Figure 3. Cyclic voltammograms of (A) Ru(dpk)$_2$Cl$_2$ and (B) [Ru-(bpy)$_2$(dpk)]$^{2+}$. Conditions: glassy-carbon electrode; scan rate 100 mv/s; DMF–TEAP (0.1 N) solution.

reduced at –0.81 V versus SCE. This is consistent with the reported data for ruthenium heterocyclic complexes where the free ligand is reduced at more negative potentials than when coordinated to ruthenium(II).[27] For the mixed-ligand complex [Ru(bpy)$_2$(dpk)]$^{2+}$, reduction occurs first at dpk, which has a lower π^* level than bpy, and the pattern of reduction is

$$[\text{Ru(bpy)}_2(\text{dpk})]^{2+} + e^- \rightarrow [\text{Ru(bpy)}_2(\text{dpk}^-)]^+$$

$$E_{1/2} = -0.82 \text{ V}$$

The cyclic voltammograms of two representative dpk complexes are shown in Figure 3. As reported earlier, for MLCT excited states where excited-state distortion is relatively small, excited-state redox potentials can be estimated from ground-state redox potentials and the excited-state emission energy by $E_{1/2}{}^{3+/2+*} = E_{1/2}{}^{3+/2+} - E_{\text{Em}}$ and $E_{1/2}{}^{2+*/+} = E_{1/2}{}^{2+/+} + E_{\text{Em}}$.[28] By this calculation, for [Ru(bpy)$_2$(dpk)]$^{2+}$, $E(\text{Ru}^{3+/2+*}) = -0.41$ V and $E(\text{Ru}^{2+*/+}) = 0.93$ V. The data suggests that [Ru(bpy)$_2$(dpk)]$^{2+*}$ is a poor reductant compared to [Ru(bpy)$_3$]$^{2+*}$ but is a better oxidant due to enhanced dπ–π^* interaction.

For the Ru(III) complexes **7**, **8**, and **11**, irreversible oxidation peaks were observed at 1.3, 1.33, and 1.14 V, respectively. These are possibly ligand-based oxidations, and oxidative degradation of the ligand leads to irreversibility.

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Hexaaza Macrocyclic Metal Complexes Containing Biimidazole. 1. Synthesis and Characterization of Nickel(II), Copper(II), and Palladium(II) Complexes of 2,7-Dimethyl-3–6-(1,1′-(2,2′-biimidazolo))-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene

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New Ni(II), Cu(II), and Pd(II) metal complexes of the macrocycle 2,7-dimethyl-3–6-(1,1′-(2,2′-biimidazolo))-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene have been synthesized and characterized. The Pd(II) complex, which is proposed to contain three 5-membered rings, one 9-membered ring, and two imine linkages, was obtained as an air-stable, insoluble, yellow, diamagnetic compound. Corresponding orange to blue Ni(II) complexes were obtained as the diamagnetic iodide or perchlorate species and paramagnetic chloro and bromo complexes. The Cu(II) complex was obtained as a blue paramagnetic perchlorate complex. FT-IR, NMR, and electronic spectral data have been used to confirm macrocycle formation from metal–trien complexes reacting with 1,1′-diacetyl-substituted 2,2′-biimidazole in water/dioxane or 2-propanol/dioxane mixtures at pH 5. The formation of these amorphous complexes demonstrates how ring formation can be achieved over 1,1′-diacetyl-2,2′-biimidazole hydrolysis due to the metal ion template effect.

Introduction

Metal template syntheses of multidentate and macrocyclic ligands have been established over the last two decades as offering high-yielding and selective routes to new ligands and their complexes.[1] Transition-metal complexes involving triethylenetetramine (trien) have received a large amount of attention because of the several configurations in which the tetradentate ligand can coordinate metal centers.[2–4] Considerable attention has also been given to the metal complexing ability of 2,2′-biimidazole.[5–8]

Because of the ease of formation of alkanyl derivatives of 2,2′-biimidazole,[9] the formation of polydentate Schiff-base ligands is made possible by the reaction of metal–trien complexes with derivatives of biimidazole. In this paper we report the preparation and spectral characterization of three new 16-membered macrocyclic complexes based on the reaction of 1,1′-diacetyl-2,2′-biimidazole (I) and Ni(II)–, Cu(II)–, and Pd(II)–triethylene-

