experimental observations. Structure determinations of selected metalloporphyrins to further test these ideas are contemplated.

Computational Details

Calculations were carried out with the charge iterative extended Hückel method[12a] with standard atomic parameters.[12b] Initial coordinates for [Fe(P)(2-MeHIm)], [Fe(P)(2-MeHIm)]$^+$, [Co(P)(HIm)], [Fe(P)-(2-MeHIm)$_2$]$^+$, [Fe(P)(HIm)$_2$], [Fe(P)(HIm)$_2$]$^+$, [Ni(P)(HIm)$_2$], and [Fe(P)(CN)$_2$]$^-$ were taken from their respective crystallographic structure determinations and transformed to the coordinate system shown in Figure 1. Peripheral groups of the porphyrins were replaced by hydrogen atoms with idealized C–H distances of 1.08 Å. All other C–H bond lengths were also idealized. Ligand rotations were made around the axial M–N(Im) bond and no additional idealization of geometry was imposed. For [Fe(P)(CO)], whose structure is unknown, a Fe–C bond distance[23] of 1.70 Å and an out-of-plane displacement of the iron atom of 0.21 Å was assumed. For [Fe(P)(CO)(HIm)], a planar porphyrin core, an in-plane iron atom and Fe–C and Fe–N(HIm) distances of 1.77 and 2.01 Å were assumed. For the [Fe(NH$_2$)$_4$(2-MeHIm)]$^-$ model calculation, H atoms were placed 1.02 Å along the N–C bonds of [Fe(P)(2-MeHIm)]$^+$. A reviewer has asked about the convergence of the calculations. The default criterion for convergence was to stop the calculation when all atomic charges change by less than 0.010 from one iteration to the next. Some exploratory calculations with a more strigent criterion of 0.005 showed that the reported overlap populations are indeed well converged.

(23) This distance was estimated from the known structure of [Fe(OEP)(CS)] and discussion found in the following: Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208–1211.

Acknowledgment. We thank Prof. Martin Gouterman and Dr. J. A. Shelnutt for providing a VAX version of the extended Hückel program. W.R.S. thanks Prof. T. P. Fehlner for helpful discussions. We thank Dr. Richard Korszun for a preprint of ref 4. W.R.S. gratefully acknowledges support of this work by the National Institutes of Health (HL-15627). D.M.C. acknowledges support of this work by the Office of Basic Energy Science of the U.S. Department of Energy. This is Document No. NDRL-2664 from the Notre Dame Radiation Laboratory.

Coordination Chemistry of Cyclamphosphorane. Access to Transition-Metal Cyclamphosphoranides. Crystal and Molecular Structure of CpMo(CO)$_2$(cyclamphosphoranide)

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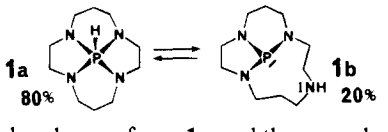
Contribution from the Laboratoire de Chimie Moléculaire, Unité Associée au CNRS, Parc Valrose, 06034 Nice, France, and Laboratoires de Chimie, Unité Associée au CNRS, Département de Recherche Fondamentale, CENG, 38041 Grenoble, France. *Received April 9, 1985*

Abstract: In solution, cyclamphosphorane **1a** is in equilibrium with ca. 20% of the open cyclamphosphine form **1b**. This equilibrium can be shifted under the action of transition-metal derivatives to yield adducts of **1b**. Three situations were encountered: (i) With Fe(NO)$_2$(CO)$_2$, only phosphorus-bound adducts were formed; both Fe(NO)$_2$(CO)(**1b**) and Fe(NO)$_2$(**1b**)$_2$ were isolated. (ii) The phosphorus- and nitrogen-bound chelates **6** were obtained under the action of [Rh(CO)$_2$Cl]$_2$. (iii) With CpM(CO)$_3$Cl, a more complex situation was found: with M = W, one CO was substituted to yield a mixture of diastereoisomeric neutral P-bound cis adducts, **8**; under the action of NaBPh$_4$, the NH site quantitatively displaced the chloride ion to give a mixture of phosphorus- and nitrogen-bound diastereoisomeric salts, **10**; when M = Mo, the reaction yielded a 3:1 mixture of the neutral P-bound only and of the ionic P- and N-bound diastereoisomers; this mixture can also be quantitatively converted to the ionic diastereoisomeric chelates, **9**. Complexes **3** and **4**, which formally contain the cyclamphosphoranide ligand **13**, i.e., a 10-electron valence-shell, monoanionic, 4-coordinated phosphorus(III) species, were isolated in over 90% yields from the reaction of the cationic chelates **9** and **10** after abstraction of the N-borne proton by LiMe. Only one diastereoisomer (an enantiomeric pair) appears to form. The phosphoranides could not be obtained directly from LiMe and the neutral adducts **7a** or **8**, in which the NH site is not coordinated. The phosphoranides are thermally fairly stable (dec 150 and 200 °C) and only moderately air-sensitive. They are characterized by high-field ^{31}P chemical shifts, ca. 173 ppm upfield from those of their precursors **9** and **10**. Adduct **3**, (C$_5$H$_5$)Mo(CO)$_2$(C$_{10}$H$_{20}$N$_4$P), crystallized in the monoclinic space group $P2_1/n$ with a = 13.736 (1) Å, b = 9.354 (2) Å, c = 15.577 (2) Å, β = 113.05 (1)°, and Z = 4. Its most notable features are the 5-connected character (i.e., phosphoranide nature of the metal-bound phosphorus atom, with a short (2.44 Å) Mo–P bond), the coordination of a P-bound nitrogen atom to the same molybdenum (2.22 Å) to form a P(M)—N cycle, the long P–N bond within this cycle (1.85 Å) contrasting with the shortness of the other apical P–N bond (1.70 Å), which compares in length with the equatorial P–N bonds (1.67 and 1.70 Å), the close to planar configuration of the uncoordinated apical nitrogen atom, the close to bipyramidal arrangement of bonds around phosphorus in spite of the five cycles to which this phosphorus belongs, and the unusual "negative" distortion of this bipyramid on Berry's ideal trigonal-bipyramid/square-pyramid low-energy path.

Cyclamphosphorane **1a**[2] has many interesting features, among which are its polycyclic structure and its equilibrium with an open tautomeric form, **1b**, in solution (eq A). We reported recently



that both the phosphorane form, **1a**, and the open phosphine form, **1b**, can exhibit bidentate behavior in the presence of diborane.[3] In the first case, **2a**, two BH$_3$ groups are coordinated on the two apical nitrogen atoms of the bipyramidal phosphorus center, while in the second case, **2b**, the BH$_3$ groups are linked one to the phosphine and the other to the secondary amine sites. The two adducts form simultaneously; then the first slowly converts to the second in the solution. We also briefly reported on the possibility of coordinating transition metals *across* a P–N bond of the closed cyclamphosphorane as in **3** and **4**.[4] It was therefore interesting

(1) (a) Université de Nice. (b) Membre de l'Université Scientifique et Médicale de Grenoble.

