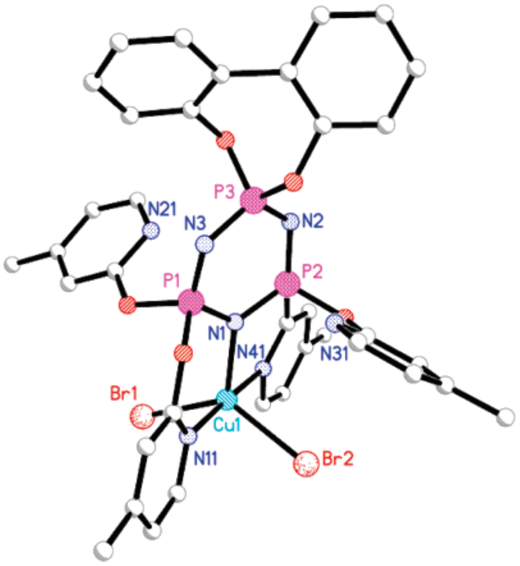


Figure 2. [CuL^{2}Br$_2$] with hydrogen atoms removed.

[HgL^{5}Cl$_2$]·CH$_2$Cl$_2$. To a solution containing L^5 (0.1 g, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) was added HgCl$_2$ (29 mg, 0.11 mmol), and the mixture was stirred at room temperature. The mixture was taken to dryness, and diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the residue afforded a pure crystalline crop of the complex. Yield: 0.07 g (54%). Anal. Calcd for: $C_{47}H_{34}Cl_4N_6O_8P_4Hg$:C, 44.20; H, 2.68; N, 6.58. Found: C, 44.78; H, 2.57; N, 6.57. ESMS: *m*/*z* 1157, [HgL^{5}Cl]$^+$. ^{31}P{^{1}H} NMR (CDCl$_3$): 7.9 to 6.7 ppm (m, 3P), −10.8 to −11.3 ppm (m, P). ^{1}H NMR (CDCl$_3$): δ 8.45 (m, 2H), 7.66 (m, 2H), 7.50 (m, 2H), 7.47 − 7.42 (m, 4H), 7.35 (m, 2H), 7.30 − 7.12 (m, 16H), 7.06 − 7.00 (m, 4H). υ/cm^{-1} (PN): 1237, 1189.

[CuL^{5}Cl$_2$]. To a solution containing L^5 (0.092 g, 0.1 mmol) in CH$_2$Cl$_2$ (25 mL) was added CuCl$_2$ (0.013 g, 0.1 mmol), and the mixture was stirred at room temperature over 2 h. The solution was filtered and taken to dryness on a rotary evaporator. The residue was dissolved into MeCN, and vapor diffusion of Et$_2$O into this solution produced a crop of crystalline material that was collected by filtration and dried under vacuum. Yield: 0.08 g (76%). Anal. Calcd for $C_{46}H_{32}Cl_2CuN_6O_8P_4$: C, 52.36; H, 3.06; N, 7.96. Found: C, 52.48; H, 3.19; N, 7.99. ESMS: *m*/*z* 983 [CuL^5]$^+$, 1018 [CuL^{5}Cl]$^+$. υ/cm^{-1} (PN): 1238, 1188.

[Cu$_2$L^{6}Cl$_4$]·2H$_2$O. To a solution containing L^6 (0.092 g, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL) was added CuCl$_2$ (0.026 g, 0.2 mmol), and the mixture was stirred at room temperature over 2 h. The solution was filtered and taken to dryness on a rotary evaporator. The residue was dissolved in MeCN, and vapor diffusion of Et$_2$O into this solution produced a crop of crystalline material that was collected by filtration and dried under vacuum. Yield: 0.067 g (54%). Anal. Calcd for $C_{48}H_{44}Cl_4Cu_2N_8O_{10}P_4$: C, 44.84; H, 3.45; N, 8.72. Found: C, 44.92; H, 3.22; N, 8.76. ESMS: *m*/*z* 1043 [CuL^7]$^+$, 1078 [CuL^{6}Cl]$^+$, 1143 [Cu$_2$L^{6}Cl]$^+$. υ/cm^{-1} (PN): 1246, 1190.

Crystallography. The X-ray data were collected on a Siemens P4 four-circle diffractometer, using a Siemens SMART 1K CCD area detector. The crystals were mounted in an inert oil and irradiated with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) X-rays. The data were collected by the *SMART* program and processed with *SAINT* to apply Lorentz and polarization corrections to the diffraction spots (integrated three dimensionally). Crystal data are given in Table 1. The structures were solved by direct methods

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Complexes of L^2

	$[CoL^2Cl_2]\cdot$ 1.27MeCN	$[CoL^2Br_2]\cdot$ 1.21MeCN	$[CuL^2Br_2]\cdot$ CH_2Cl_2
M−N1	2.0482(16)	2.044(2)	2.070(4)
M−N11	2.2064(17)	2.213(2)	2.087(4)
M−N41	2.2294(17)	2.239(2)	2.098(4)
M−X1	2.2765(5)	2.4171(4)	2.4653(8)
M−X2	2.2882(5)	2.4363(4)	2.4705(8)
N1−M−N41	89.79(6)	89.75(8)	90.19(16)
N1−M−N11	89.61(6)	89.70(8)	91.28(16)
N41−M−N11	178.55(6)	178.37(8)	178.00(17)
N1−M−X2	120.14(5)	116.40(6)	115.05(12)
N41−M−X2	89.70(4)	92.06(6)	88.95(12)
N11−M−X2	91.75(2)	89.54(6)	90.20(12)
N1−M−X1	116.38(5)	116.40(6)	117.54(12)
N41−M−X1	89.97(4)	89.00(6)	91.54(12)
N11−M−X1	89.11(4)	89.87(6)	88.98(12)
X2−M−X1	123.48(2)	123.296(17)	127.40(3)
P1−N1	1.6116(17)	1.607(2)	1.602(4)
P2−N1	1.6057(17)	1.616(2)	1.602(4)
P1−N3	1.5640(17)	1.557(2)	1.560(4)
P2−N2	1.5589(17)	1.561(2)	1.564(4)
P3−N2	1.5839(17)	1.581(2)	1.591(4)
P3−N3	1.5806(17)	1.585(2)	1.594(4)
P1−N1−P2	120.28(10)	120.13(13)	120.7(3)
P2−N2−P3	121.74(11)	121.73(14)	121.1(3)
P1−N3−P3	121.73(11)	121.85(14)	121.4(3)
N1−P1−N3	117.62(9)	117.97(12)	118.1(2)
N1−P2−N2	117.91(9)	117.60(12)	117.8(2)
N2−P3−N3	117.98(9)	117.94(12)	118.0(2)

