only one of them is presented (Figure 2).

The positional parameters for all non-hydrogen atoms of both compounds are listed in Tables I and II. Selected bond distances and angles are reported in tables III–VI, respectively.

The tetragonally distorted octahedrally coordinated divalent metal ion, M (M = Ni Co), is placed at the crystallographic inversion center. It is coordinated with two pyridine groups in the axial direction and by four oxygen atoms of the β-diketone moieties of the two $bhpp^{3-}$ ligands in the basal plane. The M–O bond lengths are quite normal for high-spin Ni(II) and Co(II) metal ions. Both exhibit almost the same metal–oxygen distance (2.020 Å on average) as in the case of Lintvedt's complexes.[1] Similar distances are found in simple acetylacetonate complexes, $M(acac)_2$.[12–14] The M–N axial bond distance slightly increase in the order Ni < Co (2.141 and 2.179 Å, respectively).

The uranyl ions occupy the outer coordination positions with two ketonic oxygens, two phenolic oxygens, and one pyridine nitrogen comprising the five equatorial donor atoms in a distorted-pentagonal-bipyramidal coordination sphere geometry. The bond distances and angles around the uranium atoms in both commpounds are virtually identical. The by symmetry identical U–Ni and U–Co distances are 3.587 (3) Å in both cases.

The ligand molecule and the three metal atoms are essentially coplanar. Two additional pyridine molecules are occupying interstitial lattice positions.

The most significant conclusion to draw from the structural results is that the ligand molecule is able to accommodate with little trouble three metal ions showing a polynucleating behavior. The flexibility of the carbon backbone is sufficient to permit metal–oxygen bond lengths as different as the ≃2.50 Å observed for U–O and the ≃2.02 Å in M–O (M = Ni, Co). This is accomplished by forcing the ends of the ligands out so that the four oxygens atoms (the two ketonics and the two phenolics) of each molecule are not linear, as is evident in Figure 2. On the other hand the synthesis-directing capacity is emphasized in the formation of mononuclear complexes and heterotrinuclear complexes of the type M′–M–M′.

Acknowledgment. This work has been supported by Grant No. 409/84 (CAICYT) from the Spanish Government.

Registry No. $[(UO_2)_2Co(bhpp)_2]\cdot 6py$, 118474-61-6; $[(UO_2)_2Ni(bhpp)_2]\cdot 6py$, 118474-63-8; $[(UO_2)_2Zn(bhpp)_2]\cdot 6py$, 118474-64-9; $Zn(bhppH_2)_2\cdot 2MeOH$, 118474-65-0; $Co(bhppH)_2\cdot 2MeOH$, 93401-36-6; $Ni(bhppH_2)_2\cdot 2MeOH$, 118474-66-1.

Supplementary Material Available: Listings of anisotropic thermal parameters (2 pages); listings of observed and calculated structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

---

(12) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 2316.
(13) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 1117.
(14) Onuma, S.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2395.

Contribution from the Department of Chemistry,
Southern Methodist University, Dallas, Texas 75275

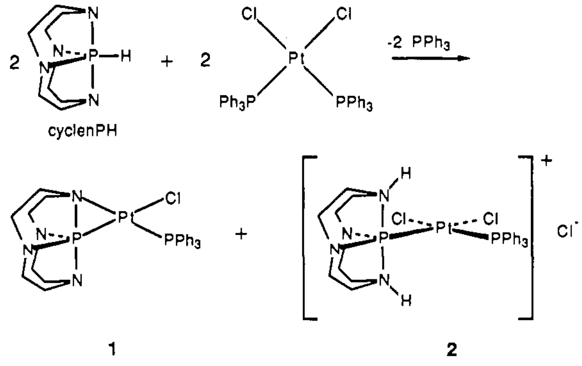
Phosphoranide Ligands with Variable Coordination Modes. Synthesis, Properties, and X-ray Crystal Structures of $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ and $[(H_2cyclenP)PtCl_2PPh_3]Cl$

Dilip V. Khasnis, Michael Lattman,* and Upali Siriwardane

Received July 29, 1988

The complex $(\eta^2\text{-cyclenP})Pt(Cl)PPh_3$ (**1**) is readily formed by the deprotonation of $[(H_2cyclenP)PtCl_2PPh_3]Cl$ (**2**) with NaOH in CH_2Cl_2. Both complexes contain phosphoranide ($R_4P{:}^-$) ligands. Complex **1** reacts with HBF_4 to give the monoprotonated derivative $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ (**3**), a species in which one of the P–N bonds of the cyclenP unit is cleaved and the proton is attached to that nitrogen. Treatment of **3** with HCl in THF gives $[(H_2cyclenP)PtCl_2PPh_3]BF_4$ (**4**) (which contains a cation identical with that of **2**), while treatment of **3** with NaCl in Me_2SO leads to **1** and **2** via disproportionation. The X-ray crystal structures of **2** and **3** were obtained. Data for **2** indicate that the axial nitrogens are protonated and the cyclenP unit is oriented with its P–N axial bonds perpendicular to the platinum coordination plane. Data for **3** show that the HcyclenP unit is coordinated to the platinum via phosphine and amine linkages and that the phosphorus is four-coordinate. X-ray data: $C_{26}N_4P_2Cl_3Pt$ (**2**), orthorhombic, space group *Pcab*, $a = 15.391$ (4) Å, $b = 17.021$ (6) Å, $c = 25.226$ (14) Å, $Z = 8$, $R = 0.087$, $R_w = 0.089$; $C_{26}H_{31}BN_4F_4P_2ClPt$ (**3**), monoclinic, space group $P2_1/c$, $a = 14.873$ (3) Å, $b = 13.021$ (3) Å, $c = 15.723$ (3) Å, $\beta = 106.654$ (14)°, $Z = 4$, $R = 0.044$, $R_w = 0.046$.