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Scheme I
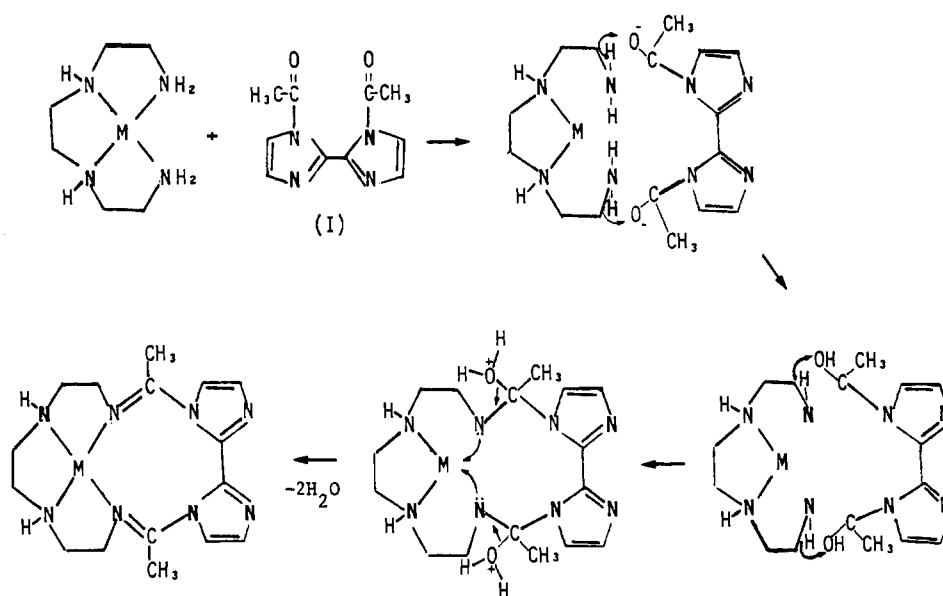
Table I. Summary of Properties for Ni(II), Cu(II), and Pd(II) Macrocyclic Complexes[a]

| complex | color | anal. | | | | | μ, μ_B | λ_{max}, nm | infrared data, cm^{-1} | | |
		% C	% H	% N	% X	% M			ν(N—H)	ν(C=N)	ν(biim)
[Ni16N6]I$_2$	brown	30.1	3.5	17.5	39.9	9.0	diamg	438, 286	3441, 3211	1575	1468
		(30.0)	(3.7)	(17.4)	(39.6)	(9.2)					1431
[Ni16N6]Br$_2$	blue	34.8	4.5	20.7	29.7	10.5	3.14	704, 583, 483, 355	3440, 3210	1579	1408
		(35.1)	(4.4)	(20.5)	(29.3)	(10.7)					
[Ni16N6]Cl$_2$H$_2$O	blue	39.9	5.4	23.3	15.0	12.1	3.18	710, 572, 496, 360	3442, 3212	1580	1408
		(40.4)	(5.4)	(23.5)	(14.9)	(12.3)					
[Cu16N6](ClO$_4$)$_2$	blue	32.8	3.9	18.7	12.3	10.6	1.88	591, 275, 262, 196	3272	1578	1465
		(32.5)	(4.1)	(18.9)	(12.0)	(10.8)					1427
[Pd16N6]Cl$_2$	yellow	38.1	4.9	22.0	14.0	20.9	diamg	404, 360	3210, 3178	1545	1469
		(37.9)	(4.8)	(22.2)	(14.1)	(21.1)					1436

[a] Magnetic measurements were obtained at room temperature. UV/vis spectra were obtained from Nujol mulls. IR spectra were obtained by using a KBr matrix. Elemental percentages in parentheses are theoretical.

tetramine complexes. The formation of complexes of 2,7-dimethyl-3–6-(1,1'-(2,2'-biimidazolo))-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene demonstrates the operation of the template effect to promote ring closure through Schiff-base formation.[10]