and refined using the *SHELXTL* program.[24] Hydrogen atoms were calculated at ideal positions. The structure of $[CuL^5Cl_2]$ contained a well-defined MeCN molecule and disordered Et_2O molecules in the asymmetric unit. The contributions from the Et_2O molecules were removed using *PLATON/SQUEEZE*.[25] A total of 390 electrons/cell were removed, corresponding to 2.3 molecules of Et_2O, and 924.9 Å^3 were left by the void. The structure of $[Cu_2L^6Cl_4]$ was initially refined with one water molecule in the asymmetric unit disordered over three positions. Disorder in the spirocyclic biphenol ring was modeled in two orientations. This solution left solvent-accessible voids in the structure of 2691 Å^3 but with no significant peaks of residual electron density. When *PLATON/SQUEEZE* was applied to the data, electron density corresponding to 1369 electrons/cell was removed, leaving a void of 2791.3 Å.^{3}

Results and Discussion

Syntheses of Ligands and Complexes. The new ligands, L^1−L^6 (Schemes 1and 2), were prepared in good yield from the reaction of 2-hydroxypyridine or 4-methyl-2-hydroxypyridine with the appropriate spirocyclic-substituted precursor in the presence of base. The base-solvent systems used were Cs_2CO_3 in acetone or THF and NaH in THF. It is also possible to undertake the syntheses as one-pot processes by the stepwise addition of 2,2′-biphenol and hydroxypyridine derivatives to the chlorophosphazene precursors in the presence of a carbonate base. However, we found it preferable to perform the hydroxypyridine substitution on an isolated sample of the spirocyclic precursor, which avoids the formation of other spirocyclic derivatives and allows for easier purification of the final products.

We isolated the pyridyloxy derivative, L^6, from a cis/trans mixture (i.e., where the 2,2′-dioxybiphenyl substituents are either adjacent or opposite to each other on the phosphazene ring) of $[N_4P_4(biph)_2Cl_4]$ (biph = 2,2′-dioxybiphenyl)[11] by first treating it with the sodium salt of 2-hydroxypyridine, followed by purification using column chromatography on alumina. The *trans*-L^6 isomer was eluted with CH_2Cl_2, whereas the cis isomer could not be removed from the column (Experimental Section). A satisfactory separation was not achieved using silica or more-active alumina, where higher polarity solvent systems were required as eluents. It is possible that hydrolytic degradation of the cis isomer occurs on the alumina because we[5c,6b] (and vide infra) and others[26] have observed hydrolysis of cyclophosphazene derivatives containing 2-pyridyloxy or 2-oxy-1,10-phenanthroline pendant groups in the presence of Lewis acids such as metal ions.

Metal complexes of the ligands were obtained (Schemes 1 and 2) from their reaction with metal(II) halides in CH_2Cl_2, and their microanalyses, along with mass spectral and IR data, are given in the Experimental Section. The monosubstituted, 2,2′-dioxybiphenyl cyclotriphosphazene ligands, L^1 and L^2, form five-coordinate 1:1 adducts with copper(II) and cobalt(II) halides with pure samples of the complexes being obtained by recrystallization from hot MeCN or by layering CH_2Cl_2 solutions with hexane. Hydrolysis of the complex $[CoL^2Cl_2]$ after standing in MeCN solution over several months yielded the dimetallic species $[\{CoL^{2a}Cl\}_2]$ ($L^{2a} = [N_3P_3(biph)(OPy)_3(O)]^-$, OPy = 2-oxypyridine). The reactions of the disubstituted, 2,2′-dioxybiphenyl cyclotriphosphazene ligands, L^3 and L^4, with $ZnCl_2$ produced four-coordinate 1:1 adducts with crystalline materials being obtained from vapor diffusion of Et_2O into MeCN solutions of the complexes. We attempted to prepare copper(II) and cobalt(II) complexes of L^3 and L^4 in a similar manner but were unable to characterize the products satisfactorily or obtain crystals suitable for diffraction experiments. Four-coordinate mercury(II) and copper(II) adducts of 1:1 stoichiometry were obtained with the trisubstituted 2,2′-dioxybiphenyl cyclotetraphosphazene ligand, L^5, and a dimetallic species, $[Cu_2L^6Cl_4]$, was obtained from the reaction of two equiv of $CuCl_2$ with the *trans*-disubstituted 2,2′-dioxybiphenyl cyclotetraphosphazene ligand, L^6. Typically, the positive-ion electrospray mass spectra of the complexes showed the loss of a halide ion with peaks assignable to $[MLX]^+$ ions being observed. In the case of the dimetallic complex, $[Cu_2L^6Cl_4]$, less intense peaks corresponding to $[Cu_2L^6Cl]^+$ ions, are also seen. As expected,[5a] very strong P−N phosphazene ring stretching absorptions are seen in the IR in the 1150−1250 cm^{-1} region.