We recently reported the synthesis of the new phosphoranide[1,2] complexes $(\eta^2\text{-cyclenP})Pt(Cl)PPh_3$ (**1**) and $[(H_2cyclenP)PtCl_2PPh_3]Cl$ (**2**) according to reaction 1.[3a,b] In addition, we found that **1** could be converted directly to **2** by reaction with HCl. However, attempts to isolate a monoprotonated intermediate in this conversion were unsuccessful since addition of less than 2 equiv of HCl led to only **2** and unreacted **1**. Moreover, a monoprotonated adduct of **1** may be important in reaction 1 as well.



(1)

Isolation of this species is important to the understanding of the mechanism of the syntheses and reactions of transition-metal complexes with phosphoranide ligands.[3] We herein report (1) the synthesis, reactions, NMR properties, and X-ray crystal structure of a monoprotonated adduct of **1**, $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$

---

(1) Phosphoranide ions are 10-P-4 phosphorus anions, isoelectronic with the neutral sulfuranes. See ref 2 and references therein.
(2) Lattman, M.; Olmstead, M. M.; Power, P. P.; Rankin, D. W. H.; Robertson, H. E. *Inorg. Chem.* **1988**, *27*, 3012.
(3) (a) Lattman, M.; Chopra, S. K.; Burns, E. G. *Phosphorus Sulfur* **1987**, *30*, 185. (b) Lattman, M.; Burns, E. G.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Inorg. Chem.* **1987**, *26*, 1926. (c) Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M. *Organometallics* **1986**, *5*, 2383. (d) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (e) de Meester, P.; Lattman, M.; Chu, S. S. C. *Acta Cryst., Sect. C* **1987**, *C43*, 162.

0020-1669/89/1328-0681$01.50/0 © 1989 American Chemical Society

(**3**), (2) a new method for the deprotonation of phosphoranide ligands, which leads to the direct conversion of **2** to **1**, and (3) the X-ray crystal structure of **2**, which allows a detailed comparison of three different coordination modes of cyclenP. Also reported is the synthesis of [$(H_2cyclenP)PtCl_2PPh_3]BF_4$ (**4**), which is the BF_4 salt of the cation of **2**.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The starting material **1** was prepared by the literature method.[3b] All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer resonating at 200.13 (^1H) and 81.026 (^{31}P) MHz. ^{31}P spectra are proton-decoupled unless otherwise indicated. ^1H resonances were measured relative to residual proton solvent peaks, referenced to Me_4Si, while ^{31}P resonances were measured relative to external 85% H_3PO_4. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Conversion of [$(H_2cyclenP)PtCl_2PPh_3]Cl$ (2) to (η^2-cyclenP)Pt(Cl)PPh_3 (1). A slurry of **2** (210 mg, 0.275 mmol) and dry, finely powdered NaOH (20 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was stirred for 12 h in the presence of 3-Å molecular sieves (to absorb water) and then filtered. The resulting solution was concentrated and crystallized by the slow addition of diethyl ether to give spectroscopically pure **1** (175 mg, 100%).

Synthesis of [(η^2-HcyclenP)Pt(Cl)$PPh_3]BF_4$ (3). A solution of **1** (169 mg, 0.244 mmol) in CH_2Cl_2 (5 mL) was treated dropwise with 85% $HBF_4 \cdot O(C_2H_5)_2$ (48 μL, 0.28 mmol; Aldrich) and stirred for 12 h. The mixture was then filtered to remove some solid that had formed. Evaporation of the volatiles from the filtrate yielded white crystals of air-stable **3** (120 mg, 63%). **3** is soluble in THF, CH_3CN, CH_2Cl_2, and CH_3OH. Dec pt: 195–197 °C. Anal. Calcd for $C_{26}H_{32}BClF_4N_4P_2Pt$: C, 40.04; H, 4.14; N, 7.18. Found: C, 39.98; H, 4.06; N, 6.87. ν_{NH} (KBr, cm^{-1}): 3205 (w).

Synthesis of [$(H_2cyclenP)PtCl_2PPh_3]BF_4$ (4). A solution of **3** (78 mg, 0.10 mmol) in THF (3 mL) was treated dropwise with a THF solution of HCl until precipitation was complete. The mixture was stirred for 4 h. The solid was filtered out and dried under vacuum, yielding white crystals of hygroscopic **4** (74 mg, 91%). **4** is soluble in Me_2SO. Dec pt: 230–232 °C. Anal. Calcd for $C_{26}H_{33}BCl_2F_4N_4P_2Pt$: C, 38.26; H, 4.07; N, 6.86. Found: C, 37.66; H, 3.97; N, 7.17.

X-ray Structure Determination and Refinement. Colorless crystals (clusters of plates) of **2** were grown by gas-phase diffusion of THF into a Me_2SO solution of **2**. The crystals were quite difficult to handle since they would decompose upon removal from the mother liquor. Several attempts were made to obtain a crystal that would hold up during data collection. Sealing in a capillary with the mother liquor, as well as coating the crystal with one layer of epoxy, led to crystal decomposition within 24 h. Finally, the crystal for which data was collected was prepared by coating it immediately with epoxy followed by mounting and centering on the goniometer head. Then the crystal was recoated several times with layers of epoxy before data collection. Colorless plates of **3** were grown from a solution of methylene chloride/ether (1/4 v/v) at −35 °C.

Details relating to the crystals, data collection, and refinement are provided in Table I. The unit cell parameters were determined by a least-squares fit of 15 reflections in the range $15 \leq 2\theta \leq 25°$. The systematic absences were consistent with the space groups. Three standard reflections were remeasured during the data collection after every 100 reflections. The crystal of **2** showed significant decay (30%) at the end of data collection. All data were corrected for decay and Lorentz-polarization effects. Data for **3** were corrected for absorption based on ψ scans. An absorption correction for **2** was not possible due to crystal decomposition and inability in locating faces or measuring dimensions accurately. The structures were solved by direct methods using SHELXTL-PLUS[4] and subsequent difference Fourier methods. Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[5] Full-matrix least-squares refinements were carried out by using only the observed reflections $I > 3\sigma(I)$, the function minimized being $\sum w(|F_o| - |F_c|)^2$. For **3**, all non-hydrogen atoms were refined anisotropically; hydrogens on carbon atoms were included in calculated positions with fixed isotropic parameters. The hydrogen atom attached to N(1) in **3** was located and included with fixed parameters. For **2**, the Pt, Cl, and P atoms were refined anisotropically; the rest of the non-hydrogen atoms were refined isotropically. Hydrogen atoms were not included in the refinement of **2**.