(2) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333. Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

(3) (a) Dupart, J. M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051. (b) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776.

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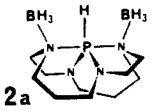
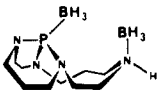
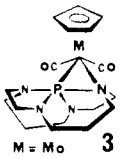


2a



2b



M = Mo 3
M = W 4

to further evaluate the coordination ability of cyclamphosphorane and its open tautomeric form toward transition-metal derivatives capable of accommodating more than one coordination site.

We now report various types of transition-metal complexes of the cyclamphosphine form **1b** with concomitant displacement of the tautomeric equilibrium A toward **1b**. Compound **1b** is an asymmetric bidentate ligand with two donor sites of distinctly different character: σ-donating and π-accepting at the softer P site and σ-donating only at the harder NH site. In all the adducts we obtained, the transition metal was bound to the phosphorus site; coordination through the nitrogen site was less straightforward but could in certain cases and conditions be forced. Full details are also given on the synthesis of the cyclamphosphoranides **3** and **4** as well as a complete single-crystal X-ray diffraction study of **3**.

Experimental Section

Melting points were determined with a Reichert microscope in sealed capillaries. Microanalyses were performed by the Centre de Microanalyse du CNRS. NMR spectra were recorded on a Bruker WH-90 instrument, and chemical shifts are given relative to internal tetramethylsilane (^{1}H) and external H_3PO_4 85% (^{31}P). Mass spectra were obtained with a VG Micromass 70-70F (Centre de Microanalyse du CNRS) or a R10 Ribermag L10 and IR spectra with a Perkin-Elmer 577 spectrophotometer.

All experimental procedures were carried out under nitrogen. The solvents were freshly distilled under nitrogen from appropriate drying agents. Molar conductances were determined with an electronic conductometer Tacussel CD6NG.

$(NO)_2(CO)Fe$(cyclamphosphine) (5). A solution of cyclamphosphorane (0.38 g, 1.7 mmol) in toluene (10 mL) was added to a solution of iron nitrosyl carbonyl (0.29 g, 1.7 mmol) in toluene (10 mL), and the mixture was stirred for 3 h at 80 °C. The dark solution was filtered and then evaporated, and the gummy residue was taken up with pentane to give a dark red powder, which was isolated by filtration and washed with cold pentane to yield 0.44 g (70%) of **5** as a red-brown powder, soluble in $CHCl_3$, slightly soluble in pentane: mp 130 °C; IR (KBr pellet, cm^{-1}) ν(NH) 3340 (w), ν(CO) 1994 (s), ν(NO) 1747 (s), 1695 (s); MS (chemical ionization with NH_3), m/e MH$^+$ (100%), (M − NO)H$^+$ (8.7%), (M − CO)H$^+$ (19%), LH$^+$ (18.3%); ^{31}P NMR ($CHCl_3$) δ +159 (s). Anal. Calcd for $C_{11}H_{21}N_6O_3PFe$: C, 35.50; H, 5.69; N, 22.58; P, 8.32. Fe 15.01. Found: C, 35.38; H, 5.75; N, 22.32; P, 8.41; Fe, 15.13.

$(NO)_2Fe$(cyclamphosphine)$_2$ (5′). Cyclamphosphorane (0.68 g, 3.0 mmol) in toluene (15 mL) was added to a solution of iron nitrosyl carbonyl (0.26 g, 1.5 mmol) in toluene (15 mL). The mixture was refluxed under stirring for about 24 h, then cooled to room temperature, and filtered. The filtrate was evaporated, and the residue was taken up with pentane. After filtration, 0.64 g (75%) of a red-brown powder was isolated. The microcrystalline powder is rather soluble in CH_2Cl_2: mp 210 °C; IR (KBr pellet, cm^{-1}) ν(NH) 3340 (w), 3120 (w), ν(NO) 1692 (s), 1640 (s); MS (DIC, chemical ionization with NH_3), m/e MH$^+$ (5.7%), LH$^+$ (100%); ^{31}P NMR (CH_2Cl_2) +175 (s). Anal. Calcd for $C_{20}H_{42}N_{10}O_2P_2Fe$: C, 41.97; H, 7.39; N, 24.47; P, 10.82; Fe, 9.76. Found: C, 41.75; H, 7.45; N, 24.21; P, 10.38; Fe 9.49.

Rh(CO)Cl(cyclamphosphine) (6). A solution of cyclamphosphorane (0.70 g, 3.0 mmol) in toluene (10 mL) was added dropwise to a stirred red-orange solution of $[Rh(CO)_2Cl]_2$ (0.57 g, 1.46 mmol) in toluene (10 mL) at room temperature. The solution immediately turned dark green, and a dark precipitate formed. The evolution of 67 mL (3.0 mmol) of CO was observed. The precipitate was filtered and washed repeatedly with toluene and then with small portions of acetonitrile until the filtrate became colorless, yielding 0.71 g (60%) of **6** as a yellow powder, slightly soluble in Me_2SO and CH_3CN, unstable in solution, and reasonably stable in air: dec ~300 °C; IR (KBr pellet, cm^{-1}) ν(NH) 3190 (w), ν(CO), 1970 (vs), ν(RhCl), 285 (w). MS, m/e M$^+$ (19%), M$^+$ − CO (100%), presence of two isotopic peaks in 3:1 ratio at M$^+$ and M$^+$ + 2 characteristic of a chlorine atom. ^{31}P NMR (Me_2SO) δ +130 (d, $^1J_{P-Rh}$ = 200 Hz). Anal. Calcd for $C_{11}H_{21}N_4OPClRh$: C, 33.48; H, 5.36; N, 14.20; P, 7.85; Cl, 8.98; Rh, 26.08. Found: C, 33.38; H, 5.48; N, 14.25; P, 7.74; Cl, 8.66; Rh, 23.08.

$(C_5H_5)Mo(CO)_2Cl$(cyclamphosphine) (7). A solution of cyclamphosphorane (0.68 g, 3.0 mmol) in THF (60 mL) was added to the red solution of $CpMo(CO)_3Cl$ (0.84 g, 3.0 mmol) in THF (40 mL). After the mixture was stirred for 24 h at room temperature, half of the solvent was evaporated and 50 mL of pentane added. The precipitate which formed was filtered, yielding 0.98 g (68%) of **7** as an orange-red powder (mp 200 °C dec), fairly stable in air, less stable in solution, soluble in CH_2Cl_2, and slightly soluble in Et_2O and acetone: IR (KBr pellet, cm^{-1}) ν(NH) 3297 (w), ν(CO), 1948 (vs), 1875 (vs). MS (chemical ionization with NH_3), m/e (M − Cl)H$^+$ (6.4%), (M − CO)H$^+$ (6.2%), (M − CO − Cl)H$^+$ (6.8%), (M − 2CO)H$^+$ (7.2%), LH$^+$ (87%); each fragment except the last one displayed the characteristic isotopic pattern of molybdenum. ^{31}P NMR (CH_2Cl_2) δ +150 (s, 75%), +145 (s, 25%); ^{1}H NMR (CD_2Cl_2) δ(N–H) 8.6, δ(Cp) 5.83 (s, 48%), 5.78 (s, 22%), 5.59 (s, 22%), 5.54 (s, 8%). Anal. Calcd for $C_{17}H_{26}N_4O_2PClMo$: C, 42.47; H, 5.45; N, 11.65; P, 6.44; Cl, 7.38; Mo, 19.95. Found: C, 42.54; H, 5.57; N, 11.65; P, 6.72; Cl, 7.33; Mo 18.30. Molar conductance (10^{-3} m in acetone): 12.0 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

