Phosphorus–carbon linkages within three PMe_3 ligands are normal, ranging from 1.806 (10) to 1.868 (8) Å and averaging 1.824 [19] Å. Contrasting significantly with this are the phosphorus–carbon distances within the phosphonium ylide moiety, ranging from 1.748 (7) to 1.782 (9) Å and averaging 1.772 [16] Å. Furthermore, the P(4)–C(4) linkage is the shortest of these, accounting for the diminished inductive trans effect of the alkyl ligand. The decrease in phosphorus–carbon bond lengths within a phosphoylide has been observed previously.[26]

Other geometrical features within the molecule are normal. Structural parameters for the ordered CO ligand are W–C(3) = 1.957 (8) Å, C(3)–O(3) = 1.158 (9) Å, and W–C(3)–O(3) = 176.0 (8)°; bond lengths for the disordered carbonyls are similar, with W–C(1) = 1.968 (19) Å, C(1)–O(1) = 1.110 (21) Å, W–C(2) = 1.940 (19) Å, and C(2)–O(2) = 1.153 (21) Å. These values are entirely consistent with previously obtained results[27] on seven-coordinate tungsten carbonyl complexes. The tungsten–chlorine distances are also normal, with W–Cl(1) = 2.557 (5) Å and W–Cl(2) = 2.527 (5) Å.

Acknowledgment. This work was made possible by a grant from the National Science Foundation (CHE80-23448, to M.R.C.). We also thank Professor R. R. Schrock for providing the sample and for continuing collaborative work.

Registry No. $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3][CF_3SO_3]$, 82880-78-2.

Supplementary Material Available: Tables of calculated hydrogen atom positions (Table II-S), anisotropic thermal parameters (Table III), and observed and calculated structure factor amplitudes and Figures 1 and 2 (28 pages). Ordering information is given on any current masthead page.

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[26] (a) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 2614–2621. (b) Churchill, M. R.; Rotella, F. J.; Abel, E. W.; Mucklejohn, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 5820–5821.

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[28] Supplementary data.

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and Institut für Anorganische Chemie, Universität München, D-8000 München 2, Germany

Bridgehead Phosphorane Structure of a Chlorodiazadiphosphetidine with Fused Five-Membered Rings[1]

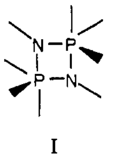
ROBERTA O. DAY,[†] ALFRED SCHMIDPETER,[‡] and ROBERT R. HOLMES*[†]

Received January 26, 1982

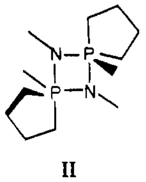
Single-crystal X-ray analysis of 10-chloro-9,10-dihydro-1,2′,9-trimethyl-3,5′,7-triphenylspiro[1*H*-[1,3,2λ^5,4λ^5]diazadiphospheto[2,1-*c*:2,3-*c*′]bis[1,2,4,3λ^5]triazaphosphole-5,3′-[2*H*][1,2,4,3λ^5]triazaphosphole], $(PhCN_3Me)_3P_2Cl$ (IX), containing both a pentacoordinate and tetracoordinate phosphorus center incorporated in the phosphetidine ring with attached 1,2,4,3-triazaphosphole rings, reveals a partial meridonal, partial cis-facial ring arrangement around the five-coodinated phosphorus atom. The compound crystallizes in the monoclinic crystal system, space group $C2/c$, with $Z = 8$, $a = 33.229$ (4) Å, $b = 9.685$ (2) Å, $c = 17.677$ (3) Å, and $\beta = 111.96$ (1)°. Refinement including all hydrogen atoms gave $R = 0.035$, $R_w = 0.045$ for the 2881 reflections having $I \geq 2\sigma_I$. The geometry around the pentacoordinate phosphorus atom is about 40% along the coordinate from an idealized trigonal bipyramid with the chlorine atom situated equatorially toward a square pyramid with the chlorine atom in the apical position. The tendency of tricoordinated nitrogen atoms to reach planarity in the partially unsaturated rings is cited as the principal influence leading to the observed structure. NMR data indicate the structure is retained in solution.