Crystallography. The Five-Coordinate Complexes of L^2. X-ray-quality crystals were obtained by MeCN/Et_2O vapor diffusion for the complex cyclotriphosphazene complexes, $[CoL^2Cl_2]$ (Figure 1) and $[CoL^2Br_2]$. The crystals are isomorphous, and the structures were refined with one complete and one fractional MeCN molecule in the asym-

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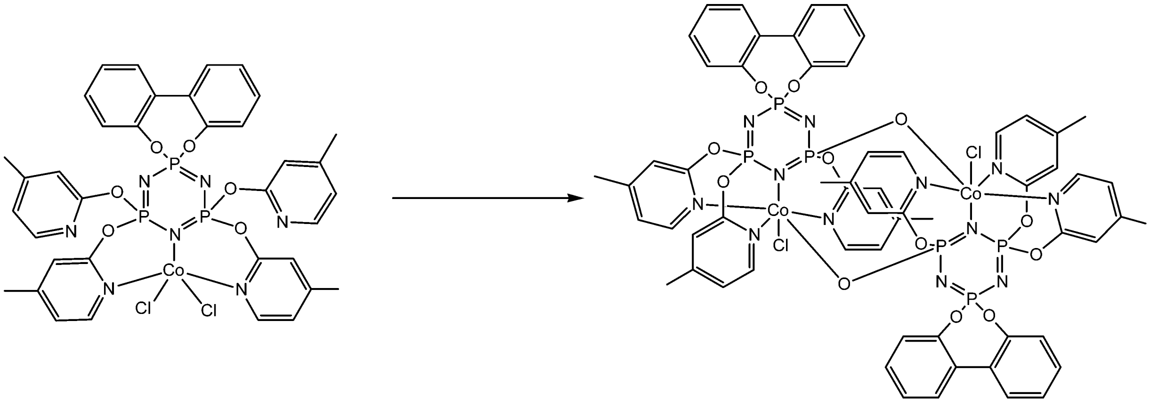
[24] Sheldrick, G. M. *SHELXL, Suite of Programs for Crystal Structure Analysis*; Institüt für Anorganische Chemie der Universität: Göttingen, Tammanstrasse 4, Germany, 1998.

[25] Van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

[26] Chandrasekhar, V.; Pandian, B. M.; Azhakar, R. *Inorg. Chem.* **2006**, *45*, 3510−3518.

Scheme 3



metric unit (0.27 and 0.21 occupancy in [CoL^2Cl_2] and [CoL^2Br_2], respectively). Crystals of the [CuL^2Br_2] (Figure 2) complex were grown from CH_2Cl_2/hexane solution, and the complex crystallizes with one molecule of CH_2Cl_2 in the asymmetric unit. In all of complexes, the metal(II) ions are in similar five-coordinate trigonal-bipyramidal N_3Cl_2 environments. The ligand coordinates in a nongeminal trans fashion, using a phosphazene ring nitrogen atom and nitrogen atoms from the pyridine arms of different phosphorus atoms approaching from opposite sides of the phosphazene ring. The pyridine nitrogens are axial, and the phosphazene nitrogen and halide ions are equatorial. Selected bond lengths and angles are given in Table 2.

For both cobalt(II) complexes, the equatorial $Co-N_{phosphazene}$ distances are similar [2.0482(16) and 2.044(2) Å for the chloro and bromo adducts respectively] and significantly shorter than the axial $Co-N_{pyridine}$ distances [ranging between 2.2064(17) and 2.239(2) Å]. The coordination environment differs slightly in the copper(II) complex where the equatorial $Cu-N_{phosphazene}$ bond length [2.070(4) Å] is similar to the axial $Cu-N_{pyridine}$ bond lengths [2.087(4) and 2.098(4) Å]. The structural index[27] τ is 0.92 for [CoL^2Cl_2], 0.84 [CoL^2Br_2], and 0.84 for [CuL^2Br_2], indicating only slight distortions from regular trigonal-bipyramidal geometry in all of the cases. In agreement with this is the fact that the angle at the metal between the axial $M-N_{pyridine}$ bonds is close to 180 ° [178.00(17) to 178.55(6) °] for all three complexes.

As pointed out above, the coordination environments for the two metals in [CoL^2Br_2] and [CuL^2Br_2] are slightly different. However, the complexes crystallize in the same space group ($P2_1/c$) with very similar cell dimensions (Table 1) and are isomorphous (although the occluded solvent molecules are different in each case). Thus, the molecular packing arrangements and intermolecular contacts are the same. Whereas the L^2 phosphazene ligand imposes a trigonal-bipyramidal geometry on the metal halides, it is sufficiently flexible to allow the differences in the electronic configurations to influence the differences between the axial and equatorial bond distances. It should be noted that such pairs of cobalt(II) and copper(II) complexes are rare, although the tris(2-dimethylaminoethyl)amine complexes (Me_6tren) [M(Me_6tren)Br]Br (M = Co and Cu) are isomorphous (space group $P2_13$) with the metal in a trigonal-bipyramidal environment. For this pair, the axial Co−N distance [2.15(2) Å] is also greater than the equatorial distances [2.08(2) Å], and the two analogous Cu−N distances are not significantly different [2.10(1) and 2.13(1) Å, respectively].[28a,b] A tridentate, nitrogen-donor ligand, which furnishes a similar stereochemical requirement to the ligands, L^1 and L^2, as found in the above cyclotriphosphazene trigonal-bipyramidal complexes is tripyridinedimethane (tpdm). Its copper(II) complex, [Cu(tppm)Cl_2], also exhibits similar axial and equatorial Cu−N bond distances [2.0338(18)−2.0730(17) Å].[28c]

The structures of the cobalt complexes are comparable with [$CoLBr_2$] [L = hexakis(2-pyridyloxy)cyclotriphosphazene], which exhibits a similar five-coordinate geometry[5d] that arises from an identical, nongeminal trans ligand binding mode. However, the $Co-N_{phosphazene}$ bond lengths in [CoL^2Cl_2] and [CoL^2Br_2] are significantly shorter [2.0482(16) and 2.044(2) Å] than the $Co-N_{phosphazene}$ bond length in [Co(MeL)Br_2] (MeL = hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene) of 2.0895(19) Å. This is consistent with the larger displacement of the cobalt(II) ion from the mean plane of the phosphazene ring in [Co(MeL)Br_2], which is 0.812 Å compared to [CoL^2Cl_2] and [CoL^2Br_2], where the out-of-plane displacements of the metal ions are minimal at 0.0412 and 0.0494 Å, respectively. There is also a difference between the copper(II) coordination observed in the [$CuLCl_2$] complex[5b] and [CuL^2Br_2]. In [$CuLCl_2$], the preference is for nongeminal cis coordination (where the coordinated pyridine arms on different phosphorus atoms approach from the same side of the phosphazene ring), which results in long $Cu-N_{phosphazene}$ bonds of 2.264(2) Å because the metal is held 1.180 Å out from the mean plane of the phosphazene ring. The nongeminal trans mode observed in [CuL^2Br_2] allows the closer metal-phosphazene approach of 2.070(4) Å.

