Synthesis and Characterization of Mononuclear Nickel(II) and Cobalt(II) Complexes of 2,2,4,4-Tetrakis(3,5-dimethylpyrazolyl)-6,6-diphenyl-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene L: Crystal Structure of [NiLCl$_2$]†

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Three complexes [NiLCl$_2$] **2a**, [NiLBr$_2$] **2b** and [CoLCl$_2$] **2c**, where L is the potentially multidentate ligand 2,2,4,4-tetrakis(3,5-dimethylpyrazolyl)-6,6-diphenyl-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene, have been prepared and characterized spectroscopically (IR, ^{1}H and ^{31}P NMR) and in the case of **2a**, crystallographically. The Ni^{II} atom in **2a** has been shown to exist in a distorted trigonal-bipyramidal geometry in which the halide atoms and a ring nitrogen atom define the equatorial plane; the axial positions are occupied by two nitrogen atoms derived from two pyrazolyl rings. Crystals of **2a** are monoclinic with space group *C*2/*c* and unit cell dimensions: a = 38.190(8), b = 9.225(3), c = 21.830(4) Å, β = 108.29(2)° and Z = 8. The structure was refined to final R = 0.045 for 4414 observed data.

Recently we have initiated a program of study involving the co-ordination chemistry of pyrazolylcyclotriphosphazenes.[1,2] This interest stems from the fact that they have multiple donor sites in the form of exocyclic pyrazolyl pyridine nitrogen atoms and the ring nitrogen atoms. The versatile nucleophilic substitution reaction chemistry of halogenocyclotriphosphazenes[3] allows the design and assembly of a variety of pyrazolyl containing cyclotriphosphazene ligands.[4] Previously, we studied the interaction of 2,2,4,4,6,6-hexakis(3,5-dimethylpyrazolyl)-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene L′ with copper(II) halides which co-ordinates in a facial N$_3$ mode in both mononuclear (**1a**) and dinuclear derivatives.[1,2] It was felt that reducing the number of donor sites would enable a selective assembly of mononuclear derivatives. With this objective in mind, we have chosen to study the co-ordination response of 2,2,4,4-tetrakis(3,5-dimethylpyrazolyl)-6,6-diphenyl-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene L, with various metal derivatives. Herein, we report the synthesis of the mononuclear derivatives, [MLX$_2$] [M = Ni, X = Cl **2a** or Br **2b**; M = Co, X = Cl **2c**]; the crystal structure of **2a** is also reported.

Experimental

General.—3,5-Dimethylpyrazole, 2,2-N$_3$P$_3$Ph$_2$Cl$_4$, [Ni(PPh$_3$)$_2$X$_2$] (X = Cl or Br) and [Co(PPh$_3$)$_2$Cl$_2$] were synthesised using literature methods.[5–8] Hexachloro-λ^5-cyclotriphosphazene, N$_3$P$_3$Cl$_6$ was obtained from Aldrich and used after purification by recrystallization from hexane. Reagent grade dichloromethane, benzene and acetonitrile were dried (P$_2$O$_5$) and stored over molecular sieves. Diethyl ether and hexane were dried (Na) immediately before use.

Instrumentation.—Infrared spectra of the compounds were recorded as KBr pellets on a Perkin-Elmer 1320 spectrophotometer using polystyrene film as a calibrant. Proton NMR spectra were recorded on a Bruker spectrometer at 80 MHz. Phosphorus NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 36.43 MHz. Chemical shifts are reported in ppm with reference to SiMe$_4$ (proton) and external 85% H$_3$PO$_4$ (phosphorus). Melting points were obtained by the use of a Toshniwal melting-point apparatus and are uncorrected. Metal analyses were carried out by complexometric titration with ethylenediaminetetraacetate after decomposing the complexes with concentrated H$_2$SO$_4$; C, H and N analyses were obtained from the microanalytical centre at the Indian Institute of Technology, Kanpur and the Central Drug Research Institute, Lucknow.