Table I. Crystal Data and Data Collection Parameters for **2** and **3**

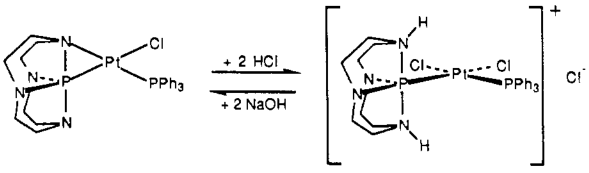
	2	**3**
formula	$C_{26}N_4P_2Cl_3Pt$	$C_{26}H_{31}BN_4F_4P_2ClPt$
fw	731.7	778.8
color and habit	colorless plates	colorless plates
cryst system	orthorhombic	monoclinic
space group	*Pcab*	$P2_1/c$
a/Å	15.391 (4)	14.873 (3)
b/Å	17.021 (6)	13.021 (3)
c/Å	25.226 (14)	15.723 (3)
β/deg		106.654 (14)
V/Å^3	6608 (5)	2917.3 (10)
Z	8	4
temp/K	295	295
d_{calcd}/g cm^{-3}	1.47	1.77
radiation, λ/Å	0.71073	0.71073
μ/mm^{-1}	4.65	5.11
cryst dimens/mm	0.2 × 0.2 × 0.1	0.23 × 0.15 × 0.50
scan mode	2θ	2θ
min, max scan speed/deg min^{-1}	3.5, 14.7	3.0, 14.7
min, max 2θ/deg	3, 45	3, 50
no. of measd reflcns	4939	5835
no. of unique reflcns	4295	5581
no. of obsd reflcns	1521	5136
no. of params refined	175	383
cryst decay, %	30	1
max, min transmission coeff		1.00, 0.586
R_{int} for multiply measd reflcns	0.134	0.017
h range	0→16	−17→16
k range	0→18	0→15
l range	0→27	0→18
R^a	0.087	0.044
R_w	0.089	0.046
k^a	0.0036	0.0025

[a] $R = \sum||F_o| - |F_c||/\sum w|F_o|$, $R_w = [w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$, and $w = 1/\sigma^2(F_o) + k(F_o)^2$.

Atomic coordinates and isotropic thermal parameters for **2** and **3** are given in Tables II and III, respectively.

Results and Discussion

1. Reactions. Attempts to convert **2** to **1** by heating under vacuum or reaction with butyllithium led to decomposition.[6] However, stirring a finely divided slurry of NaOH with **2** in CH_2Cl_2 led cleanly to **1** within 12 h. Thus, **1** can be converted to **2** reversibly according to reaction 2. However, in either direction, a monoprotonated intermediate could not be isolated, or even observed. For example, reaction of 1 with less than 2 equiv of HCl led to only **2** and unreacted **1**. The usual mechanism of HCl addition to square-planar platinum(II) complexes involves formation of a six-coordinate platinum(IV) species that may further react, for example, by undergoing reductive elimination.[7] A similar sequence could be involved in (the forward) reaction



1 **2**

(2)

---

(4) Sheldrick, G. M. "SHELXTL-Plus88, Structure Determination Software Programs"; Nicolet Instrument Corp.: 5225-5 Verona Road, Madison, WI 53711, 1988.

(5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(6) Alkyllithium reagents have been used successfully in similar deprotonations: (a) Dupart, J.-M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167. (b) Vierling, P.; Riess, J. G. *Organometallics* **1986**, *5*, 2543. (c) Dupart, J.-M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316. (d) Jeanneaux, F.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 4272. (e) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 284.

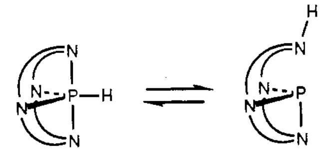
(7) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publishers, Ltd.: London, 1973; pp 62, 84.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters for **2** ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Pt	1518 (1)	101 (1)	2142 (1)	34 (1)
Cl(1)	2262 (8)	1109 (6)	1667 (5)	44 (5)
Cl(2)	2066 (9)	685 (6)	2914 (6)	58 (5)
Cl(3)	-5944 (9)	-1156 (7)	2233 (6)	72 (6)
P(1)	1038 (9)	-910 (7)	2663 (5)	36 (5)
P(2)	970 (9)	-220 (7)	1337 (5)	40 (5)
N(1)	-87 (21)	-484 (17)	2852 (15)	34 (9)
N(2)	563 (25)	-1671 (19)	2431 (15)	42 (10)
N(3)	2101 (26)	-1499 (22)	2611 (16)	51 (11)
N(4)	1230 (20)	-939 (19)	3311 (13)	28 (9)
C(1)	-757 (31)	-858 (28)	2544 (21)	56 (16)
C(2)	-381 (40)	-1770 (32)	2472 (25)	79 (18)
C(3)	954 (35)	-2425 (30)	2384 (18)	65 (16)
C(4)	1965 (36)	-2193 (28)	2222 (22)	69 (16)
C(5)	2405 (33)	-1780 (27)	3139 (22)	55 (15)
C(6)	2144 (35)	-1104 (29)	3486 (23)	66 (16)
C(7)	706 (33)	-457 (27)	3657 (22)	60 (15)
C(8)	-241 (32)	-515 (26)	3440 (20)	54 (15)
C(9)	1764 (24)	-631 (20)	870 (15)	19 (10)
C(10)	2683 (28)	-691 (22)	1062 (18)	32 (12)
C(11)	3238 (31)	-1054 (26)	682 (20)	51 (14)
C(12)	3083 (41)	-1276 (33)	173 (25)	77 (18)
C(13)	2232 (39)	-1209 (31)	58 (24)	72 (18)
C(14)	1472 (42)	-838 (33)	354 (23)	80 (18)
C(15)	25 (33)	-869 (25)	1212 (19)	44 (14)
C(16)	-828 (41)	-579 (33)	1144 (23)	80 (19)
C(17)	-1497 (44)	-1053 (34)	1104 (23)	83 (18)
C(18)	-1289 (45)	-1999 (38)	1158 (27)	96 (23)
C(19)	-520 (41)	-2230 (30)	1204 (21)	65 (17)
C(20)	251 (35)	-1770 (27)	1261 (20)	54 (15)
C(21)	617 (33)	675 (28)	1020 (21)	53 (14)
C(22)	744 (30)	908 (25)	489 (19)	41 (13)
C(23)	549 (43)	1667 (37)	273 (27)	94 (21)
C(24)	23 (38)	2194 (31)	632 (24)	74 (17)
C(25)	-222 (33)	1948 (26)	1145 (20)	48 (14)
C(26)	91 (32)	1201 (26)	1361 (19)	47 (14)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