$(C_5H_5)W(CO)_2Cl$(cyclamphosphine) (8). The same procedure, applied to cyclamphosphorane (0.52 g, 2.33 mmol) and $CpW(CO)_3Cl$ (0.82 g, 2.3 mmol), yielded, after 24 h of refluxing, 0.90 g (70%) of an orange powder, fairly stable in air: mp 215 °C dec; IR (KBr pellet, cm^{-1}) ν(NH) 3300 (m), ν(CO) 1932 (vs), 1853 (vs). MS (chemical ionization with NH_3), m/e MH$^+$ (9.2%), (M − CO)H$^+$ (4.6%), (M − Cl)H$^+$ (38.9%), LH$^+$ (100%); each fragment, except the last one, displayed the characteristic isotopic pattern of tungsten. ^{31}P NMR ($CHCl_3$) δ +122 ($^1J_{P-^{183}W}$ = 330 Hz); ^{1}H NMR ($CDCl_3$) δ(Cp) 5.70 (s,87%), 5.98 (s,13%). Anal. Calcd for $C_{17}H_{26}N_4O_2PClW$: C, 35.90; H, 4.61; N, 9.85; P, 5.45; Cl, 6.23; W, 32.33. Found: C, 36.15; H, 4.53; N, 9.74. P, 5.44; Cl, 6.33; W, 29.65. Molar conductance (10^{-3} m in acetone): 7.3 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

$[(C_5H_5)Mo(CO)_2$(cyclamphosphine)$]BPh_4$ (9). A solution of $NaBPh_4$ (0.24 g, 0.7 mmol) in water (10 mL) was added to the orange-red solution of 0.18 g (0.4 mmol) of **7** in 10 mL of ethanol. A yellow precipitate formed immediately. Water (10 mL), was added and the solution was stirred for 3 h at room temperature. The precipiate was filtered, washed with water to eliminate traces of NaCl and $NaBPh_4$, and dried overnight at 80 °C on a vacuum line, yielding 0.28 g (92%) of **9**: mp 180 °C dec (rather soluble in CH_3CN); IR (KBr pellet, cm^{-1}) ν(CO) 1964 (vs), 1954 (vs), ν(B–Ph) 1480 (m), 1425 (m), 740 (s), 710 (s); ^{31}P NMR (CH_3CN) δ +145 (s); ^{1}H NMR (CD_3CN) δ(Cp), 5.73 (s, 30%), 5.60 (s, 70%). Anal. Calcd for $C_{41}H_{46}N_4O_2PBMo$: C, 64.41; H, 6.06; N, 7.33; B, 1.41; P, 4.05. Found: C, 64.15; H, 6.19; N, 7.32; B, 1.43; P, 4.02. Molar conductance (10^{-3} m in acetone): 84.0 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

$[(C_5H_5)W(CO)_2$(cyclamphosphine)$]BPh_4$ (10). The same procedure as above was applied to $NaBPh_4$ (0.35 g, 1.0 mmol) and **8** (0.32 g, 0.56 mmol). The mixture was heated at 70 °C for 3 h to yield 0.45 g (95%) of a yellow microcrystalline powder (mp 225 °C dec), fairly soluble in CH_3CN and acetone: IR (KBr pellet, cm^{-1}) ν(CO), 1954 (vs), 1850 (vs), ν(B–PH), 1475 (m), 1420 (m), 740 (s), 710 (s); ^{31}P NMR (acetone) +118 (s); ^{1}H NMR (CD_3CN) δ(Cp), 5.86 (s, 54%), 5.72 (s, 46%). Anal. Calcd for $C_{41}H_{46}N_4O_2PBW$: C, 57.77; H, 5.44; N, 6.57; P, 3.63; W, 21.57. Found: C, 57.59; H, 5.23; N, 6.63; P, 3.67; W, 21.57. Molar conductance (10^{-3} m in acetone): 70.4 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

$(C_5H_5)Mo(CO)_2$(cyclamphosphoranido) (3). (a) From 7: A solution (1.6 M) of LiMe in ether (0.20 mL, 0.33 mmol) was added to a solution of **7** (0.14 g, 0.30 mmol) in THF (10 mL) at room temperature. The initial red solution immediately turned brown, with evolution of CH_4 (6.7 mL, 0.30 mmol), identified by IR spectroscopy. After 5 h, the solvent was evaporated, and the residue was extracted with ether or pentane. The solution was filtered and evaporated to yield 0.027 g (20%) of a yellow-orange powder, soluble in THF and $CHCl_3$, slightly soluble in ether, pentane, and CH_2Cl_2, unstable in solution, but indefinitely stable in the solid state under dry nitrogen or argon (mp 150 °C dec).

(b) From 9: A solution of LiMe (1.6 M) in ether (0.20 mL, 0.33 mmol) was added to a suspension of **9** (0.23 g, 0.30 mmol) in THF (20 mL). The solution, initially not homogeneous, turned clear as the addition proceeded and was stirred for 1 h at room temperature. The THF was evaporated, and pentane (50 mL) was added to the residue. The solution was filtered and evaporated to yield a yellow microcrystalline powder (0.12 g, 90%): IR (KBr pellet, cm^{-1}) ν(CO) 1906 (vs), 1802 (vs).

(4) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.

Table I. Summary of Crystal Data, Intensity Collection (at 20 °C), and Structure Solution and Refinement for $(C_5H_5)MoCO_2$(cyclamphosphoranido)

formula	$C_{17}H_{25}O_2N_4PMo$
M_r	444.3
space group	$P2_1/n$
a, Å	13.736 (1)
b, Å	9.354 (2)
c, Å	15.577 (2)
α, deg	90.0
β, deg	113.05 (1)
γ, deg	90.0
Z	4
V, Å^3	1841.7
d_c, g cm^{-3}	1.60
d_0, g cm^{-3}	1.58
crystal size, mm	0.2 × 0.2 × 0.25
2θ limits, deg	50
λ, Å	0.7107
μ, cm^{-1}	4.83
no. of unique data	3253
data with $I > 3\sigma(I)$	2315[34]
refined parameters	241
R	0.067[35]
R_w	0.034[35]
scan mode	$\theta/2\theta$
scan width, deg	2
goodness of fit	1.3

MS (chemical ionization with NH_3), m/e MH^+ (4.6%), $(M - CO)H^+$ (2.7%); each of these fragments displayed the characteristic isotopic pattern due to molybdenum. ^{31}P NMR (THF) δ −31 (s); ^1H NMR (C_6D_6) δ(Cp) 5.1 (s). Anal. Calcd for $C_{17}H_{25}O_2N_4PMo$: C, 45.95; H, 5.67; N, 12.61; P, 6.97; Mo, 21.60. Found: C, 45.46; H, 5.71. N, 12.48; P, 6.94; Mo, 19.88.