Synthesis.—2,2,4,4-*Tetrakis*(3,5-*dimethylpyrazolyl*)-6,6-*diphenyl*-2λ^5,4λ^5,6λ^5-*cyclotriphosphaza*-1,3,5-*triene*, L. A modified procedure for the synthesis of L used throughout this study is reported. The phosphazene *gem*-N$_3$P$_3$Ph$_2$Cl$_4$ (2.16 g, 5.0 mmol) dissolved in benzene (60 cm^3) (**CAUTION**: benzene is a known carcinogen) was added to a solution of 3,5-dimethylpyrazole (1.92 g, 20 mmol) and triethylamine (3.03 g, 30 mmol) at 25 °C. The reaction mixture was heated under reflux for 50 h. The reaction mixture was cooled and triethylamine hydrochloride was filtered off. The solvent was removed *in vacuo* leaving a residue which was washed with water (3 x 30 cm^3), and diethyl ether (2 x 20 cm^3) and subsequently dried *in vacuo*. The solid obtained was recrystallized from acetonitrile–dichloromethane (1:1) (2.7 g, 65%). M.p. 219 °C (lit.,[9] 217.5–219 °C). NMR(CDCl$_3$): ^{31}P, δ 20.3 (t, PPh$_2$) and −5.4 [d, P(Me$_2$C$_3$HN$_2$)$_2$, ^2J(P–P) 25.2 Hz]; ^{1}H, δ 7.3 (m, Ph), 5.88 (s, CH), 2.26 (s, Me) and 2.15 (s, Me). IR (KBr, cm^{-1}): 3060w, 3000m, 2840m, 1560vs, 1457s, 1430s, 1408s, 1369s, 1295vs, 1220vs, 1175s, 1088vs, 960vs, 868m, 798s, 755s, 745s, 730s and 620w.

The complexes were synthesised by mixing L with metal halides or [M(PPh$_3$)$_2$X$_2$] (X = Cl or Br) in dichloromethane solution. Typical procedures are given for [NiLCl$_2$].

[NiLCl$_2$]. To a solution of L (0.134 g, 0.2 mmol) in dichloromethane (40 cm^3) was added anhydrous NiCl$_2$ (0.026 g,

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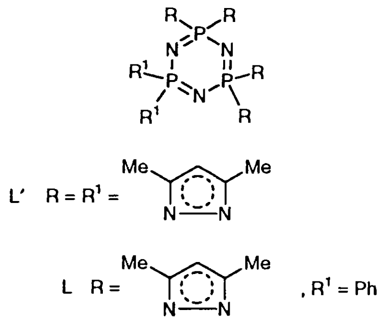
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

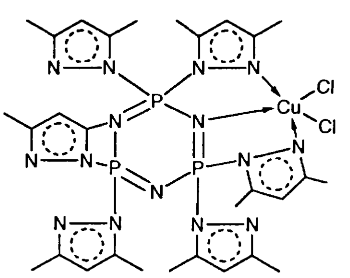
2 mmol). The resulting mixture was stirred for 48 h. The solution was filtered to remove unreacted $NiCl_2$ and concentrated to about 2 cm^3 *in vacuo*. Addition of hexane (10 cm^3) afforded a pink solid identified as **2a** (0.11 g, 69%); m.p. 315 °C. Crystals for X-ray analysis were grown by the slow vapour diffusion of hexane into a dichloromethane solution of the compound (Found: C, 48.15; H, 4.80; N, 19.35; Ni, 7.55. Calc. for $C_{32}H_{38}Cl_2N_{11}NiP_3$: C, 48.10; H, 4.75; N, 19.30; Ni, 7.35%). IR (KBr, cm^{-1}): 2935w, 1565vs, 1452m, 1439s, 1400s, 1369m, 1318w, 1303(sh), 1290vs, 1195s, 1110s, 1080(sh), 1038s, 968s, 953s, 860s, 802m, 769m, 690s, 660m and 623w.

An example of an alternative procedure is as follows: to a solution of L (0.134 g, 0.2 mmol) in dichloromethane (20 cm^3) was added $[Ni(PPh_3)_2Cl_2]$ (0.131 g, 0.2 mmol) dissolved in dichloromethane (10 cm^3) dropwise with vigorous stirring. After the addition was complete the reaction mixture was stirred further for 1 h and filtered. The filtrate was concentrated to *ca.* 3 cm^3 and diethyl ether (10 cm^3) was added affording **2a** (0.145 g, 91%).