2, where two oxidative additions and reductive eliminations at the platinum center transfer protons to the nitrogens with displacement of the nitrogen from platinum and coordination of one of the chloride anions. An alternative, or perhaps additional, possibility with **1** is the ability of the cyclenP ligand to open and close during reaction. This feature was first demonstrated by Richman and Atkins for the cyclic tetraaminophosphorane N_4PH systems, as illustrated in equilibrium 3.[8] For cyclenPH, only the five-coordinate phosphorane species is observed in solution; addition of more CH_2 groups between the nitrogens favors the open phosphine form, and in the species with four $(CH_2)_3$ bridges, only the open phosphine species is found.



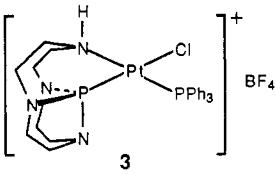
(3)

Since the chloride anion is a strongly coordinating ligand that may drive the reaction toward dual protonation, use of a noncoordinating anion might facilitate isolation of a monoprotonated species. In fact, reaction of **1** with 1 equiv of tetrafluoroboric acid yields a species **3** with ^{31}P chemical shifts at 13 and 94 ppm (Table IV). Each resonance shows platinum satellites and two-bond phosphorus–phosphorus coupling. The small $^2J_{PP}$ value is indicative of a cis arrangement of phosphorus atoms around the platinum,[9] while the 94 ppm chemical shift is far downfield of the corresponding resonances in **1** and **2** (Table IV). The disappearance of the upfield negative resonance and the appearance of a downfield one are consistent with coordination of the open form of the cyclenP ligand and have been observed previously with rhodium complexes.[3c] The ^1H NMR spectrum shows (in addition to the expected phenyl and methylene resonances) a broad peak at δ 6.06, which integrates to one proton. These spectra are consistent with P–N bond cleavage and coordination of the open form of cyclenP with one of the nitrogens protonated. The structure of $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ (**3**) was confirmed by X-ray crystallography (see later).

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters for **3** ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Pt	3810 (1)	6270 (1)	5948 (1)	26 (1)
Cl	4241 (1)	5440 (1)	7335 (1)	43 (1)
P(1)	3855 (1)	7143 (1)	4763 (1)	29 (1)
P(2)	2276 (1)	5820 (1)	5520 (1)	31 (1)
N(1)	5248 (3)	6784 (4)	6337 (3)	35 (2)
N(2)	4102 (4)	8343 (4)	5092 (4)	40 (2)
N(3)	3083 (4)	7420 (4)	3781 (3)	41 (2)
N(4)	4631 (4)	6548 (4)	4349 (3)	38 (2)
C(1)	5789 (5)	6178 (5)	5835 (5)	42 (2)
C(2)	5634 (5)	6498 (6)	4890 (5)	46 (3)
C(3)	4465 (6)	6859 (6)	3411 (5)	49 (3)
C(4)	3431 (6)	7007 (6)	3056 (5)	51 (3)
C(5)	2870 (6)	8538 (6)	3762 (5)	56 (3)
C(6)	3673 (7)	9092 (6)	4423 (5)	65 (4)
C(7)	4586 (6)	8580 (5)	6015 (5)	45 (3)
C(8)	5448 (5)	7930 (5)	6373 (5)	45 (3)
C(9)	1955 (4)	4909 (5)	4594 (4)	37 (2)
C(10)	1792 (6)	3891 (6)	4721 (6)	54 (3)
C(11)	1541 (7)	3218 (7)	3975 (7)	71 (4)
C(12)	1492 (6)	3590 (6)	3138 (6)	64 (3)
C(13)	1692 (6)	4609 (7)	3034 (5)	58 (3)
C(14)	1894 (5)	5263 (6)	3743 (4)	45 (3)
C(15)	1497 (4)	6915 (5)	5134 (4)	34 (2)
C(16)	585 (5)	6783 (6)	4569 (5)	45 (2)
C(17)	-8 (5)	7609 (6)	4344 (5)	59 (3)
C(18)	305 (7)	8583 (7)	4673 (7)	69 (4)
C(19)	1183 (6)	8722 (5)	5235 (6)	60 (4)
C(20)	1797 (5)	7896 (5)	5470 (5)	46 (3)
C(21)	1848 (4)	5265 (5)	6398 (4)	34 (2)
C(22)	2273 (5)	4389 (5)	6842 (5)	48 (3)
C(23)	1975 (6)	3992 (7)	7527 (6)	64 (3)
C(24)	1268 (6)	4432 (8)	7796 (6)	70 (4)
C(25)	846 (5)	5317 (7)	7357 (5)	57 (3)
C(26)	1124 (5)	5728 (6)	6653 (5)	47 (3)
B	7058 (7)	6184 (8)	8771 (7)	57 (4)
F(1)	6922 (6)	5253 (6)	8399 (6)	151 (5)
F(2)	7959 (5)	6351 (7)	9035 (7)	161 (5)
F(3)	6663 (6)	6905 (7)	8173 (6)	152 (4)
F(4)	6655 (9)	6216 (5)	9426 (7)	164 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.