In all three of the new complexes, the phosphazene rings remain essentially planar, and the bond angles in the rings are typical. The P−N distances in the ring show the expected[5] trends caused by coordination of a metal ion to a phosphazene ring nitrogen. Hence, the P−N bonds P1−N1 and

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[27] Addison, A. W.; Rao T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

[28] (a) di Vaira, M.; Orioli, P. L. *Inorg. Chem.* **1967**, *6*, 955−957. (b) di Vaira, M. *Acta Crystallogr.* **1968**, *B24*, 595−599. (c) Vedernikov, A. N.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2002**, *41*, 6244−6248.

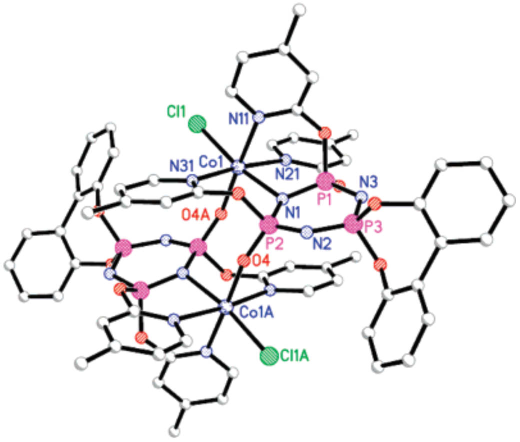

Figure 3. [{CoL^{2a}Cl}$_2$] with hydrogen atoms removed.

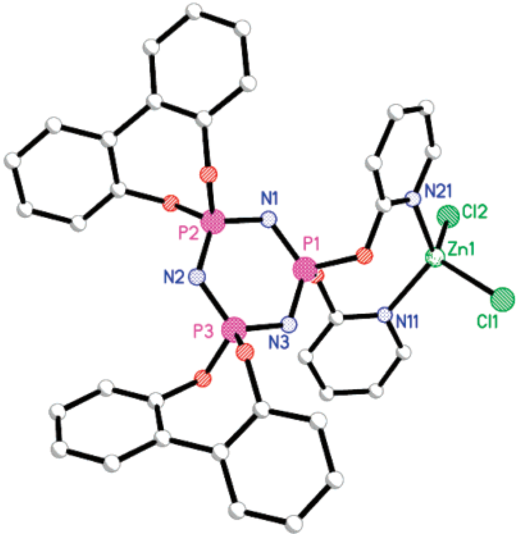

Figure 4. [ZnL^{3}Cl$_2$] with hydrogen atoms removed.

P2−N1 that flank the metal-bound N1 are in general slightly longer [in the range 1.602(4)−1.616(2) Å] than the other P−N bonds in the rings [in the range 1.594(4)−1.5589(17) Å].

The [CoL^{2}Cl$_2$] Hydrolysis Product. X-ray-quality crystals of the centrosymmetric complex [{CoL^{2a}Cl}]$_2$·4MeCN (Scheme 3 and Figure 3) were deposited from a MeCN solution containing [CoL^{2}Cl$_2$]. In this complex, the ligand L^2 has been slowly hydrolyzed and is monoanionic following the loss of a pendant pyridine arm (Scheme 3). The ligand coordinates to one cobalt(II) center in a tetradentate manner through the remaining three pyridyl arms and a phosphazene ring nitrogen. The remaining phosphazenate oxygen atom coordinates to the second, symmetry-related, cobalt(II) ion in the molecule. A monodentate chloride anion occupies the sixth coordination site, and, hence, the cobalt(II) centers have N$_4$OCl donor sets. Selected bond lengths and angles are given in Table 3.

The closest cobalt-ligand contact in the molecule is 2.035(4) Å for the bond Co−O4. The Co−N$_{\text{pyridine}}$ bonds vary between 2.206(5) and 2.408(5) Å, the shortest being for Co−N11, which is trans to the Co−O bond. The shortest Co−N contact in the molecule [2.150(5) Å] is made to the phosphazene ring and is trans to the coordinated chloride ion. The geometry about the cobalt centers is approximately octahedral, with interligand angles ranging from 170.36(14) to 175.52(18)° between the trans donors and from 82.74(18) to 95.47(18) ° between the cis donors.

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for [{CoL^{2a}Cl}$_2$]·4MeCN

Co1−N11	2.206(5)	Co1−N1	2.150(5)
Co1−N21	2.408(5)	Co1−O4#	2.035(4)
Co1−N31	2.223(5)	Co1−Cl1	2.3901(17)
P1−N1	1.594(5)	P2−N2	1.603(5)
P1−N3	1.572(5)	P3−N2	1.572(5)
P2−N1	1.646(5)	P3−N3	1.594(5)
N1−Co1−N11	82.74(18)	N31−Co1−Cl1	92.00(14)
N1−Co1−N31	91.48(18)	N21−Co1−O4	86.76(17)
N11−Co1−N31	88.81(19)	N1−Co1−N21	85.73(18)
N1−Co1−O4	93.58(17)	N11−Co1−N21	95.47(18)
N31−Co1−O4	88.74(17)	N11−Co1−N11	175.52(18)
O4−Co1−Cl1	95.48(12)	N1−Co1−Cl1	170.36(14)
N11−Co1−Cl1	88.35(14)	N31−Co1−N21	174.55(17)
N21−Co1−Cl1	91.49(13)		
P1−N1−P2	123.3(3)	N1−P1−N3	118.1(3)
P1−N3−P3	120.4(3)	N1−P2−N2	112.2(3)
P2−N2−P3	124.9(3)	N2−P3−N3	118.1(3)