Results and Discussion

The complexity presented in the preparation of the tetradentate hexaaza 16-membered macrocyclic complex from the trien complex and I lies in the reactivity of I, which has been reported to be subject to general-base- or general-acid-catalyzed hydrolysis. However, reported studies of acetylimidazole hydrolysis show that the rate of hydrolysis in zero buffer solutions at pH 5 is negligible in aqueous solution.[11]   With this consideration, macrocyclic complexes were prepared by the condensation of isolated Ni(II)–, Cu(II)–, and Pd(II)–trien complexes with I in water/dioxane, or 2-propanol/dioxane mixtures at pH 5. Attempts to conduct this condensation reaction with isolated Co(III)–trien complexes were unsuccessful. The results of these experiments illustrate macrocyclic complex formation via Schiff-base reactions and are in agreement with previous reports regarding macrocycle formation involving labile divalent metal complexes.[12] The template reaction is proposed to proceed by nucleophilic addition of semicoordinated amino groups as outlined in Scheme I.

A summary of the characteristic infrared absorptions, visible absorption maxima, and magnetic properties of these complexes is given in Table I.   The insolubility of [Pd16N6]Cl$_2$H$_2$O in common solvents did not permit solution studies of this complex.

Infrared Analysis. Infrared spectra of the condensation products show the expected vibrations attributable to the trien complex[13] and biimidazole[14] components of the macrocyclic complex. The absence of the stretching and deformation frequencies for the NH$_2$ group, the absence of the C=O stretching frequency of the carbonyl group, and the presence of a strong band at ca. 1545–1580 cm^{-1}, which is assigned to the stretching mode of the conjugated coordinated aliphatic C=N group in the infrared spectra of these complexes, provide strong evidence for the presence of a cyclic product containing Schiff-base linkages.

There are three prominent features of these infrared spectra. The values of the vibration modes in the macrocyclic complexes resulting from the imidazole rings at 1460–1470 and 1427–1436 cm^{-1} show no significant change when compared to similar absorptions at 1460 and 1431 cm^{-1} for 1,1'-diacetyl-2,2'-biimidazole.[15] This suggests that biimidazole is not involved in metal ion complexation. In addition preliminary investigation of subsequent Ni^{2+} binding by [Ni16N6]I$_2$ shows a definitive shift of the biimidazole ring mode vibration from 1468 to 1495 and from 1431 to 1405 cm^{-1}.[16] The IR absorptions due to trien undergo

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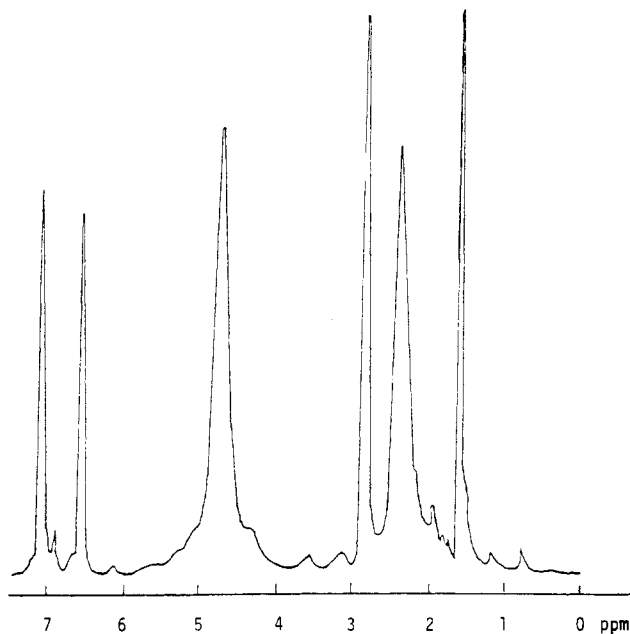(15) Petrak, K.; Beynon, P. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 783.

Figure 1. FT ^{1}H NMR spectrum of [Ni16N6]I$_2$ in D$_2$O. Chemical shifts are calibrated in ppm downfield from TMS.

variations expected for the rigid configuration adopted for macrocycle and Schiff-base formation. In comparing the infrared spectra of the Pd(II), Cu(II), and Ni(II) macrocycles, a distinctive decrease in the number and sharpness of absorptions is observed, suggesting that the influence of decreasing metal ion size and resulting ring puckering give rise to more complex intramolecular interactions.

NMR Analysis. The proton magnetic resonance spectrum for the [Ni16N6]I$_2$ macrocyclic complex in D$_2$O at pH 6.7 is shown in Figure 1. The corresponding chloro–Ni(II) and bromo–Ni(II) as well as the Cu(II)–perchlorate complexes were all found to be paramagnetic. The insolubility of the diamagnetic palladium macrocycle permitted only solids magnetic resonance measurements to be made.