3

The cation of **3** may be a key intermediate in the conversion of **1** to **2** and, possibly, in the original synthesis (reaction 1). To investigate the first possibility, **3** was treated with HCl in THF; a white precipitate of $[(H_2\text{cyclenP})PtCl_2PPh_3]BF_4$ (**4**) formed immediately. The NMR properties of **2** and **4** are virtually identical (Table IV). If the cation of **3** is also an intermediate in reaction 1, then addition of a source of chloride should lead to **1** and **2** via disproportionation. This is what is observed when a solution of **3** in $Me_2SO\text{-}d_6$ is treated with NaCl. The above reactions, summarized in Scheme I, illustrate the three different coordination modes for the cyclenP unit and the conversion of one to another.

---

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

(9) (a) Verkade, J. G. *Coord. Chem. Rev.* **1972/1973**, *9*, 1. (b) Pregosin, P. S.; Kunz, R. W. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979.

Table IV. NMR Data (ppm)[a]

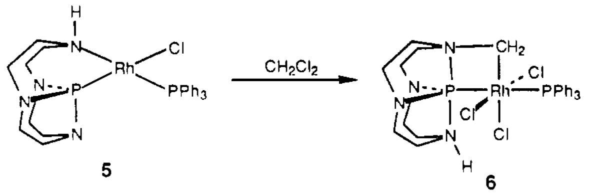
compd (solvent)	^{31}P	^{1}H
1 ($CDCl_3$)	−55 (PN, $^1J_{PtP}$ = 3612 Hz) 21 (PC, $^1J_{PtP}$ = 4702 Hz) ($^2J_{PP}$ = 2 Hz)	2.2–3.6 (comp m, CH_2, 16 H) 7.33, 7.62 (m, CH, 15 H)
2 (Me_2SO-d_6)	−59 (PN, $^1J_{PtP}$ = 5567 Hz) 15 (PC, $^1J_{PtP}$ = 4070 Hz) ($^2J_{PP}$ = 10 Hz)	1.7–3.5 (comp m, CH_2, 16 H) 7.50 (br s, CH) $\}$ (17 H)[b] 7.79 (m, CH and NH)
3 (CD_2Cl_2)	94 (PN, $^1J_{PtP}$ = 4497 Hz) 13 (PC, $^1J_{PtP}$ = 3733 Hz) ($^2J_{PP}$ = 19 Hz)	2.3–3.7 (comp m, CH_2, 16 H) 6.06 (br pseudo t, NH, 1 H) 7.3–7.7 (m, CH, 15 H)
4 (Me_2SO-d_6)	−59 (PN, $^1J_{PtP}$ = 5570 Hz) 15 (PC, $^1J_{PtP}$ = 4087 Hz) ($^2J_{PP}$ = 10 Hz)	1.7–3.5 (comp m, CH_2, 16 H) 7.5–7.8 (br m, CH and NH, 17 H)[b]

[a] Data for **1** and **2** taken from ref 3b. [b] Phenyl and N–H protons overlapping.

Table V. Selected Internuclear Distances (Å) and Angles (deg) for **2** and **3**

Bond Lengths for 2			
Pt–Cl(1)	2.386 (12)	Pt–Cl(2)	2.343 (13)
Pt–P(1)	2.289 (12)	Pt–P(2)	2.265 (13)
P(1)–N(1)	1.936 (34)	P(1)–N(2)	1.598 (37)
P(1)–N(3)	1.924 (42)	P(1)–N(4)	1.663 (35)
Bond Angles for 2			
Cl(1)–Pt–Cl(2)	86.5 (4)	Cl(1)–Pt–P(1)	169.9 (5)
Cl(2)–Pt–P(1)	87.6 (4)	Cl(1)–Pt–P(2)	84.4 (4)
Cl(2)–Pt–P(2)	168.8 (4)	P(1)–Pt–P(2)	102.3 (4)
Pt–P(1)–N(1)	98.6 (11)	Pt–P(1)–N(2)	123.2 (15)
N(1)–P(1)–N(2)	89.1 (17)	Pt–P(1)–N(3)	94.5 (13)
N(1)–P(1)–N(3)	166.5 (17)	N(2)–P(1)–N(3)	86.6 (18)
Pt–P(1)–N(4)	122.0 (13)	N(1)–P(1)–N(4)	85.8 (16)
N(2)–P(1)–N(4)	114.6 (18)	N(3)–P(1)–N(4)	84.3 (17)
Bond Lengths for 3			
Pt–Cl	2.353 (2)	Pt–P(1)	2.200 (2)
Pt–P(2)	2.264 (2)	Pt–N(1)	2.156 (5)
P(1)–N(2)	1.653 (5)	P(1)–N(3)	1.678 (5)
P(1)–N(4)	1.670 (6)		
Bond Angles for 3			
Cl–Pt–P(1)	163.0 (1)	Cl–Pt–P(2)	98.0 (1)
P(2)–Pt–P(1)	98.9 (1)	Cl–Pt–N(1)	84.0 (1)
P(1)–Pt–N(1)	79.2 (1)	P(2)–Pt–N(1)	176.9 (1)
Pt–P(2)–C(9)	114.5 (2)	Pt–P(2)–C(15)	112.7 (2)
C(9)–P(2)–C(15)	104.2 (3)	Pt–P(2)–C(21)	114.7 (2)
C(9)–P(2)–C(21)	106.0 (3)	C(15)–P(2)–C(21)	103.6 (3)
Pt–P(1)–N(2)	106.4 (2)	Pt–P(1)–N(3)	135.4 (2)
N(2)–P(1)–N(3)	96.7 (3)	Pt–P(1)–N(4)	106.4 (2)
N(2)–P(1)–N(4)	116.3 (3)	N(3)–P(1)–N(4)	96.1 (3)
Pt–N(1)–C(1)	109.0 (4)	Pt–N(1)–C(8)	118.9 (4)
C(1)–N(1)–C(8)	114.0 (6)		

Most reactions of cyclenPH with transition metals yield species wherein the pentacoordinate, "closed" form of cyclenP coordinates as a phosphoranide ligand.[3] This is in marked contrast to the chemistry of cyclamPH,[10] where initial reactions with transition metals yield complexes of the open form exclusively.[6] In only two cases, **3** and (η^2-HcyclenP)Rh(Cl)PPh_3 (**5**),[3c] has the open form of cyclenPH been stabilized. Yet even here, subsequent reaction recloses the ring to give pentacoordinate derivatives (see above and reaction 4). The isolation of **3** and **5** shows that cyclenP can