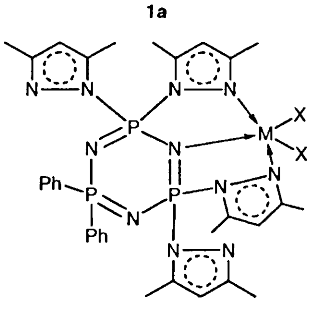
$[NiLBr_2]$. M.p. 280–285 °C (decomp.) (Found: C, 43.40; H, 4.15; N, 17.65; Ni, 6.45. Calc. for $C_{32}H_{38}Br_2N_{11}NiP_3$: C, 43.25; H, 4.30; N, 17.35; Ni, 6.60%). IR (KBr, cm^{-1}): 2938m, 1569vs, 1459m, 1430s, 1405s, 1373m, 1320w, 1305(sh), 1290vs, 1220vs (br), 1175vs (br), 1112s, 1079(sh), 1040vs, 969vs, 957vs, 888w, 865m, 810m, 782m, 698s and 668m.

$[CoLCl_2]$. M.p. 318 °C (decomp.) (Found: C, 48.20; H, 4.65; N, 19.35; Ni, 7.45. Calc. for $C_{32}H_{38}Cl_2CoN_{11}P_3$: C, 48.10; H, 4.80; N, 19.25; Ni, 7.35%). IR (KBr, cm^{-1}): 2938m, 1560vs, 1450m, 1425s, 1400s, 1370m, 1315w, 1300(sh), 1285vs, 1220vs (br), 1170vs (br), 1090vs, 1030s, 973m, 960s, 900s, 880m, 860s, 845w, 800s, 765m, 750m, 745w, 732m, 720s, 695(sh), 688s, 660w, 622w and 610w.





1a



	M	X
2a	Ni	Cl
2b	Ni	Br
2c	Co	Cl

Crystallography.—Intensity data for a maroon crystal of $[NiLCl_2]$ **2a** (0.13 × 0.24 × 0.50 mm) were measured at room temperature (21 °C) on an Rigaku AFC6R diffractometer fitted with Mo-Kα radiation (graphite monochromator), λ = 0.710 73 Å. The ω–2θ scan technique was employed to measure data to a maximum Bragg angle of 27.5°; no significant decomposition of the crystal occurred during the data collection. Lorentz and polarization corrections were applied[10] as was an empirical absorption correction such that the maximum and minimum transmission coefficients were 0.845 and 1.125, respectively.[11] Crystal data are summarized in Table 1. The structure was solved by direct methods[12] and refined by a full-matrix least-squares procedure based on *F*.[10] Anisotropic thermal parameters were employed for all non-H atoms, H atoms were included in the model at their calculated positions (C–H 0.97 Å) and the refinement was continued until convergence employing sigma weights; final refinement details are listed in Table 1. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been employed.

Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Fig. 1 which was drawn with the ORTEP[13] program at 30% probability ellipsoids. Scattering factors were those incorporated in the TEXSAN package[10] which was installed on an Indigo workstation.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Spectra.—Phosphazene L reacts with nickel(II) and cobalt(II) halides to afford mononuclear complexes. Higher yields are obtained when L is treated with the phosphino precursors, $[M(PPh_3)_2X_2]$ [equation (1); M = Ni, X = Cl or

$$[M(PPh_3)_nX_2] + L \longrightarrow [MLX_2] + nPPh_3 \qquad (1)$$

Br; M = Co, X = Cl; n = 0 or 2]. Failure to isolate any dinuclear derivatives rules out exclusive co-ordination by exocyclic pyrazolyl nitrogen atoms and suggests the participation of cyclotriphosphazene ring nitrogen atoms also, in an analogous manner to that found in $[CuL'Cl_2]$ **1a**.[2]

Crystal Structure of $[NiLCl_2]$ **2a**.—The molecular structure of **2a** is shown in Fig. 1 and selected interatomic parameters are listed in Table 3. The lattice is comprised of essentially discrete molecules of **2a**, there being no significant intermolecular