$(C_5H_5)W(CO)_2$(cyclamphosphoranido) (4). The same procedure as above (b) was applied to **10** to yield the phosphoranide **4** (88%): mp 200 °C dec; IR (KBr pellet, cm^{-1}) ν(CO), 1900 (vs), 1780 (vs). MS (chemical ionization with NH_3), m/e MH^+ (19.0%), $(M - 2CO)H^+$ (45.6%), each of these fragments displayed the characteristic isotopic pattern of tungsten. ^{31}P NMR (THF) δ −52 ($^1J_{P-^{183}W}$ = 250 Hz); ^1H NMR ($CDCl_3$) δ(Cp) 5.3 (s). Anal. Calcd for $C_{17}H_{25}O_2N_4PW$: C, 38.36; H, 4.73; N, 10.53; P, 5.82; W, 34.54. Found: C, 38.31; H, 4.72; N, 10.60; P, 5.88; W, 33.98.

Crystallographic Analysis of 3. Parallelepipedic orange crystals of **3** were obtained from a saturated solution of **3** in pentane at 0 °C. Preliminary unit cell dimensions and space group $P2_1/n$ were determined from Weissenberg photographs. Cell parameters were refined by a least-squares fitting of the angular position of 25 reflections. Crystal data are recorded in Table I.

The intensity of 3253 reflections (2° < θ < 25°) was collected on an automatic Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. The intensity of three standard reflections was recorded periodically, and no decrease was observed during the data collection. The data were corrected for Lorentz and polarization factors and for anomalous dispersion of the molybdenum atom, but not for absorption.

The structure was solved by the heavy-atom method. Fourier synthesis allowed the location of all the non-hydrogen atoms. The structure was refined by using the XFLSN program,[5] with Mo, P, N, C, and O atoms anisotropic (anomalous scattering factor included for Mo).

Refinement with 2315 reflections ($I > 3\sigma(I)$) reached the $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ values of 0.044 and 0.068, respectively. At this stage of refinement a Fourier difference map showed the hydrogen atoms; they were introduced isotropically (6 Å^2) in the refinement but not refined. Finally, the R_w and R factors reached the values of 0.034 and 0.067.

The final atomic coordinates and thermal parameters are reported in Table II, with esd's in parentheses. The numbering scheme is the same as in Figure 1, which shows two ORTEP views of the molecule. Interatomic distances and angles are given in Table III.

Results and Discussion

Aspects of the coordination chemistry of cyclamphosphorane/cyclamphosphine mixtures, displacement of the tautomeric equilibria A, and mono- and bidentate behavior of **1b** are discussed.

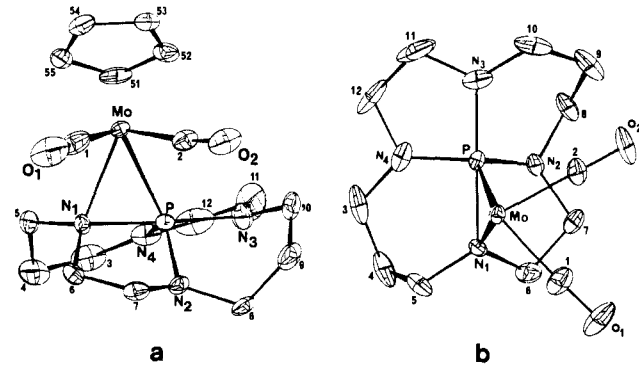
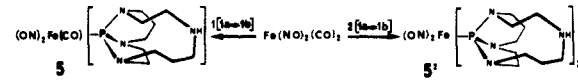


Figure 1. ORTEP representations and atomic numbering for two views of **3** showing the trigonal-bipyramidal arrangement of the bonds on phosphorus and the $\overset{Mo}{N}$—P bridge (in b, the C_5H_5 ring has been omitted for clarity).

Iron and Nitrosyl Adducts. Coordination through Phosphorus Only. It is well established that tertiary phosphines readily replace one or two CO groups in $Fe(NO)_2(CO)_2$ to yield $Fe(NO)_2(CO)PR_3$ and $Fe(NO)_2(PR_3)_2$, while adducts of type $Fe(NO)_2(CO)L$, where L is an amine, could seldom be isolated because of their instability.[6] Previous experience in a situation similar to that found with cyclamphosphorane, in which other phosphorane precursors led to adducts of tautomeric phosphane/amine ligand, showed that the carbonyl groups of $Fe(NO)_2(CO)_2$ could be substituted by these ligands, which then acted as monodentates through their phosphorus donor site only.[7,8]

Depending on the stoichiometry used, the reaction of $Fe(NO)_2(CO)_2$ with solutions of cyclamphosphorane **1a** in toluene at 80 °C did indeed afford the mono- or disubstitution products **5** or **5′** (eq B) in which the ligand **1b** is bound solely through



phosphorus. In both cases the high yields indicate that equilibrium A had been displaced toward the initially minor open tautomer **1b**.

The proposed formulations of **5** and **5′** are ascertained by their elemental analysis and mass spectra. The ^{31}P NMR spectra display single signals at +159 and +175 ppm for **5** and **5′**, respectively, significantly shifted toward lower fields with respect to **1b** (+111 ppm). In comparison with the IR spectrum of $Fe(NO)_2(CO)_2$, those of **5** and **5′** show the disappearance of one or two CO groups, respectively, and a gradual shift toward lower frequencies of the remaining carbonyl and of the nitrosyl vibrations, as expected from the substitution of the carbonyls by less π-accepting ligands (each substitution provoking a ca. 50-cm^{-1} shift of the remaining CO and NO absorptions). The low ν(CO) and ν(NO) values of **5** and **5′**, close to those of analogous trialkylphosphine iron adducts, indicate, according to the usual σ/π bonding model, that cyclamphosphine has high-donor/low-acceptor character, which can be rationalized as resulting from strong Np_π–Pd_π interactions inside the ligand. The high frequency of the ν(NH) vibration at 3340 cm^{-1} in solution is typical of a free NH vibrator. The occurrence of two ν(NH) absorptions in **5** in the solid state (3340 and 3120 cm^{-1}) is not uncommon[8] and may reflect intermolecular interactions, as through hydrogen bonds, in the crystal structure.