The phosphazene ring remains reasonably flat (the mean deviation of the ring atoms from their mean plane is 0.0724 Å, with the largest being 0.1110 Å) and PNP and NPN angles within the ring lie in the usual ranges. The P−N bond lengths show some variation, lying between 1.572(5) and 1.646(5) Å with the longest being P2−N1, the bond between the phosphazenate phosphorus atom and the coordinated ring nitrogen. The bond P2−O4 of the phosphazenate ligand is considerably shorter [1.488(4) Å] than the other P−O bonds in the molecule [between 1.595(4) and 1.633(4) Å]. Similar trends have been reported in two structures containing related hydrolyzed phosphazene ligand systems.[6a,26]

Four-Coordinate Complexes of L^3, L^4, L^5, and L^6. The X-ray structures of the disubstituted, 2,2′-dioxybiphenyl cyclotriphosphazene ligand complexes [ZnL^{3}Cl$_2$] (Figure 4) and [ZnL^{4}Cl$_2$] exhibit essentially the same distorted-tetrahedral zinc(II) coordination geometries. The zinc(II) centers have N$_2$Cl$_2$ donor sets with both nitrogen ligands arising from the geminally substituted pyridine arms. The ligands form eight-membered bidentate rings with bite angles of 117.75(5) and 117.27(8)° respectively for L^1 and L^2. These angles are slightly larger than the N−Zn−N angle [106.3(2) °] observed in [Zn(py)$_2$Cl$_2$] (py = pyridine) and similar to the four-coordinate zinc(II) moiety observed in [(ZnCl$_2$)$_2$L] (L = hexakis(2-pyridyloxy)cyclotriphosphazene).[5d] The Cl−Zn−Cl angles are similar at 117.66(2) and 117.42(3)° respectively for [ZnL^{3}Cl$_2$] and [ZnL^{4}Cl$_2$], whereas the other angles in the coordination sphere are closer to a regular tetrahedral geometry, varying between 100.05(6) and 109.73(4)°. The Zn−N bond lengths in the complexes are similar and vary in the range of 2.051(2) to 2.076(2) Å. Selected bonds and angles for both complexes are given in Table 4.

X-ray-quality crystals of the tris(2,2′-dioxybiphenyl)-cyclotetraphosphazene ligand complexes, [HgL^{5}Cl$_2$]·CH$_2$Cl$_2$ and [CuL^{5}Cl$_2$]·MeCN·2.3Et$_2$O were obtained from CH$_2$Cl$_2$/hexane and MeCN/Et$_2$O solvent systems, respectively. In both structures (Figure 5), the ligands bind in a manner comparable to L^3 and L^4 in the zinc complexes described

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for the Zinc(II) Complexes

	$[ZnL^3Cl_2]\cdot MeCN\cdot 0.5Et_2O$	$[ZnL^4Cl_2]\cdot 2MeCN$
Zn1−N11	2.7037(15)	2.051(2)
Zn1−N21	2.0628(14)	2.076(2)
Zn1−Cl1	2.2288(5)	2.2320(7)
Zn1−Cl2	2.2213(5)	2.2592(7)
P1−N1	1.5653(14)	1.577(2)
P1−N3	1.5636(14)	1.5765(19)
P2−N1	1.5800(14)	1.589(2)
P2−N2	1.5728(15)	1.5848(19)
P3−N2	1.5750(14)	1.581(2)
P3−N3	1.5822(14)	1.593(2)
N11−Zn1−N21	117.75(5)	117.27(8)
N21−Zn1−Cl2	102.47(4)	100.05(6)
N11−Zn1−Cl2	109.73(4)	108.59(6)
N21−Zn1−Cl1	108.21(4)	105.96(6)
N11−Zn1−Cl1	101.77(4)	107.86(6)
Cl1−Zn1−Cl2	117.66(2)	117.42(3)
N1−P1−N3	121.33(8)	120.65(11)
N1−P2−N2	117.84(7)	117.72(10)
N2−P3−N3	118.34(8)	118.01(10)
P1−N1−P2	120.26(9)	120.54(12)
P2−N2−P3	122.52(9)	122.82(13)
P1−N3−P3	119.64(9)	120.12(13)

above. The mercury(II) and copper(II) ions are both four-coordinate, bound in a bidentate manner by the geminally substituted pyridyl arms to form an eight-membered chelate ring. Selected bond lengths and angles are given for both complexes in Table 5.

In $[HgL^5Cl_2]$, the mercury(II) ion lies in a distorted-tetrahedral environment with Cl1−Hg−Cl2 and N11−Hg−N21 angles of 141.04(3) and 110.70(8)°, respectively. The ligand bite angle here is similar to that previously reported in the $HgCl_2$ adduct of a thio-bridged bis-pyridyl ligand that also forms an eight-membered ring.[29] Both of the Hg−N bond lengths in the molecule are similar [2.406(2) and 2.419(3) Å] as are both Hg−Cl distances [2.3655(8) and 2.343(8) Å], and packing in the crystal is such that the $HgCl_2$ moieties are isolated from one another.

The copper(II) center in $[CuL^5Cl_2]$ shows considerable distortion toward tetrahedral geometry from the square-planar geometry that normally is preferable for the stereoelectronic requirements of copper(II) with this donor set. The N−Cu−N [134.8(3)°] and Cl−Cu−Cl [137.29(9)°] angles are approximately half way between those required for regular cis or trans geometries. The other interligand angles lie between 95.75(19) and 101.79(18)°, and the dihedral angle between the N11−Cu−N21 and Cl1−Cu−Cl2 bonding planes is 88°. The Cu−N bond lengths [1.972(6) and 2.004(5) Å] and Cu−Cl bond lengths [both 2.210(2) Å] are typical.