Introduction

Diazadi-λ^5-phosphetidines I are stabilized relative to a monomeric formulation if substituents of sufficient electronegativity are attached[2,3] to phosphorus. The addition of cyclic substituents, as in II, contributes to the stabilization of the

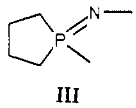


I



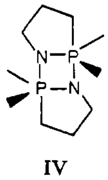
II

diazadiphosphetidine, presumably due to ring strain reduction relative to the monomeric form III.[4,5]

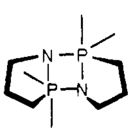


III

Recent work with fused-ring systems revealed two variations of the dimeric form, a meridonal conformer[6,7] IV and a facial-cis placement of the fused rings V.[3] The use of acyclic



IV



V

[†] University of Massachusetts.

[‡] Universität München.

[1] (a) Pentacoordinated Molecules. 46. (b) Previous paper in the series: Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 2379.

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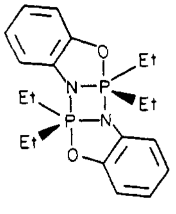
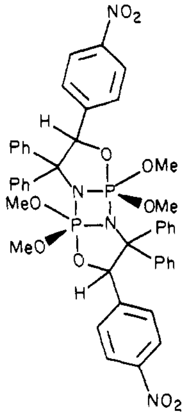
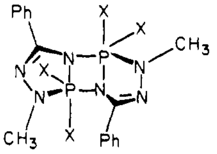
ligands of low apicophilicity favors the formation of the meridonal form IV, especially since the tendency for nitrogen to attain planarity is possible only for IV.[3] In keeping with these trends, the meridonal conformation is found for VI[6] and VII[7] by X-ray analysis. In the latter, VII, the apicohilicities of the endocyclic and exocyclic ligands are not sufficiently different. However, use of halogen atoms as endocyclic ligands and nitrogen in place of the oxygen atoms in the fused ring system leads to the cis-facial arrangement V, established by crystal structure determinations of VIII.[3]



VI



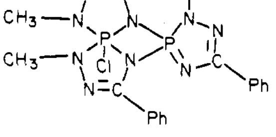
VII



VIIIa, X = F
b, X = Cl

Evidently, because of ring unsaturation and the tendency of nitrogen to reach planarity, the structures VIII are almost midway between the idealized trigonal bipyramid and square pyramid.[3] The latter structure is reached by executing a Berry[8] pseudorotation using equatorial halogen atoms as pivotal ligands.[9]

An interesting extension is found in the chlorodiazadiphosphetidine IX which has the fused five-membered rings constrained at the pentacoordinated phosphorus center so that one is in the meridonal configuration and the other one is in the facial arrangement. The other phosphorus atom is tetracoordinated and is bound by one five-membered triaza ring. The crystal structural analysis is reported here.



IX

Experimental Section

Preparation of 10-Chloro-9,10-dihydro-1,2′,9-trimethyl-3,5′,7-triphenylspiro[1*H*-[1,3,2λ^5,4λ^5]diazadiphospheto[2,1-*c*:2,3-*c*′]bis-[1,2,4,3λ^5]triazaphosphole-5,3′-[2*H*][1,2,4,3λ^5]triazaphosphole] (IX). A mixture of 2.48 g (5.0 mmol) of VIIIb and 0.88 g (5.0 mmol) of 2-methyl-5-phenyl-1,2,4,3-triazaphosphole, Ph(CN$_3$P)Me (X),[10] were heated to 150 °C. A clear melt formed, and after 3 h 0.69 g (5.0 mmol) of PCl$_3$ had distilled off. After cooling, the glassy residue was dissolved in 5 mL of chloroform. Addition of 10 mL of acetonitrile gave 1.70 g (63%) of colorless crystals. $^{31}P\{^1H\}$ NMR (CHCl$_3$): two AB spin systems $\delta_A = 26.0, 25.0$ and $\delta_B = -34.0, -36.0$ ($J_{PP} = 85.0, 84.0$ Hz).