Bidentate Behavior of Cyclamphosphine in the Presence of Rhodium Carbonyl Chloride. Rhodium dicarbonyl chloride, when allowed to react with phosphine/amine ligands or precursors

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Table II. Atomic Coordinates and Anisotropic Thermal Parameters with esd's (in parentheses)[a] for $(C_5H_5)Mo(CO)_2$(cyclamphosphoranido)

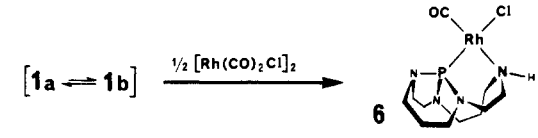
atom	x	y	z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Mo	7945 (1)	8403 (1)	9739 (1)	47 (1)	78 (1)	25 (1)	−9 (1)	11 (1)	2 (1)
P	7165 (1)	6170 (2)	9982 (1)	43 (1)	84 (3)	27 (1)	−9 (1)	14 (1)	−6 (1)
N1	6517 (4)	7894 (6)	10022 (3)	47 (3)	110 (9)	31 (3)	27 (5)	14 (3)	9 (4)
N2	7248 (5)	5854 (7)	11081 (4)	56 (5)	110 (9)	29 (3)	3 (6)	10 (3)	17 (5)
N3	7819 (7)	4648 (7)	9946 (6)	111 (8)	114 (11)	91 (6)	25 (8)	58 (6)	−11 (7)
N4	6111 (6)	5530 (8)	9098 (4)	100 (7)	162 (12)	42 (4)	−49 (8)	29 (5)	−25 (6)
C1	8113 (8)	9941 (10)	10621 (6)	150 (10)	103 (13)	64 (6)	−48 (10)	45 (7)	−9 (7)
C2	9167 (6)	7876 (9)	10811 (6)	55 (6)	138 (14)	48 (5)	−33 (7)	8 (5)	10 (6)
C3	4986 (8)	5961 (14)	8690 (6)	64 (8)	331 (25)	54 (6)	−58 (12)	−15 (5)	29 (10)
C4	4683 (7)	7241 (15)	9109 (7)	43 (7)	354 (26)	65 (7)	−11 (11)	1 (5)	42 (10)
C5	5516 (6)	8335 (11)	9275 (5)	60 (6)	188 (14)	62 (5)	45 (10)	23 (5)	44 (8)
C6	6472 (7)	8105 (9)	10948 (6)	86 (7)	145 (16)	63 (5)	24 (9)	49 (5)	0 (7)
C7	7263 (6)	7134 (8)	11615 (5)	94 (8)	125 (13)	37 (4)	−24 (8)	35 (5)	−16 (6)
C8	7865 (6)	4657 (9)	11606 (5)	54 (6)	151 (14)	57 (5)	−9 (8)	7 (5)	58 (7)
C9	8945 (7)	4535 (11)	11592 (8)	68 (8)	210 (18)	106 (8)	24 (10)	8 (7)	88 (10)
C10	8874 (9)	4414 (10)	10590 (9)	113 (10)	93 (14)	158 (11)	43 (10)	74 (9)	44 (10)
C11	7386 (13)	3896 (12)	9081 (10)	286 (20)	150 (19)	128 (11)	56 (17)	114 (13)	−44 (11)
C12	6298 (11)	4322 (13)	8639 (7)	240 (16)	158 (19)	70 (7)	−91 (15)	85 (10)	−70 (10)
O1	8249 (6)	10840 (7)	11183 (5)	237 (10)	153 (11)	96 (5)	−85 (9)	83 (6)	−62 (6)
O2	9972 (4)	7628 (7)	11440 (4)	63 (5)	275 (13)	59 (3)	−48 (6)	−16 (3)	46 (5)
C51	7370 (9)	7904 (11)	8148 (5)	92 (9)	230 (20)	24 (4)	−60 (10)	21 (5)	8 (7)
C52	8423 (8)	7607 (10)	8551 (6)	102 (10)	138 (15)	53 (5)	−10 (10)	52 (6)	−12 (7)
C53	8974 (6)	8802 (10)	8877 (5)	55 (6)	165 (17)	40 (4)	−22 (8)	19 (4)	10 (7)
C54	8257 (9)	9915 (9)	8676 (6)	118 (10)	119 (14)	56 (6)	−14 (10)	45 (6)	14 (7)
C55	7245 (8)	9374 (13)	8218 (6)	66 (8)	261 (21)	52 (6)	58 (11)	30 (6)	77 (9)

[a] Anisotropic thermal parameters are of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Table III. Selected Bond Lengths (Å) and Angles (deg) with esd's for $(C_5H_5)Mo(CO)_2$(cyclamphosphoranido)

P–Mo	2.444 (2)	$MoPN_1$	60.5 (2)
$P–N_1$	1.854 (5)	$MoPN_2$	116.4 (2)
$P–N_2$	1.697 (6)	$MoPN_3$	116.2 (2)
$P–N_3$	1.696 (7)	$MoPN_4$	118.0 (2)
$P–N_4$	1.670 (7)		
		N_1PN_3	176.6 (3)
N_1–Mo	2.223 (5)	N_2PN_4	117.6 (3)
$N_1–C_5$	1.470 (8)	N_1PN_2	87.8 (3)
$N_1–C_6$	1.482 (8)	N_1PN_4	93.8 (3)
		N_2PN_3	93.5 (3)
$Mo–C_1$	1.940 (9)	N_3PN_4	88.4 (4)
$Mo–C_2$	1.911 (8)		
$C_1–O_1$	1.175 (9)	MoN_1P	73.0 (2)
$C_2–O_2$	1.178 (8)	MoN_1C_5	114.1 (4)
		MoN_1C_6	122.7 (4)
$N_2–C_7$	1.453 (9)		
$N_2–C_8$	1.448 (9)	$PMoN_1$	46.5 (1)
$N_3–C_{10}$	1.421 (12)	$PMoC_1$	117.5 (2)
$N_3–C_{11}$	1.426 (13)	$PMoC_2$	86.1 (2)
$N_4–C_3$	1.478 (11)	C_1MoC_2	75.6 (4)
$N_4–C_{12}$	1.414 (12)		
		PN_1C_6	110.6 (5)
$C_3–C_4$	1.499 (14)	$C_6N_1C_5$	110.5 (5)
$C_4–C_5$	1.480 (13)	C_5N_1P	122.0 (5)
$C_8–C_9$	1.498 (12)		
$C_9–C_{10}$	1.529 (14)	PN_2C_7	114.5 (5)
$C_6–C_7$	1.484 (10)	$C_7N_2C_8$	116.1 (6)
$C_{11}–C_{12}$	1.435 (16)	C_8N_2P	119.8 (5)
$C_{51}–C_{52}$	1.361 (12)	PN_3C_{10}	120.9 (7)
$C_{52}–C_{53}$	1.334 (10)	$C_{10}N_3C_{11}$	121.6 (9)
$C_{53}–C_{54}$	1.383 (11)	$C_{11}N_3P$	114.5 (8)
$C_{54}–C_{55}$	1.385 (12)		
$C_{55}–C_{51}$	1.395 (12)	PN_4C_3	132.8 (7)
		$C_3N_4C_{12}$	111.5 (8)
		$C_{12}N_4P$	115.6 (7)