Methyl Protons. The spectrum consists of four distinct regions that are in agreement with the expected proton environments in the macrocyclic complex. These include methyl, methylene, amine, and imidazole protons.

The intense methyl resonance appears in the high-field portion (1.85 ppm from TMS) of the spectrum for the iodo–Ni(II) macrocycle. This assignment is consistent with molecular models and previously reported assignments of equivalent pendant methyl groups bound to carbons adjacent to metal coordinated nitrogens in macrocyclic and noncyclic quadridentate complexes.[17]

Methylene Protons. The absorptions at ca. 2.35 and 2.85 ppm are assigned to the various methylene protons in the iodo–Ni(II) complex.[18] The observed 1:2 (i.e. 6:12) ratio of integrated methyl to methylene protons supports these assignments.

Amine Protons. The broad intense signal at ca. 4.7 ppm is attributed to the N–H protons. This absorption is obscured by the HDO resonance.

Biimidazole Protons. Chemical shifts at ca. 6.7 and ca. 7.2 ppm have been assigned to the aromatic protons of biimidazole.

The solids carbon-13 nuclear magnetic resonance spectra of 1,1′-diacetyl-2,2′-biimidazole and [Pd16N6]Cl$_2$H$_2$O are shown in Figures 2 and 3 and a comparison of the spectral data along with those for [Ni16N6]I$_2$ is made in Table II. The observed close comparison of specific carbon shifts of standard reference compounds with the prepared compounds strongly support mac-
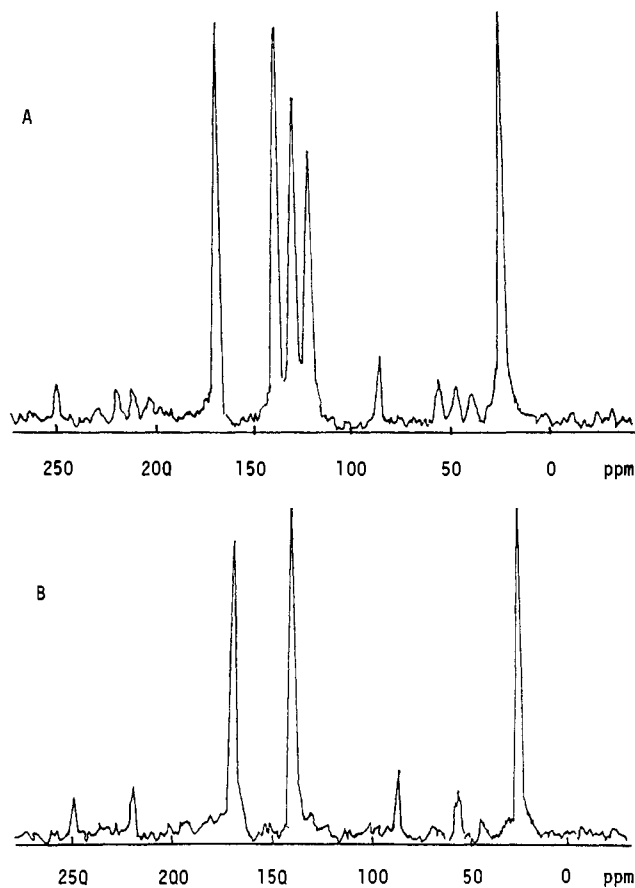
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Figure 2. Solid-state ^{13}C NMR spectra of 1,1′-diacetyl-2,2′-biimidazole: (A) complete carbon spectrum; (B) proton-decoupled spectrum.