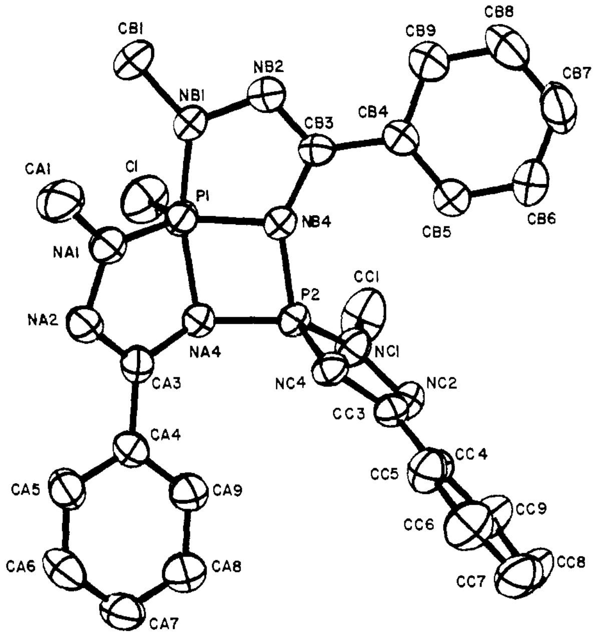


Figure 1. ORTEP plot of $C_{24}H_{24}N_9P_2Cl$ (IX), with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

The X-ray crystallographic study was done with use of an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda_{K\alpha_1} = 0.70930$ Å, $\lambda_{K\alpha_2} = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[11]

A colorless crystal of IX, cut from a polycrystalline mass (0.25 × 0.25 × 0.35 mm) and mounted inside a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray studies.

Crystal Data for $C_{24}H_{24}N_9P_2Cl$: space group $C2/c$ (C_{2h}^6-No. 15),[12] from $2/m$ diffraction symmetry, extinctions, and successful solution and refinement; $a = 33.229$ (4) Å, $b = 9.685$ (2) Å, $c = 17.677$ (3) Å, $\beta = 111.96$ (1)°, $Z = 8$, $\mu_{\mathrm{Mo}\,K\alpha} = 0.302$ mm^{-1}; 3876 independent reflections ($+h,+k,\pm l$) measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{Mo}\,K\alpha} \leq 47°$; no corrections made for absorption.

The structure was solved by using direct methods (MULTAN) and refined by full-matrix least squares.[13] The 36 independent nonhydrogen atoms were refined anisotropically while the 24 independent

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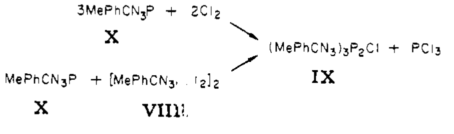
(8) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(9) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*, 225.

(10) While exhaustive chlorination of the 2-methyl-5-phenyl-1,2,4,3-triazaphosphole X gives the dimer VIIIb of its 3,3-dichloro derivative[3] as the sole product, complex mixtures of products are obtained if less than 1 mol of chlorine is added. One of the products isolated originates, according to its analysis, from 3 mol of X and 2 mol of chlorine by loss of 1 mol of phosphorus trichloride.



It may consequently also be prepared from equimolar amounts of X and VIIIb. See: Schmidpeter, A.; Nayibi, M.; Renoth, P.; Tautz, H. "Abstracts", 3rd International Symposium on Inorganic Ring Systems, Graz, Austria, Aug 1981; Verein Österreichischer Chemiker: Graz, Austria, 1981; p 30.

(11) Sau, A. C.; Day, R. O; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; p 101.

(13) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 12, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Cl and P were taken from the same source, pp 149–150.