thereof, readily gave adducts in which the ligand displays a bidentate chelating behavior.[9] Immediate evolution of carbon monoxide was observed when the equilibrated mixture **1a** ⇌ **1b** was added to $[Rh(CO)_2Cl]_2$ in a Rh/**1** ratio of 1:1 in toluene at room temperature; no **1a** was left in the reaction mixture once the reaction was complete, and the phosphorus- and nitrogen-bound rhodium chelate **6** (eq C) was indeed formed. The ana-



lytical and spectral data of **6** agree with the opening of the phosphorane form and with the bidentate character of the resulting ligand, which is assessed in particular in the IR spectrum by the absence of a ν(PH) vibration, the presence of a single ν(NH) vibration and its position at 3190 cm^{-1}, and by the presence of single ν(CO) and single ν(RhCl) absorptions at 1970 and 285 cm^{-1}. The single ^{31}P chemical shift at +130 ppm lies in the range usually found for metal-bound tris(dialkylamino)phosphines[10] and displays a $^1J_{P-Rh}$ coupling of 200 Hz. Only one positional isomer was detected, the same in the crude reaction mixture and in solutions of the isolated crystalline material, to which structure **6** (with the NH site trans to the carbonyl group) has been assigned on the basis of the antisymbiotic rule,[11] as well as by analogy with the structures established by X-ray diffraction analysis for related rhodium chelates.[9,12]

Formation of Both Neutral Phosphorus-Bound and Ionic Phosphorus- and Nitrogen-Bound Adducts from Cyclopentadienylmolybdenum Tricarbonyl Chloride. The substitution reactions of η^5-$CpMo(CO)_3Cl$ with bidentate group VA (15) ligands[36] have been thoroughly investigated. The most π-accepting diphosphines tend to substitute for carbonyls only;[13a] diamines such as bipyridines, on the contrary, displace the chloride ion to give cationic products,[13b] while both neutral and ionic compounds are obtained with the moderately π-accepting diphosphines.[13c] The open cyclamphosphine form, which offers a combination of π-accepting and non-π-accepting sites, was expected to yield a carbonyl and chloride substituted cationic chelate favorable to proton abstraction to yield phosphoranide adducts (see next section).

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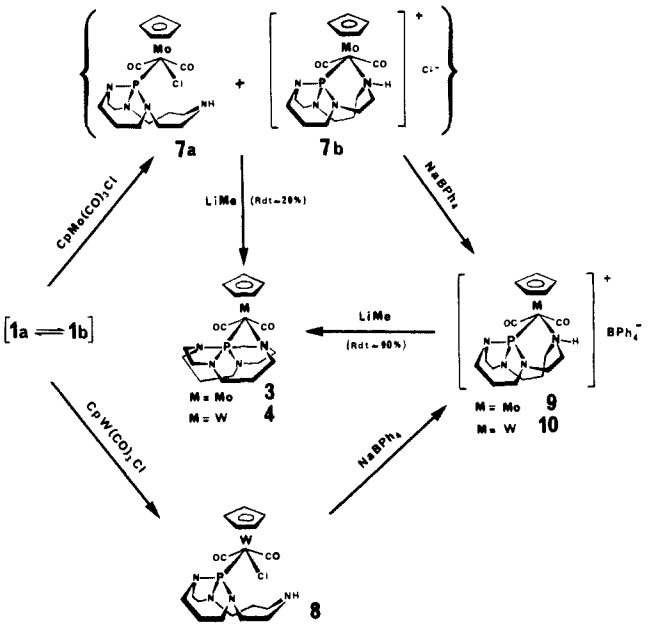
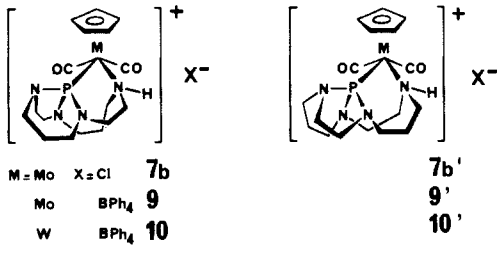
Scheme I



One equivalent of carbon monoxide was evolved when a THF solution of $CpMo(CO)_3Cl$ and cyclamphosphorane was stirred at room temperature. The elemental analysis and mass spectrum of the isolated orange-red compound support of $CpMo(CO)_2$-(cyclamphosphine)Cl formulation. The ^{31}P NMR spectrum (with two signals at 150 (75%) and 145 (25%) ppm) and the conductometric measurements in acetone, which indicate the presence of an ionic species (20% if calculated for **7b**), point to the existence

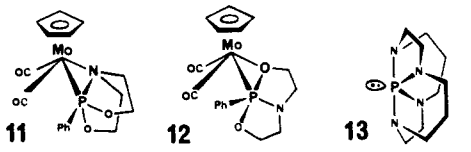


in solution of a mixture of constitutional isomers (Scheme I), a covalent one (**7a**), corresponding to a monodentate phosphorus-bound behavior of **1b**, and an ionic one (**7b**), in which the ligand acts as a phosphorus- and nitrogen-bound bidentate. The infrared spectrum measured on the orange-red powder exhibits two ν(CO) vibrations (1948 and 1875 cm^{-1}) and only one ν(NH) absorption, at 3297 cm^{-1}, characteristic of a noncoordinated nitrogen atom. The ^1H NMR pattern of **7** in CD_2Cl_2 is complex. In the Cp region it shows four singlets, which were attributed to the presence of a pair of cis diastereoisomers both in the case of **7a** (48% + 22%) and in that of **7b** (22% + 8%) (**7b** and **7b'**) (Mo, P, and NH are all asymmetric, but P and NH not independently). The trans isomers, which usually exhibit J_{HP} couplings,[14,15] were not detected.

The same reaction when carried out with $CpW(CO)_3Cl$ led to the neutral product **8** only. Conductometric data exclude the presence of any significant amount of ionic compound in the material isolated. The ^{31}P NMR spectrum exhibits a singlet at 121.5 ppm with the expected two satellite peaks ($^1J_{P-^{183}W}$ = 330 Hz). The ^1H NMR spectrum shows two signals in the Cp region, attributed to the presence of both cis diastereoisomers of the neutral form in which the ligand displays monodentate behavior. The absorption at 3300 cm^{-1} in the IR spectrum corresponds to an uncoordinated ν(NH) vibration.

Formulations **7a** + **7b** and **8** are further confirmed by their quantitative conversion, under the action of $NaBPh_4$, to the spectroscopically closely related ionic molybdenum and tungsten adducts **9** and **10**.

Access to Transition-Metal Cyclamphosphoranides. The phosphoranide ions are 10-electron valence-shell, monoanionic, 4-coordinated phosphorus(III) species.[16] Their lone electron pair and partially vacant d orbitals make them potential σ-donor π-acceptor ligands.[17] Coordination to transition metals can also be envisaged as a means of stabilizing them. The first transition-metal complexes of phosphoranide ligands, **11** and **12**, were



derived from bicyclic aminophosphoranes.[17-19] The approach used to achieve this new class of compounds was to abstract a N-bound proton from a phosphine/secondary amine metal chelate and to provoke the intramolecular addition of the resulting amide ligand to the metal-bound phosphorus atom.