(4)

open and close during reaction and suggests that the open form

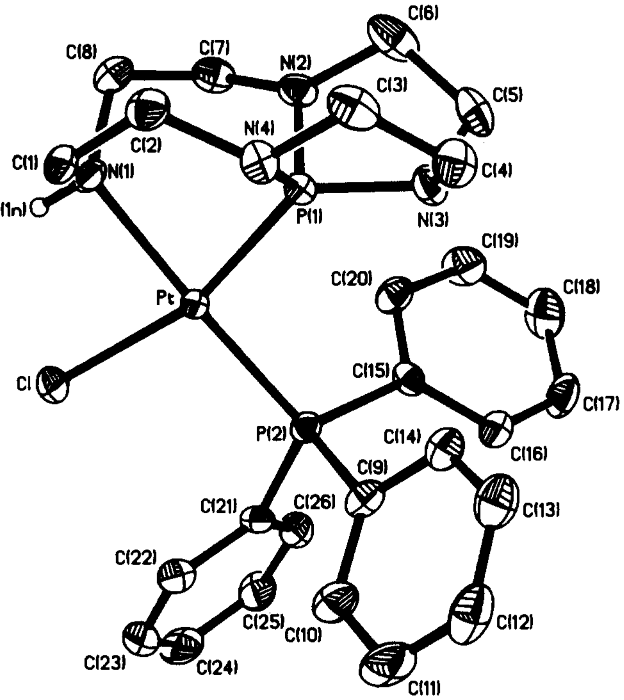
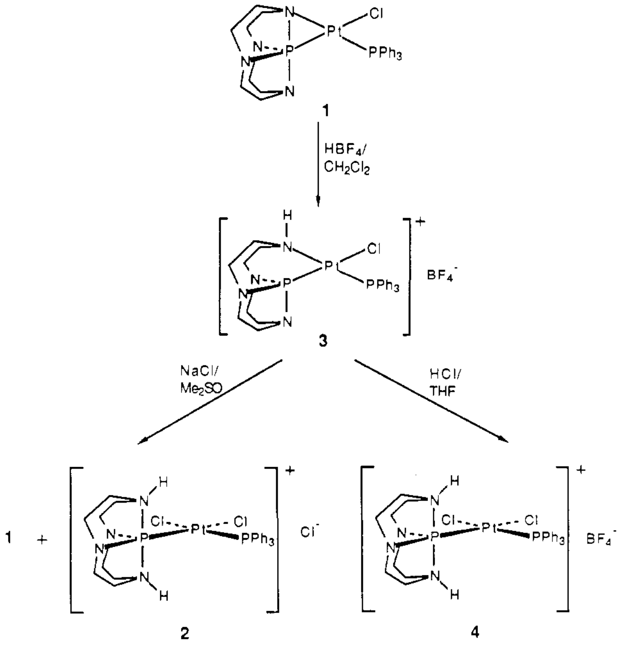


Figure 1. ORTEP drawing of the cation of **3**, showing the molecular configuration and numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity, except for H(1n), the hydrogen bonded to N(1).

Scheme I



---

(10) cyclamPH is the cyclic tetraaminophosphorane with alternating $(CH_2)_3$ and $(CH_2)_2$ bridges between the nitrogens.

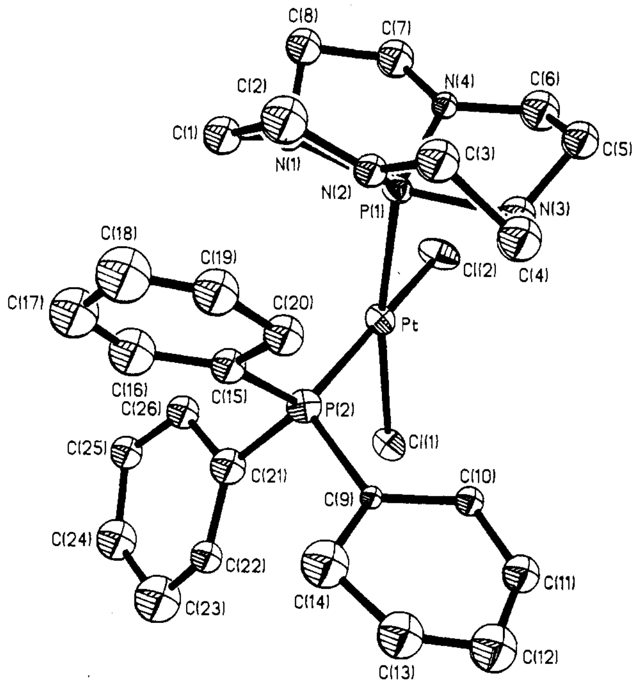


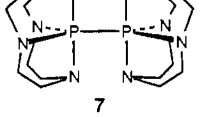
Figure 2. ORTEP drawing of the cation of **2**, showing the molecular configuration and numbering scheme. Thermal ellipsoids are drawn at the 35% probability level.

may be a key intermediate in many reactions of cyclenP derivatives.

2. Structural Descriptions and Comparisons. Selected internuclear distances and angles for **3** and **2** are listed in Table V, and their structures are illustrated in Figures 1 and 2, respectively. In **3**, all four atoms directly bonded to Pt lie in the plane with the metal, as is clear from the sum of the bond angles about Pt, 360.1 (2)°. The geometry about P(1) is distorted tetrahedral; cleavage of the P(1)–N(1) bond is evident from the long P–N distance of 2.775 (6) Å, an increase of 0.90 Å from that of **1**. Accompanying this bond rupture is a large increase of 28.2° in the P(1)–Pt–N(1) bond angle, compared to the corresponding angle in **1**.