Table I. Atomic Coordinates in Crystalline $C_{24}H_{24}N_9P_2Cl$ (IX)[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
Cl	1765.2 (3)	6213.3 (9)	2374.9 (6)
P1	1936.0 (3)	4128.3 (8)	2593.6 (5)
P2	1245.1 (2)	2589.1 (8)	1984.6 (5)
NA1	2198 (1)	3832 (3)	3579 (2)
NA2	1941 (1)	3739 (3)	4061 (2)
NA4	1453 (1)	3686 (2)	2762 (1)
NB1	2359 (1)	4148 (3)	2269 (1)
NB2	2265 (1)	3582 (3)	1489 (2)
NB4	1678 (1)	3096 (2)	1774 (1)
NC1	772 (1)	2926 (2)	1285 (1)
NC2	506 (1)	1743 (3)	1127 (1)
NC4	1159 (1)	1032 (2)	2138 (1)
CA1	2661 (1)	3685 (6)	4062 (3)
CA3	1535 (1)	3603 (3)	3594 (2)
CB1	2703 (1)	5183 (4)	2467 (3)
CB3	1890 (1)	2976 (3)	1228 (2)
CC1	625 (1)	4121 (4)	752 (3)
CC3	735 (1)	769 (3)	1614 (2)
CA4	1198 (1)	3371 (3)	3929 (2)
CA5	1310 (1)	3289 (4)	4773 (2)
CA6	998 (1)	2964 (4)	5086 (2)
CA7	572 (1)	2751 (4)	4583 (2)
CA8	458 (1)	2865 (4)	3752 (2)
CA9	766 (1)	3177 (4)	3422 (2)
CB4	1726 (1)	2210 (3)	458 (2)
CB5	1393 (1)	1265 (4)	282 (2)
CB6	1269 (1)	486 (4)	−426 (2)
CB7	1477 (1)	639 (4)	−960 (2)
CB8	1803 (2)	1593 (5)	−795 (2)
CB9	1923 (1)	2393 (4)	−101 (2)
CC4	535 (1)	−590 (3)	1616 (2)
CC5	784 (1)	−1683 (3)	2041 (2)
CC6	592 (1)	−2948 (4)	2060 (3)
CC7	156 (1)	−3120 (4)	1658 (3)
CC8	−96 (1)	−2053 (4)	1225 (3)
CC9	94 (1)	−788 (4)	1195 (3)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

Table II. Selected Bond Lengths (Å) and Bond Angles (Deg) for $C_{24}H_{24}N_9P_2Cl$ (IX)[a, b]

P1–Cl	2.094 (1)	NA1–NA2	1.416 (3)
P1–NA1	1.656 (3)	NB1–NB2	1.406 (3)
P1–NB1	1.704 (3)	NC1–NC2	1.409 (3)
P1–NB4	1.705 (2)	NA2–CA3	1.299 (4)
P1–NA4	1.790 (2)	NB2–CB3	1.295 (4)
P2–NA4	1.669 (2)	NC2–CC3	1.311 (4)
P2–NB4	1.688 (2)	CA3–NA4	1.394 (4)
P2–NC1	1.628 (2)	CB3–NB4	1.398 (3)
P2–NC4	1.577 (2)	CC3–NC4	1.391 (3)
NA1–CA1	1.461 (4)	CA3–CA4	1.469 (4)
NB1–CB1	1.463 (4)	CB3–CB4	1.465 (4)
NC1–CC1	1.457 (4)	CC3–CC4	1.474 (4)

NB1–P1–NA4	164.0 (1)	CA3–NA2–NA1	109.9 (2)
NA1–P1–NB4	133.8 (1)	NA2–NA1–P1	116.5 (2)
Cl–P1–NA1	111.2 (1)	NA2–NA1–CA1	112.4 (3)
Cl–P1–NB4	113.1 (1)	CA1–NA1–P1	131.0 (2)
NB1–P1–Cl	97.3 (1)	P2–NB4–P1	100.5 (1)
NA4–P1–Cl	93.6 (1)	P2–NB4–CB3	145.1 (2)
NB1–P1–NB4	86.4 (1)	P1–NB4–CB3	114.3 (2)
NA4–P1–NA1	86.3 (1)	NB4–CB3–NB2	112.5 (3)
NB1–P1–NA1	100.4 (1)	NB4–CB3–CB4	125.0 (2)
NA4–P1–NB4	78.7 (1)	CB4–CB3–NB2	122.4 (3)
NA4–P2–NB4	82.6 (1)	CB3–NB2–NB1	110.9 (2)
NC4–P2–NC1	97.9 (1)	NB2–NB1–P1	114.7 (2)
NA4–P2–NC4	120.9 (1)	NB2–NB1–CB1	111.6 (3)
NB4–P2–NC1	115.7 (1)	CB1–NB1–P1	126.7 (2)
NA4–P2–NC1	118.9 (1)	P2–NC4–CC3	105.3 (2)
NB4–P2–NC4	122.7 (1)	NC4–CC3–NC2	119.9 (3)
P2–NA4–P1	97.9 (1)	NC4–CC3–CC4	120.5 (3)
P2–NA4–CA3	133.6 (2)	CC4–CC3–NC2	119.6 (2)
P1–NA4–CA3	110.8 (2)	CC3–NC2–NC1	106.8 (2)
NA4–CA3–NA2	114.3 (3)	NC2–NC1–P2	110.1 (2)
NA4–CA3–CA4	123.8 (3)	NC2–NC1–CC1	118.9 (2)
CA4–CA3–NA2	121.9 (3)	CC1–NC1–P2	130.3 (2)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