The solid-state structures of $[HgL^5Cl_2]$ and $[CuL^5Cl_2]$ contain phosphazene rings with remarkably similar configurations, given that the packing motifs in the crystals are quite different. The spirocyclic 2,2′-dioxybiphenyl groups on opposite sides of the phosphazene rings in both cases have opposite (RS) configurations, and the phosphazene rings are irregularly puckered. However, the rings have comparable sets of P−N−P−N torsion angles with similar magnitudes (34.2 and 20.2, 56.9 and 70.1, 5.3 and 1.6, 85.3 and 87.0°), and the same is true of the N−P−N−P torsion angles (33.9 and 37.8, 85.5 and 83.7, 17.6 and 21.9, 46.3 and 54.0°). Comparable pairs of PNP angles (which generally deviate over a wider range than the NPN angles in cyclophosphazene tetramers) are also similar, viz. 123.92 and 124.16, 140.64 and 144.74, 136.44 and 133.65, 139.22 and 141.25. These data suggest that a certain amount of rigidity may be imparted on the phosphazene ring configuration with the presence of four spirocyclic moieties, in contrast to the conformational flexibility we observed in $[N_4P_4(biph)_2Cl_4]$ or $[N_4P_4(biph)_3Cl_2]$.[11]

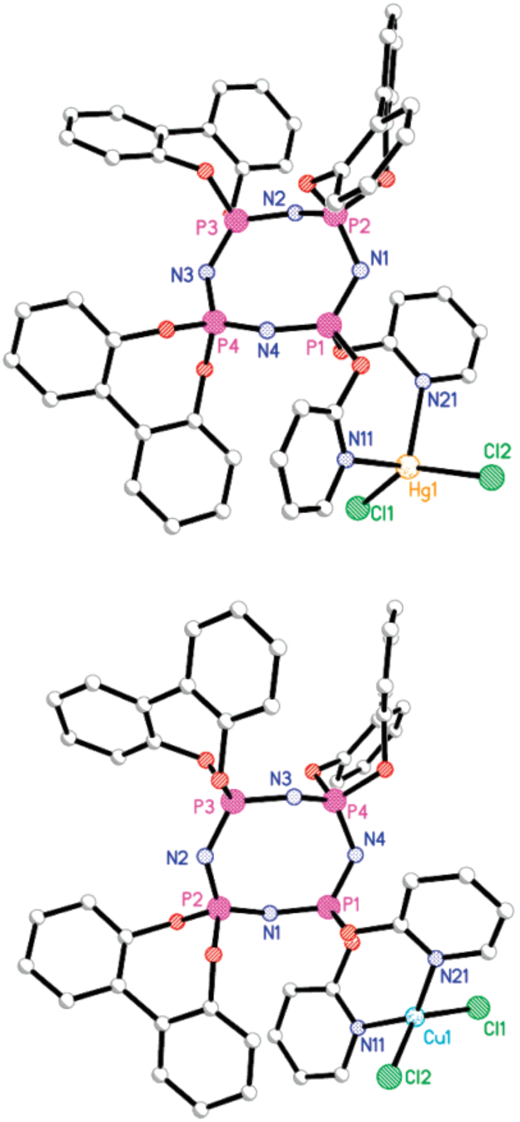

Figure 5. $[HgL^5Cl_2]$ and $[CuL^5Cl_2]$ with hydrogen atoms removed.

X-ray-quality crystals of the dimetallic complex, $[Cu_2L^6Cl_4]$, were grown from vapor diffusion of Et_2O into a solution of the complex dissolved in MeCN. In this complex (Figure 6), the ligand bridges two symmetry-related $CuCl_2$ centers, coordinating to each one via a set of geminal pyridine arms in a bidentate manner similar to that observed in $[CuL^5Cl_2]$. Selected bond lengths and angles are given in Table 5.

Tetrahedral distortion of the copper(II) center is also apparent in this complex. The N−Cu−N angle is 137.07(12)°, and the Cl−Cu−Cl angle is 137.73(4)°. The other

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(29) Berry, S. M.; Bebout, D. C.; Butcher, R. J. *Inorg. Chem.* **2005**, *44*, 27−39.

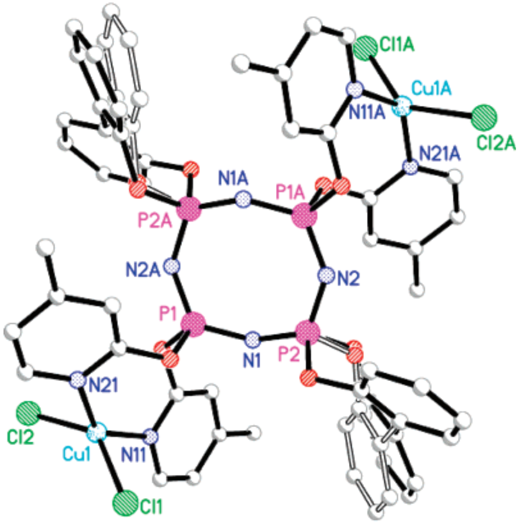

Figure 6. $[Cu_2L^6Cl_4]$ with hydrogen atoms removed.

Table 5. Selected Bond Lengths (Angstroms) and Angles (Degrees) for the Cyclotetraphosphazene Complexes