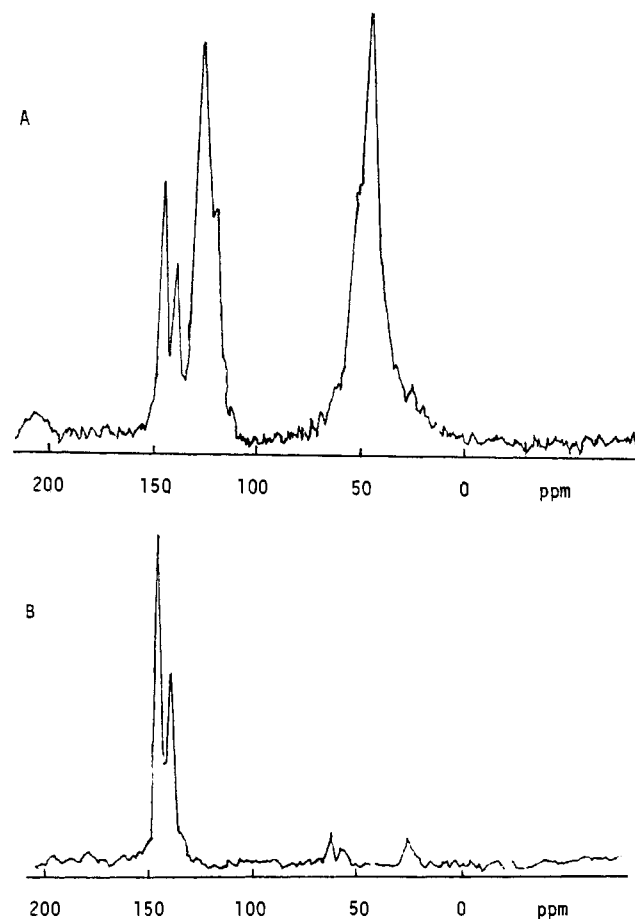**Figure 3.** Solid-state ^{13}C NMR spectra of [Pd16N6]Cl$_2$H$_2$O: (A) complete carbon spectrum; (B) proton-decoupled spectrum.

Table II. Summary of Solid-State ^{13}C NMR Shifts (ppm) for 1,1'-Diacetyl-2,2'-biimidazole and Ni(II) and Pd(II) Macrocyclic Complexes

assignt	ref shift	1,1'-diacetyl-2,2'-biimidazole exptl shift
C, carbonyl	158–175	168
C, carbonyl methyl	10–30	24
C2, imidazole	136	138
C3, imidazole	122	122
C4, imidazole	122	130

assignt	ref shift[23]	exptl shift [Pd16N6]I$_2$	[Ni16N6]I$_2$
C, methyl	~20	25	23
C, trien	40–60	45	42
C, ethylene imine	40–60	52	53
C3, imidazole	122	120	118
C4, imidazole	122	126	125
C2, imidazole	136	139	137
C, imine	140–160	145	155

rocycle formation.[19] In addition, the selective nonprotonated carbon spectra for these compounds in Figures 2b and 3b clearly show the nonprotonated carbons of biimidazole and the imine carbon resulting from Schiff-base formation. The apparent lack of diminution of the methyl carbon in the deprotonated spectrum of 1,1'-diacetyl-2,2'-biimidazole is presumably due to rapid methyl group rotation, which reduces the proton–carbon dipolar couplings.[20] The reason for the low intensity of the methyl carbon absorption at ca. 25 ppm in the [Pd16N6]Cl$_2$H$_2$O complex carbon-13 spectrum is only speculative. Presumably macrocycle formation imposes a degree of steric restraint on the methyl carbon, thus introducing shielding and rotational factors that are particularly emphasized in the solid state.

Electronic Spectral Analysis. Table I lists the magnetic moments and solid-state spectral absorption maxima for Ni(II), Cu(II), and Pd(II) macrocyclic complexes. The complexes of the formula [Ni16N6X$_2$], where X is Cl$^-$ or Br$^-$, have magnetic moments near ca. 3.2 μ_B, corresponding to two unpaired electrons and thus considered to contain axially distorted octahedral or tetragonal nickel(II) in its common triplet ground states.[21] The nickel(II) iodide and Pd(II) complexes are diamagnetic and may be considered to contain a planar metal ion in the singlet state.