After several unsuccessful attempts to obtain the cyclamphosphoranide anion **13** directly from **1** under the action of strong bases such as $NaNH_2$, LiMe, or LiBu and then coordinating it to a metal substrate, we adopted the above-mentioned approach and reported in a preliminary note that it led successfully to the cyclamphosphoranides **3** and **4** (Scheme I).[4] Further examples of transition-metal phosphoranides which use the same[20,21] or different approaches[22] have since been reported.

As starting material we chose the cationic complexes **9** and **10**, which we obtained quantitatively from **7** and **8**, respectively, under the action of $NaBPh_4$. In **9** and **10** the phosphorus and nitrogen donor sites are positioned properly on the metal to allow the envisaged intramolecular reaction to occur. Phosphoranide **3** was isolated in over 90% yields as moderately sensitive yellow-orange crystals, soluble in THF and $CHCl_3$, slightly soluble in ether, pentane, and CH_2Cl_2. It appears to be indefinitely stable at room temperature under nitrogen or argon; its stability is also shown by its relatively high decomposition point, around 150 °C. The ^{31}P NMR spectrum of **3** exhibits a single peak at −31 ppm, i.e., shifted by 22 ppm only (1 ppm only in the case of **4**) toward lower fields with respect to *phosphorane* **1a** and located 176 ppm upfield from the cationic *phosphine* adduct **9**. These shifts are in line with those measured for other transition-metal phosphoranides.[23] The ^1H NMR spectrum shows a single signal in the Cp region at 5.1 ppm, indicating that only one of the two possible diastereoisomeric structures is present. In the IR spectrum, both ν(CO) vibrations are shifted by ca. 50 cm^{-1} toward lower frequencies relative to those found in **9**, as expected from the decrease in positive charge of the metal. The structure of **3** was definitely established from an X-ray diffraction analysis.

The isolation in 90% yields of only one diastereoisomer, namely **3**, of the two possibilities **3** and **3'**, from a 70:30 mixture of the

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ionic diastereoisomers **9** and **9'** supposes an interconversion among diastereoisomers. This could occur in **9** by dissociation of the Mo–N bond followed by an inversion of the configuration at Mo; less likely would be a change of the configuration of Mo in phosphoranide **3**.

Phosphoranide **3** was also obtained directly from the mixture **7a** + **7b** under the action of LiMe but in low yields only (ca. 20%) along with unidentified decomposition products. In line with this observation, the tungsten analogue **4** could not be obtained directly from **8**, which contains solely the neutral complex. But **4** was prepared and isolated in 93% yield after **8** had been converted into the cationic product **10**, which was then treated with LiMe. The analytical and spectral characteristics of **4** are, as expected, very close to those of **3**. Again, a high-field ^{31}P chemical signal is found (−52 ppm), shifted by 1 ppm only toward lower fields with respect to **1a** and located 170 ppm upfield from the cationic phosphine adducts **10** and **10'**. The phosphorus–metal bond is further established by the $^{1}J_{P-^{183}W}$ coupling of 250 Hz. Again, a single Cp signal is found in the ^{1}H NMR spectrum, and the infrared shows for the ν(CO) absorptions the same shifts as for **3** toward lower frequencies; below 1400 cm^{-1} the infrared spectra of **3** and **4** are almost superimposable.

Crystal and Molecular Structure of Cyclopentadienyldicarbonylmolybdenum Cyclamphosphoranide (3). Compound **3** consists of discrete neutral units based on one molybdenum atom each. A summary of crystal data and intensity collections are given in Table I, the atomic coordinates, thermal parameters, and standard deviations in Table II, and selected bond lengths and bond angles in Table III.

Among the most remarkable features of structure **3** are the 5-connected character, i.e., phosphoranide nature, of the metal-bound phosphorus atom and the simultaneous coordination of one of the phosphorus-bound nitrogens to the metal to form a three-membered P(—M)—N cycle. These features establish that the expected reactions took place and in particular that a new P–N bond had formed under the action of LiMe on the cationic phosphine adduct **9**. If we postulate, in agreement with the spectral data and the diamagnetic character of **3**, that the electronic structure and oxidation state of molybdenum have not changed during this process, and since the resulting adduct is neutral, we are led to consider that the phosphorus ligand, which has substituted a chloride ion, is formally also anionic and hence must be written as a lone-pair-bearing phosphoranide ion **13** and that this phosphorus atom is in a formal oxidation state of 3.

The three-membered P(—M)—N ring is only the second example known of such an arrangement,[18] while metal-bridged hydrazido ligands N(—M)—N[24] and diphosphido ligands P(—M)—P[25] are already known. The stabilizing of a P(—M)—N cycle is notable in view of the low basicity usually displayed by phosphorus-bound nitrogen atoms.[26] This occurrence certainly results in great part from the approach used in which both phosphorus and nitrogen were coordinated to the metal before being bound together. The formation of this bridge is accompanied by a lengthening of the P–N bond (1.85 Å) with respect to "normal" ›P–N‹ single bonds. The P–N length here lies in the upper range of those found for apical

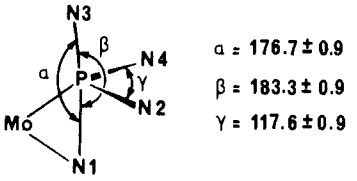

Figure 2. Valence angles around phosphorus in **3** showing the distortions from the ideal TP.

P(V)–N bonds found in other tetracyclic tetraaminophosphorane derivatives (1.70–1.87 Å).[27-29] There can be no unambiguous interpretation of this lengthening, which probably results from several contributions: the involvement of the nitrogen's lone pair in bonding with the metal prevents any significant Np_{π}–Pd_{π} contribution; apical single bonds between a bipyramidal P(III) and a tetrahedral N(III) are expected to be long, if only because the s character of the bonding orbitals at phosphorus should be low, and longer than those observed for apical P(V)–N bonds; besides, the strain of the three-membered cycle will also tend to distend the P–N bond. This ring, with a sharp Mo–N1–P angle of 73°, is probably also responsible for the flattening of the quaternized nitrogen atom's tetrahedron when compared to the quaternized apical nitrogen atoms found in bis(borane)cyclenphosphorane.[29]

The other apical P–N3 bond is notably short (1.70 Å), and comparable in length to the usually much shorter equatorial P–N bonds (1.67 and 1.70 Å). Also remarkable is the close-to-planar configuration of this N3 apical nitrogen atom (sum of angles $\sum$N3 = 357.0 ± 7.2°), which may indicate that some Np_{π}–Pd_{π} interaction has become operative. It also shows, as is often found in phosphorus chemistry, that some mechanism has set in which compensates for the longer PN1 bond in the trans position and reestablishes the electronic balance at phosphorus. It is also noteworthy that it is not the apical N3 atom but one of the equatorial ones, N2, that departs most from planarity ($\sum$N2 = 350.4 ± 4.8°). The difference between P–N4 and P–N2 is small but significant, the shorter one corresponding to the more planar nitrogen atom ($\sum$N4 = 359.9 ± 6.6°), in line with previous observations.[29]