	$[HgL^5Cl_2]\cdot CH_2Cl_2$	$[CuL^5Cl_2]\cdot MeCN\cdot 2.3Et_2O$	$[Cu_2L^6Cl_4]\cdot H_2O\cdot 3.26Et_2O$
M−N11	2.406(2)	1.972(6)	1.993(3)
M−N21	2.419(3)	2.004(5)	2.006(4)
M−Cl1	2.3655(8)	2.210(2)	2.2108(11)
M−Cl2	2.3743(8)	2.210(2)	2.2089(10)
N1−P1	1.567(2)	1.549(6)	1.550(3)
N1−P2	1.577(2)	1.563(5)	1.566(3)
N2−P2	1.558(2)	1.564(6)	1.559(3)
N2−P3	1.562(2)	1.559(6)	
N3−P3	1.566(2)	1.577(6)	
N3−P4	1.565(2)	1.533(6)	
N4−P4	1.562(2)	1.585(6)	
N4−P1	1.553(2)	1.570(6)	
N2#−P1			1.551(3)
N11−M−N21	110.70(8)	134.8(3)	137.07(12)
N11−M−Cl1	103.84(6)	101.79(18)	97.87(10)
N11−M−Cl2	97.65(6)	95.75(19)	98.17(9)
N21−M−Cl1	103.10(6)	96.54(18)	98.24(11)
N21−M−Cl2	99.02(6)	98.0(2)	96.03(10)
Cl1−M−Cl2	141.04(3)	137.29(9)	137.74(4)
N1−P2−N2	118.52(13)	121.0(3)	120.71(4)
N2−P3−N3	121.76(13)	120.4(3)	
N3−P4−N4	121.13(12)	118.7(3)	
N1−P1−N4	122.58(13)	122.7(3)	
P1−N1−P2	123.92(15)	141.2(4)	136.9(2)
P2−N2−P3	140.64(17)	133.7(4)	
P3−N3−P4	136.44(16)	144.7(4)	
P4−N4−P1	139.22(17)	124.2(3)	
N1−P1−N2#			124.91(15)
P1#−N2−P2			139.56(18)

interligand angles range between 96.03(10) and 98.24(11)°, and the dihedral angle between the Cl−Cu−Cl and N−Cu−N bonding planes is 90.7°. The Cu−N bond lengths [1.993(3) and 2.006(4) Å] and Cu−Cl bond lengths [2.108(11) and 2.089(10) Å] are similar to those in $[CuL^5Cl_2]$.

The phosphazene ring has a chair configuration with P1, P2, N2, and symmetry equivalents being nearly planar (the rms deviation of the atoms from a mean plane is 0.0455 Å), and N1 and its symmetry equivalent lie 0.4272 Å above and below this plane. The NPN angles in the ring are 120.71(14) and 124.91(15)°, and the PNP angles are 136.9(2) and 139.56(18)°. The P−N bonds lie between 1.550(3) and 1.566(3) and are in the usual range.

Table 6. ESR Spectral Parameters for the Copper Complexes

complex	$g_{\|}$	$A_{\|}$ (10^{-4}cm^{-1})	$g_{\perp}$
$[CuL^1Cl_2]^a$	2.26	165	2.09
$[CuL^1Br_2]^a$	2.29	167	2.12
$[CuL^2Cl_2]^a$	2.27	165	2.10
$[CuL^2Br_2]^a$	2.29	163	2.12
$[CuL^5Cl_2]^b$	2.28	163	2.07
$[Cu_2L^6Cl_4]^b$	2.42	134	2.08

[a] In CH_2Cl_2. [b] In $MeNO_2$.

Table 7. Magnetic Moments and Electronic Spectral Data

		λ_{max}/nm	
complex	μ_B	solution[a]	solid[b]
$[CoL^1Cl_2]$	4.48	[c]	588, 850
$[CoL^1Br_2]$	4.55	698 (176), 632 (117), 618 (131)[d]	588, 850
$[CoL^2Cl_2]$	4.26	684 (185), 588 (160)[d]	534 (sh), 585, 664, 900
$[CoL^2Br_2]$	4.24	699 (196), 633 (133), 618 (147)[d]	544 (sh), 584, 626, 900
$[CuL^1Cl_2]$	2.15	876 (104)[e]	800
$[CuL^1Br_2]$	2.22	981 (218), 652 (90)[e]	1150
$[CuL^2Cl_2]$	2.29	895 (116)[e]	848
$[CuL^2Br_2]$	2.03	938 (200), 650 (58) (sh)[e]	1120
$[CuL^5Cl_2]$		814 (75)[f]	818
$[Cu_2L^6Cl_4]$		808 (98)[f]	810

[a] Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) in parenthesis. [b] As nujol mulls. [c] Insoluble. [d] In MeCN. [e] In CH_2Cl_2. [f] In $MeNO_2$.

Physicochemical Measurements. X-band ESR spectra of the five-coordinate copper halide complexes with L^1 and L^2, which were recorded in CH_2Cl_2 at 113 K (Table 6), are typical for species having mononuclear axial symmetry with a $d_{x^2-y^2}$ ground state.[30] The data are consistent with a square-pyramidal geometry, suggesting that the compounds are all exhibiting neutral complex distortion isomerism, with the room temperature solid-state structure being trigonal bipyramidal. Absorptions at the half-field values around 1500 G ($\Delta M_s = \pm 2$), were not observed, which is consistent with the absence of magnetically interacting dimeric species. The cyclotetraphosphazene complexes were insoluble in CH_2Cl_2 and so were recorded in frozen CH_3NO_2 solutions. The ESR spectrum of the dimetallic complex, $[Cu_2L^6Cl_4]$, was typical of a monomeric axial copper(II) complex with a $d_{x^2-y^2}$ ground state with $g_{\|} > g_{\perp}$ ($g_{\perp}$ 2.08, $g_{\|} = 2.42$, $A_{\|} = 134 \times 10^{-4}$ cm^{-1}). The $g_{\|}/A_{\|}$ ratio at 180 points to the copper ions having a distorted-tetrahedral geometry.[31] However, the spectrum of $[CuL^5Cl_2]$ in the same solvent displayed $g_{\perp}$ at 2.07 and $g_{\|}$ at 2.28 with $A_{\|} = 163 \times 10^{-4}$ cm^{-1}, again consistent with a $d_{x^2-y^2}$ ground state, but suggesting a more geometrically relaxed structure, which possibly implies one that is approximately square planar or a distorted five-coordinate with a weak-field $N_2Cl_2(Y)$ donor set with Y as a solvent molecule.

The room-temperature magnetic moments for the complexes are presented in Table 7. For the trigonal-bipyramidal cobalt(II) complexes with L^1 and L^2 the magnetic moments lie in the range 4.24 − 4.55 μ_B as expected for high spin

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(30) Hathaway, B. J. In *Comprehensive Coordination Chemistry*, *First Edition*; Wilkinson, G., Ed.; Paragon Press: New York, 1987; Vol. 5, 662−663.