Table 1 Crystal data for complex **2a**

Formula	$C_{32}H_{38}Cl_2$-$N_{11}NiP_3$	$F(000)$	3312
M	799.3	μ/mm^{-1}	8.50
Crystal system	Monoclinic	θ limits/°	1.5–27.5
Space group	$C2/c$ (C^6_{2h}, no. 15)	hkl range	$+h, +k, \pm l$
a/Å	38.190(8)	No. of data collected	9391
b/Å	9.225(3)	No. of unique data	8846
c/Å	21.830(4)	No. of data $\geqslant 2.5\sigma(I)$	4414
β/°	108.29(2)	R	0.045
$U/Å^3$	7302(3)	R'	0.043
Z	8	$\rho/e\ Å^{-3}$	0.34, −0.40
$D_c/g\ cm^{-3}$	1.454		

Table 2 Fractional atomic coordinates for complex **2a**

Atom	*x*	*y*	*z*
Ni	0.107 00(2)	0.417 20(7)	0.141 64(3)
Cl(1)	0.149 72(4)	0.341 1(2)	0.233 12(6)
Cl(2)	0.061 81(4)	0.554 4(2)	0.156 94(8)
P(1)	0.142 27(3)	0.424 6(1)	0.027 19(6)
P(2)	0.104 72(3)	0.183 6(1)	0.033 93(6)
P(3)	0.174 22(3)	0.156 7(1)	0.025 51(6)
N(1)	0.113 0(1)	0.348 6(4)	0.054 7(2)
N(2)	0.137 6(1)	0.087 6(4)	0.034 0(2)
N(3)	0.173 2(1)	0.330 4(4)	0.017 1(2)
N(11)	0.140 9(1)	0.581 4(4)	0.127 2(2)
N(12)	0.157 5(1)	0.558 0(4)	0.080 8(2)
N(21)	0.121 5(1)	0.513 4(4)	−0.041 2(2)
N(22)	0.092 8(1)	0.602 0(5)	−0.038 2(2)
N(31)	0.079 4(1)	0.218 7(4)	0.131 7(2)
N(32)	0.083 8(1)	0.124 9(4)	0.085 7(2)
N(41)	0.071 7(1)	0.175 7(4)	−0.037 5(2)
N(42)	0.082 7(1)	0.139 9(5)	−0.089 9(2)
C(11)	0.145 9(2)	0.758 8(6)	0.212 0(2)
C(12)	0.156 5(1)	0.698 9(5)	0.157 8(2)
C(13)	0.183 1(1)	0.750 8(6)	0.132 0(2)
C(14)	0.183 4(1)	0.662 1(5)	0.083 7(2)
C(15)	0.205 1(2)	0.663 2(6)	0.038 1(3)
C(21)	0.146 6(2)	0.402 8(7)	−0.123 8(2)
C(22)	0.120 3(1)	0.490 9(6)	0.103 9(2)
C(23)	0.091 6(2)	0.566 5(7)	−0.138 5(2)
C(24)	0.075 2(2)	0.632 1(6)	−0.098 1(3)
C(25)	0.042 0(2)	0.724 6(9)	−0.114 9(3)
C(31)	0.054 8(2)	0.203 7(6)	0.220 6(3)
C(32)	0.062 8(1)	0.141 1(6)	0.164 8(2)
C(33)	0.056 6(2)	0.002 2(6)	0.141 1(3)
C(34)	0.070 2(1)	−0.008 5(5)	0.091 6(2)
C(35)	0.072 2(2)	−0.128 8(6)	0.048 7(3)
C(41)	0.021 0(1)	0.308 9(8)	−0.011 3(3)
C(42)	0.038 8(1)	0.246 9(6)	−0.056 4(2)
C(43)	0.028 5(1)	0.253 3(6)	−0.121 3(2)
C(44)	0.056 1(2)	0.186 6(6)	−0.138 7(2)
C(45)	0.058 4(2)	0.167 7(8)	−0.205 0(3)
C(51)	0.182 4(1)	0.074 7(5)	−0.042 7(2)
C(52)	0.161 6(1)	−0.040 1(6)	−0.072 5(3)
C(53)	0.166 8(2)	−0.098 7(6)	−0.126 2(3)
C(54)	0.192 9(2)	−0.044 0(7)	−0.149 9(3)
C(55)	0.213 9(2)	0.071 0(7)	−0.120 8(3)
C(56)	0.208 8(1)	0.130 4(6)	−0.066 8(2)
C(61)	0.212 0(1)	0.112 3(5)	0.095 5(2)
C(62)	0.210 5(1)	0.165 6(6)	0.153 4(2)
C(63)	0.237 8(2)	0.131 1(7)	0.209 7(2)
C(64)	0.265 8(1)	0.042 1(7)	0.207 3(3)
C(65)	0.267 4(1)	−0.009 9(6)	0.150 5(3)
C(66)	0.240 6(1)	0.027 1(5)	0.094 5(2)