hydrogen atoms were refined as isotropic scatters. The final agreement factors[14] were $R = 0.035$, $R_w = 0.045$, and GOF = 1.282 for the 2881 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.172 e/Å^3.

Results and Discussion

The atom labeling scheme and the molecular geometry of IX are shown in Figure 1. Atomic coordinates for non-hydrogen atoms are given in Table I. Important bond lengths and angles are given in Table II. Anisotropic thermal patameters, refined parameters for hydrogen atoms, remaining bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

The geometry about the 5-coordinated P1 lies on the coordinate connecting an idealized trigonal bipyramid (TBP), having Cl, NA1, and NB4 in equatorial positions and NB1 and NA4 in axial ones, with an idealized rectangular pyramid (RP), having four basal N atoms and an apical Cl atom. In terms of the Berry coordinate,[8] the geometry is displaced 34.1% (40.4% using unit vectors) from the TBP toward the RP,[15] where Cl is the pivotal atom in the pseudorotation process.

Except for the perturbations caused by the stereochemical center at P1, the molecule would have a pseudo mirror plane, which would ideally contain Cl, P1, P2, and the five- and six-membered "C" rings and methyl group. This pseudo mirror plane would take the "A" rings into the "B" rings, making NA1 and NA4 chemically equivalent to NB1, and NB4, respectively. Although the axial bond length P1–NB1 (1.704 (3) Å) is essentially the same as the equatorial bond length P1–NB4 (1.705 (2) Å), the established trend for relative elongation of axial bonds[16] in trigonal bipyramids is followed if bonds that are chemically equivalent, except for stereochemistry, are compared. Relative to the TBP character of IX, P1–NB1 (axial, 1.704 (3) Å) is longer than P1–NA1 (equatorial, 1.656 (3) Å) and P1–NA4 (axial, 1.790 (2) Å) is longer than P1–NB4 (equatorial, 1.705 (2) Å). The latter two values compare with similar bond distances for the four-membered ring in the chloro derivative[3] VIIIb of 1.770 (2) and 1.684 (3) Å (average values).

The five-membered ring defined by P1, NB1, NB2, CB3, and NB4 is nearly coplanar with the diazadiphosphetidine ring, the dihedral angle between the respective least-squares mean planes (planes IV and VII, Table D) being 6.7°. For the five-membered ring P1, NA1, NA2, CA3, and NA4, the corresponding dihedral angle with the plane of the four-membered ring (planes IV and V, Table D) is 44.3°. This is consistent with the presence of ring unsaturation (at N2–C3) and the observation that equatorially placed nitrogen atoms attached to phosphorus tend to be planar.[3,16] For NA1, the angular sum is 359.9 (7)°, while for NB4, the sum is 359.9 (5)°.[17]

For the axial nitrogen atoms bonded to P1, the geometry around nitrogen becomes progressively less planar on going from NB1 (angular sum of 353.0 (7)°) to NA4 (angular sum of 342.3 (5)°). The latter effect is seen for other phosphoranes containing axial nitrogen atoms.[3,16,18]

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(14) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = 2881 and NV = 421.

(15) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318. Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

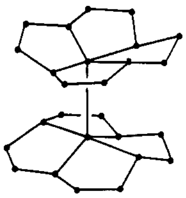
(16) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*, 12–33, 48–50.