(31) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600−608.

complexes with this stereochemistry[30,32] The magnetic moments of the analogous five-coordinate copper complexes (2.03 − 2.29 μ_B) are also as expected.[30]

The room-temperature electronic spectra (nujol mull transmittance) for the cobalt complexes (Table 7), display *d*−*d* bands in the 850−900 nm and 588−657 nm regions, consistent with a trigonal-bipyramidal structure, as found by X-ray crystallography.[30,32] However, in MeCN or CH_2Cl_2 the solutions become a more-intense blue color and exhibit d−d absorptions at about 698, 632, and 618 nm, with high extinction coefficients, which are indicative of a distorted-tetrahedral stereochemistry for cobalt(II). Each of the complexes, [CuL^1Cl_2] and [CuL^2Cl_2], displays a broad d−d band around 800−850 nm, which tails into the infrared, whereas [CuL^1Br_2] and [CuL^2Br_2] have similar bands at lower energy, centered at 1150 or 1120 nm, respectively. These spectra are consistent with copper having a trigonal-bipyramidal arrangement of ligands.[32] The absorption spectra of CH_3NO_2 solutions of [CuL^5Cl_2] and [$Cu_2L^6Cl_4$] are essentially identical with the nujol mull transmittance spectra of the solid samples, implying that the distorted-tetrahedral structure for each copper as found by single-crystal X-ray crystallography is retained in this solvent at room temperature. The compounds display broad d−d absorption bands at about 800 nm, which tail toward the infrared typical of reported spectra for this geometry.[33]

Conclusion

Conformational Rigidity of the Chelate Rings. The substitution of cyclotriphosphazenes and cyclotetraphosphazenes with spirocyclic 2,2′-dioxybiphenyl groups in conjunction with 2-pyridyloxy pendant donors allows the tuning of the metal coordination sphere. Hence, the monosubstituted, 2,2′-dioxybiphenyl tricyclophosphazene ligands, L^1 and L^2, form five-coordinate 1:1 adducts with copper(II) and cobalt(II) halides. The L^1 and L^2 ligands bind in a tridentate mode by involving the phosphazene ring nitrogen and two pyridyloxy arms from flanking phosphazene phosphorus atoms. The two halide ions complete the coordination sphere. Six-membered rings are formed with the metal bite angle being relaxed at about 90°, thus giving rise to a preferred geometry around the metal in each case of trigonal bipyramidal in the solid state. However, in CH_3CN solution, the five-coordinate cobalt(II) complexes, [CoL^1X_2] and [CoL^2X_2] (X = Cl, Br), appear to dissociate one of the nitrogen donors from the metal, hence forming a tetrahedral species similar to that found for the zinc(II) complexes, [ZnL^3Cl_2] and [ZnL^4Cl_2].

The disubstituted, 2,2′-dioxybiphenyl cyclotriphosphazene ligands, L^3 and L^4, and the cyclotetraphosphazene ligands, L^5 and L^6, all only have two pyridine nitrogen donor atoms, which arise from the geminally substituted pyridine arms. Because the phosphazene ring nitrogen does not participate in the metal coordination sphere in these complexes, the ligands act in a bidentate mode. Eight-membered chelate rings with the N−Zn−N angle being about 117° for the L^3 and L^4 zinc complexes result. The corresponding angle for mercury with L^5 is 110.70(8)°, and for copper with L^5 and L^6 the angles are 134.8(3) and 137.07(12)°, respectively. The eight-membered rings all have similar distorted boat conformations. The bite angles favor tetrahedral or distorted-tetrahedral structures for all of the metals, which forces the copper away from its usually preferred square-planar geometry.

For copper, this observation cannot be explained by steric reasons associated with the ligands, and it does not seem to be electronic in origin. This leaves us with the nature of the chelate ring. Hancock[34] has noted that generally increasing the bond angle upon increasing the ring size is generally countered by a puckering of the ring. This can be limited by the introduction of double bonds for which torsion angles should be close to zero. The eight-membered chelate rings formed with all of the above ligands, L^3, L^4, L^5, and L^6, all possess two double bonds, and this will reduce the degrees of freedom for such rings. This limits the degree of puckering, and the ring is unable to adopt a conformation that gives a bond angle at the metal center of 90°. Also of note is the relative invariance of the O−P−O angle (101−103°) in the phosphazene rings, which also restricts the flexibility of the chelate ring. In the copper(II) chloride complex of 1,3-*bis*(2-pyridyl)propane (bpp, a ligand that also contains a three-atom spacer between two 2-pyridine donors), the ligand acts in a monodentate bridging manner to form the complex [$\{Cu(bmp)Cl_2\}_2$] and achieves near square-planar geometry at the copper(II) centers.[35] It is likely that the cyclic phosphazene platform provides a steric restriction to a similar binding mode in L^5 and L^6 for the reasons discussed above, and these features may be useful in the design of ligands with specific properties such as reduction potentials. The results with the bidentate cyclotriphosphazene and cyclotetraphosphazene ligands, L^3, L^4, L^5, and L^6, suggest that polymeric phosphazenes that are heavily loaded with 2,2′-dioxybiphenyl groups in conjunction with appropriate monodentate ligands will present similar distorted-tetrahedral binding sites to metal ions.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Patra, A. K.; Ray, M.; Mukherjee, R. *J. Chem. Soc., Dalton Trans.* **1999**, *15*, 2461−2466.

(33) Gouteron, J.; Jeannin, S.; Jeannin, Y.; Livage Sanchez, C. *J. Inorg. Chem.* **1984**, *23*, 3387−3393.

(34) Hancock, R. D. *Acc. Chem. Res.* **1990**, *23*, 253−257.

(35) Spodine, E.; Atria, A. M.; Calvo, V.; Manzur, J.; Garland, M. T.; Grandjean, D.; Pena, O. *Boletin de la Sociedad Chilena de Quimica* **1991**, *36*, 209−15.