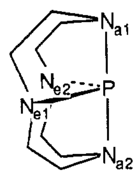
In **2**, the geometry about P(1) is a distorted trigonal bipyramid (tbp) with the P–N axial bonds longer than the equatorial bonds. Although the hydrogens on N(1) and N(3) were not located, their attachment can be confidently assumed due to the very long P–N axial bond lengths of 1.9 Å. Distances of about 1.9 Å and above for the axial P–N bonds in cyclenP derivatives are always indicative of coordination of the axial nitrogens;[2,3] for uncomplexed axial nitrogens, the bond lengths are less than 1.8 Å.[2,11] The H_2cyclenP ligand is oriented with its P–N axial bonds perpendicular to the coordination plane of the Pt due, most likely, to steric effects.

The cations of **3** and **2** represent stepwise protonation of the starting material **1**. Structural comparison among these compounds gives significant insight into three aspects of their geometries, chemistry, and electronics. Table VI collects the relevant data for the cyclenP unit in **1**, **3**, and **2** (note that N_{a1} is the metal-bonded nitrogen in **1** and **3**). Also included are corresponding data for the dimer $(\text{cyclenP})_2$ (**7**),[11] which serves as a comparison standard for a cyclenP unit without external nitrogen bonding.



7

Table VI. Comparative Geometry Data for **1**, **3**, **2**, and **7**[a]



	1	**3**	**2**	**7**
$P-N_{a1}$	1.872 (11)	2.775 (6)[b]	1.936 (34)	1.782 (2)
$P-N_{a2}$	1.698 (11)	1.678 (5)	1.924 (42)	1.782 (2)
$P-N_{e1}$	1.676 (11)	1.653 (5)	1.663 (35)	1.694 (2)
$P-N_{e2}$	1.694 (11)	1.670 (6)	1.598 (37)	1.694 (2)
$N_{a1}-P-N_{a2}$	175.2 (5)	174.9 (7)[b]	166.5 (17)	169.6 (1)
$N_{e1}-P-N_{e2}$	128.4 (6)	116.3 (3)	114.6 (18)	131.1 (1)
$N_{a1}-P-N_{e1}$	86.6 (5)	80.4 (5)[b]	85.8 (16)	87.8 (1)
$N_{a1}-P-N_{e2}$	87.0 (5)	81.3 (5)[b]	89.1 (17)	87.8 (1)
$N_{a2}-P-N_{e1}$	91.2 (5)	96.7 (3)	84.3 (17)	87.9 (1)
$N_{a2}-P-N_{e2}$	91.0 (6)	96.1 (3)	86.6 (18)	87.9 (1)

[a] Bond lengths in Å and bond angles in deg. Data for **1** and **7** taken from ref 3b and 11, respectively. N_{a1} is the metal-bonded nitrogen in **1** and **3**. [b] Nonbonded parameters.

The first structural comparison concerns the steric demands of the transition-metal moiety. In **7**, the axial bonds are about 0.1 Å longer than the equatorial bonds. The geometry about each phosphorus exhibits the usual distortion (i.e., axial N–P–N angle less than 180° and equatorial N–P–N angle greater than 120°) from a tbp to a square pyramid (sp), in this case 32.9% along the Berry coordinate. This is in contrast to the distortion of the cyclenP unit in **2**, where the equatorial angle is *less* than 120°, even though the axial angle shows the usual distortion. The contraction of the equatorial angle in pentacoordinate phosphorus derivatives with transition-metal groups has been observed before[3c,12] and is due to the steric requirements of metal-bound ligands that lie perpendicular to the P–metal bond and eclipse the P–N equatorial bonds (in the case of **2**, Cl(2) and PPh_3). Note that in species with no such ligands, such as **1**, the equatorial angle is greater than 120°.

The second comparison concerns the similarities of the geometries of the four compounds and suggests why most isolated cyclenP derivatives involve pentacoordinate phosphorus. The basic skeletal geometry of the PN_4 unit (i.e., the N–P–N angles) in all the species remains close to that of a tbp. Even the nonbonded $N_{a1}-P-N_{a2}$ angle in **3** is 174.9°. Thus, the cyclenP unit is ideally suited to accommodate the pentacoordinate tbp geometry, even when the phosphorus is only four-coordinate.

The third comparison concerns the electronics of the interaction between the cyclenP ligand and the transition metal. In **3**, the interaction appears to be simple coordination of the phosphine and amine ends of the open form of cyclenPH. In **2**, H_2cyclenP coordinates as a phosphoranide ligand. However, we have treated **1** and related derivatives as phosphoranide adducts with coordination of one of the axial nitrogen lone pairs; a closer examination of the structural data reveals that there is an alternative. Note that the $P-N_{a2}$, $P-N_{e1}$, and $P-N_{e2}$ bond lengths in **1** and **3** are all very similar and lie between 1.65 and 1.70 Å. This would be expected in **3**, where the cyclenP unit is coordinated as an ordinary phosphine; however, in **1**, this near equivalence indicates that the usual three-center/four-electron "hypervalent" bond[13]

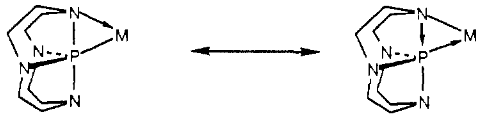
---

(11) (a) Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3378. (b) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955.

(12) (a) Lattman, M.; Anand, B. N.; Garrett, D. G.; Whitener, M. A. *Inorg. Chim. Acta* **1983**, *76*, L139. (b) Lattman, M.; Anand, B. N.; Chu, S. S. C.; Rosenstein, R. D. *Phosphorus Sulfur* **1983**, *18*, 303. (c) Chu, S. S. C.; Rosenstein, R. D.; Lattman, M.; Anand, B. N. *J. Organomet. Chem.* **1984**, *265*, 45. (d) Lattman, M.; Morse, S. A.; Cowley, A. H.; Lasch, J. G.; Norman, N. C. *Inorg. Chem.* **1985**, *24*, 1364. (e) Chopra, S. K.; Chu, S. S. C.; de Meester, P.; Geyer, D. E.; Lattman, M.; Morse, S. A. *J. Organomet. Chem.* **1985**, *294*, 347.