The Mo–P bond (2.44 Å) is short when compared to those found in phosphine adducts of analogous molybdenum(II) moieties (2.45–2.52 Å).[30] It is, however, impossible to apportion such effects between contributions due to the difference in hybridization of the P atom, to differences in its σ-donor and π-acceptor character, and to the effects of the strain due to the three-membered ring. The Mo–N bond falls in the range usually found for molybdenum amine adducts but is longer than that found in a molybdenum(II) adduct containing a bridging hydrazido group.[24]

In spite of the phosphorus atom's incorporation into five rings simultaneously, its bonding arrangement is surprisingly close to a regular trigonal bipyramid (Figure 1). Thus the N1, P, and N3 atoms are almost in line, and the angles in the equatorial plane are close to 120° (118.0 ± 0.6°; 116.4 ± 0.6°; 117.6 ± 0.9°) in spite of the P(—Mo)—N ring. The distortion of a trigonal bipyramid is usually described in % displacement along the Berry coordinate[31] that extends from the ideal trigonal bipyramid (TP, 0%) toward the square pyramid (SP, 100%), following the low-energy axial/equatorial bending path. Molybdenum will here be taken as the pivotal atom in the pseudorotation process. However, because of the highly strained 3-membered ring, with an internal angle at phosphorus of 61°, the idealized SP does not provide a rigorously adequate reference with respect to which distortions can

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Table IV. Concomitant Evolution of Internal Angles at Phosphorus, β and γ in Four Tetracyclic Tetraaminophosphoranes

	% along Berry coordinate	β,[a] deg	γ,[b] deg	ref
fluorocyclen-phosphorane	50	169.7[c]	145.2[c]	27
dicyclenphosphorane	32.9	169.6 ± 0.3	131.1 ± 0.3	28
bis(borane)cyclen-phosphorane	10.4	176.8 ± 0.9	125.6 ± 0.9	29
3	−15	183.3 ± 0.9	117.6 ± 0.9	this work

[a] Internal axial NPN angle at phosphorus (Figure 2). [b] Internal equatorial NPN angle at phosphorus (Figure 2). [c] No eds's were reported by the authors.

be estimated. If one nevertheless applies the dihedral angles method and unit bond lengths,[32] one finds that structure **3** is distorted by −15% along the Berry coordinate. This *negative* value means that this structure is not located between the idealized TP and SP structures but "before" the TP, i.e., that the N1-P-N3 angle closes "on the other side" with respect to the N2-P-N4 angle[33] (Figure 2). This small but significant tilt of the P-N3 bond toward the molybdenum atom may simply result from a better occupation of space after the equatorial P-Mo bond is bent down. The resulting relief in interactions between the apical/equatorial P-N bonds can also be seen in the smaller equatorial N2-P-N4 angle. The correlation between the increase in angle between the apical bonds and decrease in angle between the equatorial bonds when related molecules are compared (Table IV) is remarkable; compound **3** provides an extreme situation where the former is "larger" than 180° (183.3 ± 0.9°), and the latter is smaller than 120° (117.6 ± 0.9°).

The diastereoisomer that has formed comes as the enantiomeric pair in which the more space-demanding cyclopentadienyl ring lies on the side of a more flexible six-membered ring while the carbonyls lie atop a five-membered ring. The planar or close-to-planar geometry of the nitrogen atoms prevents satisfactory description of these five- and six-membered rings in terms of the usual chair or envelope conformations. The tetracyclic cyclam structure is distorted by the metal bridge, as shown by the difference between the angles formed by the mean planes of the fused cycles P, N4, C3, C4, C5, N1 and P, N1, C6, C7, N2 (97.6°), and by that of the fused cycles P, N3, C11, C12, N4 and P, N2, C8, C9, C10, N3 (120.5°).

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Registry No. 1a, 64317-99-3; **3**, 100016-82-8; **4**, 100016-83-9; **5**, 99829-54-6; **5′**, 99829-55-7; **6**, 99829-56-8; **7a**, 81121-01-9; **7b**, 99883-33-7; **7b′**, 99829-58-0; **8**, 99829-57-9; **9**, 81121-03-1; **10**, 81121-05-3; $Fe(NO)_2(CO)_2$, 13682-74-1; $CpMo(CO)_3Cl$, 12128-23-3; $CpW(CO)_3Cl$, 12128-24-4; $[Rh(CO)_2Cl]_2$, 14523-22-9.

Supplementary Material Available: Listings of observed and calculated structure factors, tables of atomic coordinates for hydrogen atoms, nonessential angles, and least-squares planes (17 pages). Ordering information is given on any current masthead page.

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(34) There are very few usable reflections beyond $\theta = 20°$, because of the inferior crystal quality and the use of Mo Kα radiation. This is not crucial, because there are a sufficient number of reflections left to carry out the refinement under good conditions; ten data were used to obtain each variable.
(35) The refinements were carried out with the weight $w = 1/\sigma^2$ for each reflection, and no corrections were made in the weights. The fact that the R factor is about twice the R_w factor is not unusual in such molecular crystals.
(36) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is elimination because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Crystal Structure of Bis(trimethylammonium) Decabromotetracuprate(II): A Review of Stacking Patterns in Pseudoplanar $Cu_nX_{2n+2}^{2-}$ and $Cu_nX_{2n}L_2$ Oligomers

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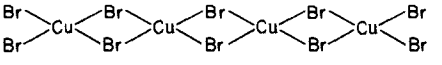
Abstract: The stacking of planar, bibridged copper(II) halide oligomers is reviewed. Within each oligomer, the copper ions assume a nearly square-planar coordination. Interoligomer contacts lead to further semicoordination, yielding a 4 + 1 or 4 + 2 coordination for the copper ions. A wide variation in stacking patterns is observed, associated with many possible ways of forming the semicoordinate bonds. A simple graphic representation illustrating the stacking patterns is introduced, as well as a more detailed formal specification of the patterns. The crystal structure of a compound containing a new variant of these stacking patterns is also presented. $[(CH_3)_3NH]_2Cu_4Br_{10}$ is monoclinic, space group $P2_1/c$ with a = 9.556 (3) Å, b = 14.703 (4) Å, c = 18.173 (5) Å, β = 99.75 (3)°, Z = 4, and ρ_{calcd} = 3.11 g/cm^3. The structure, refined to an R value of 0.049, contains the nearly planar $Cu_4Br_{10}^{2-}$ oligomers,



These stack such that three of the four copper ions have a 4 + 2 coordination geometry, while the fourth has only a 4 + 1 coordination geometry.

I. Introduction

The crystal chemistry of copper(II) halides is extremely diverse and complex. This is certainly due, at least in part, to the presence of an active Jahn-Teller effect in these d^9 electronic systems. Thus, true octahedral complexes are not known; rather distortions of the nominally six-coordinate complexes occur, leading, generally, to an elongation of the copper-ligand (Cu-L) bond lengths along one axis. This gives a typical 4 + 2 coordination geometry with

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