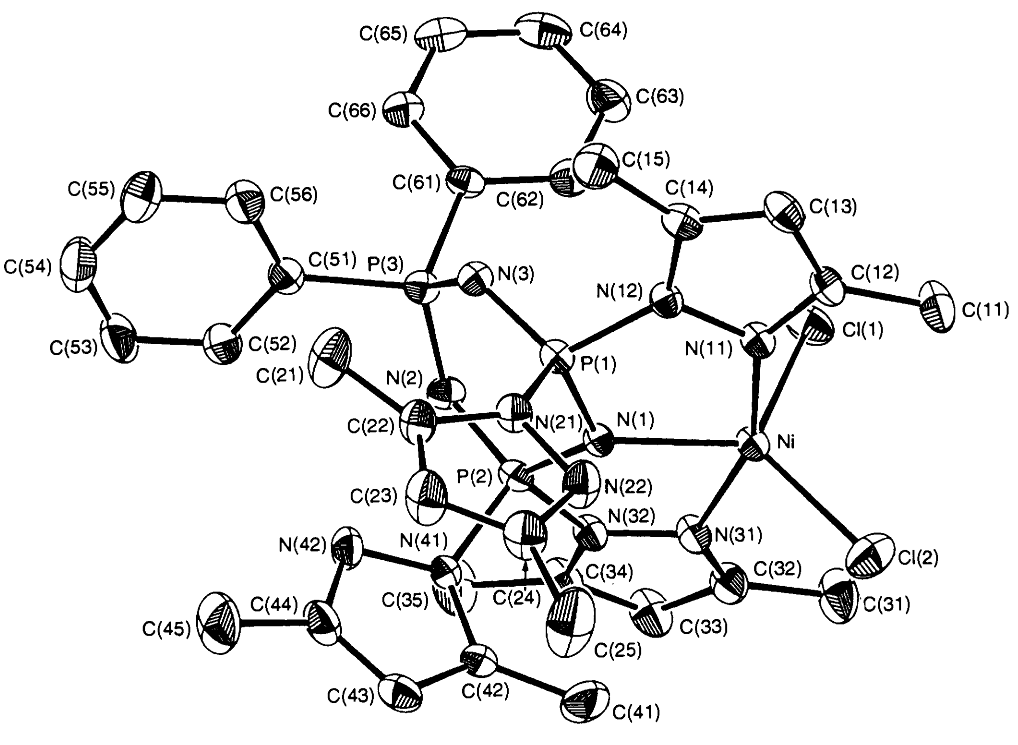


Fig. 1 Molecular structure and crystallographic numbering scheme for complex **2a**

contacts; the closest non-hydrogen contact in the lattice occurs between the N(22) and C(35′) atoms at 3.366(7) Å (symmetry operation: *x*, 1 + *y*, *z*).

The Ni atom in the complex exists in a distorted trigonal-bipyramidal geometry. The equatorial plane is defined by the two chloride atoms and a nitrogen donor atom derived from the cyclotriphosphazene ring; the nickel atom lies 0.0212(6) Å out of the equatorial plane in the direction of the N(11) atom. The axial positions are occupied by two nitrogen atoms derived from two non-geminally substituted pyrazolyl groups [N(11)–Ni–N(31) 160.0(1)°] and the planes through the two pyrazolyl groups involved in co-ordination to the Ni atom form dihedral angles of 99.7 and 78.9°, respectively with the equatorial plane. The ligand L co-ordinates in a tridentate mode and remarkable in the structure is the equivalence of the Ni–N bond distances which lie in the narrow range 2.079(3)–2.089(4) Å. These values may be compared to the range of Ni–N values [2.01(1)–2.05(1) Å] found in the structure of dibromo[bis(6-methylpyridin-2-ylmethyl)amine-*N*,*N*′,*N*″]nickel(II) which features a similar trigonal-bipyramidal geometry defined by an N_3Br_2 donor set.[14] In the analogous [$CuL'Cl_2$] complex **1a**, the axially bound nitrogen atoms formed significantly tighter Cu–N interactions [*i.e.* 1.988(5) and 1.974(5) Å] compared with the equatorially bound nitrogen atom [Cu–N 2.360(5) Å].[1]