(13) (a) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. (b) Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359. (c) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

is significantly disrupted by coordination to the metal. In addition, consider the geometry about the coordinated nitrogen in **1**: the sum of the two Pt-N-C angles and one C-N-C angle (i.e., neglecting the P-N interaction) is 353°, very close to planar.[14] The geometry about this nitrogen suggests the Pt-N interaction may be more amide-like, while the Pt-P interaction may be more phosphine-like, leaving the lone pair on nitrogen to donate to phosphorus to complete its 10-P-5 geometry. Both of the above electronic descriptions represent extremes that are illustrated below; the actual electronic situation is probably a hybrid of these.



Acknowledgment. We wish to thank the Robert A. Welch Foundation for generous financial support; M.L. and D.K. thank Thomas K. Clark for assistance in the synthesis of cyclenPH.

Registry No. **1**, 108148-24-9; **2**, 108148-25-0; **3**, 118474-27-4; **4**, 118494-04-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, and torsion angles for **2** and **3** and a table of hydrogen atom coordinates and isotropic thermal parameters for **3** (7 pages); tables of observed and calculated structure factors for **2** and **3** (35 pages). Ordering information is given on any current masthead page.

---

(14) This value can be compared to the corresponding value of 342° in **3** (neglecting the N-H interaction). Note that this represents a difference of 25°, since the N in **1** is on the same side of the C-Pt-C plane as the P, while it lies on the opposite side in **3**.

Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwain 30043, Republic of China

Steric, Inductive, and Ring-Strain Effects in Chelation Thermodynamics and Kinetics. Reactions of Copper(II) Ion with *N*-Alkyl-Substituted Diamino Diamides

Min-Shiun Chao and Chung-Sun Chung*

Received October 14, 1987

In order to study the steric, inductive, and ring-strain effects of diamino diamides on the thermodynamic, spectral, and kinetic properties of copper(II)-diamino diamide complexes, four new tetradentate ligands, 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-Me_2-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2), have been synthesized. Synthetic procedures for these new ligands are described. Their protonation constants have been determined potentiometrically in 0.10 M $NaClO_4$ at 25.0 °C. The formation of their copper(II) complexes and the Cu-O to Cu-N bond rearrangements at the two amide sites of these complexes have been investigated quantitatively by the potentiometric technique and by the measurement of their electronic spectra. The kinetics of complexation obtained by using the stopped-flow technique indicates that the first metal-nitrogen bond formation between copper(II) and the unprotonated ligands is the rate-determining step and that the proton loss is the rate-limiting step in the reactions of copper(II) with the monoprotonated ligands. The reactivity order for the dissociation reaction is $Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+} > Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+} > Cu(4\text{-}Me\text{-}L\text{-}2,2,2)^{2+} > Cu(4\text{-}Et\text{-}L\text{-}2,2,2)^{2+}$. The thermodynamic, spectroscopic, and kinetic data are discussed in relation to a combination of steric, inductive, statistical, solvation, and ring-strain effects.

Introduction

Previously, we have reported the thermodynamics and kinetics of the complexation reactions of divalent nickel ion[1] and copper ion[2] with four closely related diamino diamides, two of which are depicted in Chart I. The ligand $NH_2CO(CH_2)_nNH(CH_2)_mNH(CH_2)_pCONH_2$ is denoted by the symbol L-*n*,*m*,*p*. The current investigation is designed to gain more detailed understanding of the steric, inductive, and ring-strain effects that arise from the substitution at the amino nitrogen donor atom on the thermodynamic, spectral, and kinetic properties of copper(II)-diamino diamide complexes. Thus we have synthesized four new *N*-alkyl-substituted diamino diamides, 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-Me_2-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2). These ligands are depicted in Chart I. Their complexes with copper(II) have been studied by potentiometry and visible absorption spectrophotometry, and the reaction kinetics have been studied by stopped-flow methods.

Experimental Section

Reagents. The ligand 4-Me-L-2,2,2 was prepared from *N*-methylethylenediamine (12.4 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 80 mL of acetonitrile by refluxing for 2 h. The solution was cooled in a refrigerator for 3 weeks, and the product was filtered off, recrystallized from acetonitrile, and dried in vacuo; mp 88-89 °C. Anal. Calcd for $C_9H_{20}N_4O_2$: C, 50.0; H, 9.30; N, 25.9. Found: C, 50.8; H, 9.3; N, 26.5. The ligand 4,7-Me_2-L-2,2,2 was prepared from *N*,*N'*-dimethylethylenediamine (13.2 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 50 mL of acetonitrile by heating under reflux for 1.5 h. The solution was cooled and the product filtered off, washed with chloroform, recrystallized from chloroform, and dried in air; mp 101-102 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.8; H, 9.58; N, 24.6. The ligand 4-Et-L-2,2,2 was prepared from *N*-ethylethylenediamine (21.1 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 80 mL of acetonitrile by refluxing the mixture for 2 h. The solution was cooled in a refrigerator and the product filtered off, recrystallized from acetonitrile, and dried in vacuo; mp 81-82 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.4; H, 9.48; N, 24.8. The ligand 4-Me-L-2,3,2 was prepared from *N*-methyltrimethylenediamine (13.6 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 60 mL of acetonitrile by refluxing it for 2 h. The solution was cooled; the product was recrystallized from chloroform and dried in vacuo; mp 55-56 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.6; H, 9.51; N, 23.8. These ligands were 99.8% pure as determined by titration with a standard base. All other chemicals used were of reagent grade from Merck. A saturated solution of sodium hydroxide (reagent grade) was prepared to precipitate sodium carbonate. A sample of this was diluted with freshly boiled, distilled, deionized water and stored in a Nalgene Teflon bottle. It was standardized against weighed amounts of potassium hydrogen phthalate. Standard solutions of ligands, borate-mannitol buffers, and sodium perchlorate were prepared by weight. The copper(II) ion concentration was standardized by EDTA titration.

Measurements. For pH measurements a Radiometer PHM 64 instrument equipped with a GK 2401B combined electrode was used. The

---

(1) Liu, S.-H.; Chung, C.-S. *Inorg. Chem.* **1985**, *24*, 2368-2373.
(2) Liu, S.-H.; Chung, C.-S. *Inorg. Chem.* **1986**, *25*, 3890-3896.

0020-1669/89/1328-0686$01.50/0