(17) The nitrogen atom NC1 attached to the tetracoordinated P2 atom has ligands surrounding it in a planar arrangement (the sum of angles is 359.3 (6)°).

The implication is that less P–N π bonding is present for axial bonds compared to equatorial bonds.[19] The presence of relatively rigid five-membered rings, fused to the diazadiphosphetidine ring, and the tendency of the axial nitrogen atoms toward planarity may be responsible to some extent for the widening of the equatorial NA1–P1–NB4 angle to 133.8 (1)° and the displacement of the structure toward a square pyramid (40.4% based on unit vectors). In the case of the cis-facial structures VIII, this displacement corresponded to a structure near the midpoint between the two idealized pentacoordinated geometries.[3]

It is interesting that each of the five-membered rings tends to be coplanar with its attached phenyl ring. The dihedral angles between these pairs of planes are 7.5, 10.4, and 17.9° for phenyl rings attached at CA3, CC3, and CB3, respectively (Table D). This agrees with the double-bond character implied by the length of the C–C bond, averaging 1.470 (4) Å, at the point of attachment of the phenyl groups. However, bond distance data for both the fluoro and chloro derivatives of VIII[3] are very similar to those for IX reported here, and in these structures, the dihedral angles between planes of the five-membered rings and attached phenyl groups range from 22 to 26°.[3] Possibly, crystal-packing forces for the cis-facial structures VIII lead to the out-of-plane rotation of the phenyl groups (with respect to the five-membered rings) without appreciable loss of C–C π bonding.

The partial facial-meridonal structure for the tricyclic arrangement around P1 of IX may be compared with the completely cyclized bis(cyclenphosphorane) $(C_8H_{16}N_4P)_2$ containing two N_4 macrocycles with saturated five-membered rings (XI). In this structure,[20] the P–N axial bonds are 1.782 (2) Å, and the P–N equatorial bonds, 1.694 (2) Å.



XI

The ^{31}P NMR data for IX indicate that the solid-state structure is retained in solution. The presence of an equilibrium mixture of two diastereomers, each containing a five-coordinate and four-coordinate phosphorus atom, is supported by the observance of the two AB spin systems with appropriate chemical shifts for these coordination numbers. Assuming the retention of the basic ring triazaphosphole structure of X, it is reasonable to conclude that the pentacoordinated phosphorus atom is the spirocyclic center containing the fused five-membered rings.

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Registry No. VIIIb, 63148-50-5; IX, 82808-35-3; X, 52713-97-0.

Supplementary Material Available: Tables A–D, compilations of anisotropic thermal parameters, refined parameters for hydrogen atoms, remaining bond lengths and angles, and deviations from selected least-squares mean planes for IX and a listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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N-(2-Ammonioethyl)morpholinium Tetrachlorocuprates(II). The First Instance of Two Forms, One Green and One Yellow, Both Stable at Room Temperature

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Crystals of the green form of the title compound are monoclinic, space group $I2/a$, with a = 15.934 (3) Å, b = 13.023 (1) Å, c = 14.069 (3) Å, β = 118.89 (1)°, and Z = 8. Crystals of the yellow form are monoclinic, space group $P2_1/a$, with a = 15.909 (3) Å, b = 12.420 (3) Å, c = 6.355 (1) Å, β = 98.77 (5)°, and Z = 4. The crystal structures were determined by three-dimensional X-ray diffraction and refined to R = 0.047 and 0.045 for the green and yellow forms, respectively. In the green crystals two crystallographically independent $[CuCl_4]^{2-}$ anions are present, one of them with a flattened-tetrahedral geometry and the other square planar for symmetry requirements. In the yellow form only $[CuCl_4]^{2-}$ distorted-tetrahedral ions are present. In both modifications, the anions form hydrogen bonds with the *N*-(2-ammonioethyl)morpholinium cation, with stronger bonds being present in the green modification. The spectroscopic and magnetic properties of the complexes are explained in the light of their known crystal structures.

Introduction

The great interest in the tetrachlorocuprates(II) stems from the fact that they show a great variety of coordination numbers and geometries[2,3] and, in some cases, a discontinuous reversible thermochromic behavior.

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