Table 3 Selected bond distances (Å) and angles (°) for complex **2a**

Ni–Cl(1)	2.258(1)	Ni–Cl(2)	2.248(2)
Ni–N(1)	2.079(3)	Ni–N(11)	2.080(4)
Ni–N(31)	2.089(4)	P(1)–N(1)	1.590(4)
P(1)–N(3)	1.537(4)	P(1)–N(12)	1.672(4)
P(1)–N(21)	1.668(4)	P(2)–N(1)	1.591(4)
P(2)–N(2)	1.537(4)	P(2)–N(32)	1.667(4)
P(2)–N(41)	1.671(4)	P(3)–N(2)	1.600(4)
P(3)–N(3)	1.611(4)	N(11)–N(12)	1.370(5)
N(21)–N(22)	1.384(5)	N(31)–N(32)	1.374(5)
N(41)–N(42)	1.375(5)		
Cl(1)–Ni–Cl(2)	114.77(6)	Cl(1)–Ni–N(1)	117.2(1)
Cl(1)–Ni–N(11)	92.8(1)	Cl(1)–Ni–N(31)	91.1(1)
Cl(2)–Ni–N(1)	128.0(1)	Cl(2)–Ni–N(11)	99.0(1)
Cl(2)–Ni–N(31)	97.1(1)	N(1)–Ni–N(11)	80.3(1)
N(1)–Ni–N(31)	80.5(1)	N(11)–Ni–N(31)	160.0(1)
N(1)–P(1)–N(3)	117.9(2)	N(1)–P(1)–N(12)	101.1(2)
N(1)–P(1)–N(21)	111.2(2)	N(3)–P(1)–N(12)	113.7(2)
N(3)–P(1)–N(21)	108.7(2)	N(12)–P(1)–N(21)	103.2(2)
N(1)–P(2)–N(2)	117.6(2)	N(1)–P(2)–N(32)	102.2(2)
N(1)–P(2)–N(41)	109.4(2)	N(2)–P(2)–N(32)	112.2(2)
N(2)–P(2)–N(41)	110.6(2)	N(32)–P(2)–N(41)	103.8(2)
N(2)–P(3)–N(3)	114.8(2)	N(2)–P(3)–C(51)	108.4(2)
N(2)–P(3)–C(61)	108.1(2)	N(3)–P(3)–C(51)	109.4(2)
N(3)–P(3)–C(61)	108.0(2)	C(51)–P(3)–C(61)	108.1(2)
Ni–N(1)–P(1)	120.2(2)	Ni–N(1)–P(2)	118.9(2)
P(1)–N(1)–P(2)	114.4(2)	P(2)–N(2)–P(3)	120.9(2)
P(1)–N(3)–P(3)	122.6(2)	Ni–N(11)–N(12)	116.9(3)
Ni–N(11)–C(12)	136.6(3)	N(12)–N(11)–C(12)	105.4(4)
Ni–N(31)–N(32)	117.1(3)	Ni–N(31)–C(32)	137.4(3)
N(32)–N(31)–C(32)	104.4(4)		

Further, the Cl–Cu–Cl angle of 142.3(1) Å in **1a** is significantly greater than the analogous angle in **2a** of 114.77(6)°. Clearly, the geometry about the copper atom in **1a** approaches a tetragonally distorted square pyramid (with the ring nitrogen atom occupying the axial position), at least more so than that found in **2a**.

The P_3N_3 framework of the cyclotriphosphazene ligand is not planar, with the major deviation being found for the N(1) atom as shown in the torsion angles of 119.5(2) and −110.7(2)° for Ni–N(1)–P(1)–N(3) and Ni–N(1)–P(2)–N(2), respectively. The P–N(1) bond distances of 1.590(4) and 1.591(4) are significantly longer than the adjacent P(1)–N(3) and P(2)–N(2) bond lengths of 1.537(4) Å (× 2) consistent with the trends found when the ligands are protonated.[3]

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