Electronic absorption spectra were measured at room temperature over the 200–750 nm range. The iodo derivative of [Ni16N6]$^{2+}$ shows one absorption at 438 nm. This result is consistent with the presence of a planar Ni(II) species,[22] and the band is assigned to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$. In addition, a charge-transfer band occurs at 286 nm. This peak has previously been assigned to a transition of the π-electrons on the C=N groups.[23] The spectra of the high-spin chloro and bromo derivatives of the Ni(II) complex show absorption patterns that resemble that of *trans*-diacido–nickel(II)–tetraaza macrocyclic ligands reported by Martin et al.[24] except for a hypsochromic shift of spectral bands due to the presence of the imine functions. Although the present complexes have lower symmetry than D_{4h}, the observed spectra can be interpreted on the basis of ligand field models. According to the tetragonal ligand field model, the transition $^3B_{2g} \rightarrow {}^3B_{1g}$ corresponds, in a first approximation, to the in-plane ligand field strength (Dq_{xy}). This band is observed at 14 085 and 14 205 cm^{-1} for the chloro and bromo derivatives, respectively. In the case of the chloro derivative, it is likely that the water molecule may be hydrogen bonded to the chloride, and thus the axial ligand field is reduced, giving rise to a slightly stronger in-plane ligand field.[24,25] In addition, the spectrum shows

a band in the range 580–556 nm that is assigned to the $^3B_{1g} \rightarrow {}^3A_{2g}$ transition and a broad absorption around 500 nm that may be assigned to the $^3B_{1g} \rightarrow {}^3E_g + {}^3A_{2g}$ transition. The electronic spectrum of the Cu(II) macrocycle show bands at 591, 275, and 262 nm. These assignments are consistent with analogous complexes reported by Curtis and House.[17] The band at 196 nm shows splitting, which has been assigned to the $\pi \rightarrow \pi^*$ transition of azomethine, and suggests that the azomethine groups have different energy states.[26]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 1700 Fourier transform spectrometer (range 4000–450 cm^{-1}) by using KBr disks. Proton and carbon-13 NMR solution spectra were recorded by using a JEOL FX100 Fourier transform spectrometer. A Varian Model VXR-200 Fourier transform spectrometer, operating at 50.3 MHz in the ^{13}C mode, was used to obtain solids magnetic resonance CPMAS spectra. High-power ^{1}H decoupling was used to eliminate ^{1}H–^{13}C dipolar interactions. Selective nonprotonated carbon resonances in solid-state nuclear magnetic resonance spectra were obtained according to a previously described procedure.[20] Hexamethylbenzene was used as the external reference. Electronic spectra were obtained with a modified Cary Model 16 scanning spectrometer. C, H, N, and metal microanalyses were performed in the University of Missouri—Rolla Chemistry Department and by Galbraith Laboratories.

Preparation of Complexes. All chemicals were of ultrapure grade quality and used without further purification. **1,1'-Diacetyl-2,2'-biimidazole** was prepared according to a published procedure.[9] The white precipitate obtained was filtered and washed with anhydrous ether under under a nitrogen blanket. An ether slurry of the precipitate was placed in vials and the ether removed by evacuation in a desiccator over Drierite (mp 203–204 °C). (Triethylenetetramine)nickel(II) tetrachlorozincate, [Ni(trien)]ZnCl$_4$·H$_2$O, (triethylenetetramine)nickel(II) perchlorate, [Ni(trien)][ClO$_4$]$_2$, (triethylenetetramine)copper(II) perchlorate, [Cu(trien)][ClO$_4$]$_2$, and (triethylenetetramine)palladium(II) tetrachloropalladate, [Pd(trien)][PdCl$_4$], were prepared according to published procedures.[2–4] *Caution!* solutions containing perchlorate should not be evaporated to dryness by heating; otherwise a violent explosion may result.

Dichloro[2,7-dimethyl-3–6-(1,1'-biimidazolo)-1,3,6,8,11,14-hexaaza-cyclohexadeca-1,7-diene]palladium(II). A 1.252-g quantity of [Pd(trien)][PdCl$_4$] (2.5 mmol) was suspended in 25 mL of distilled H$_2$O and stirred at 60 °C. To this mixture was added a 0.10 M solution of trien in distilled water dropwise until a yellow solution was formed, indicating the formation of [Pd(trien)]$^{2+}$. This solution was adjusted to pH 5 by using 0.10 M HCl. A 1.090-g quantity of 1,1'-diacetyl-2,2'-biimidazole (5.0 mmol) in 25 mL of 1,4-dioxane was added with vigorous stirring and the mixture heated at 60 °C for 24 h. An excess of LiCl (0.297 g, 7.0 mmol) was added and stirring continued for an additional 12 h. The yellow product that formed was filtered and washed several times with a warm 1:1 dioxane–water mixture. The product was dried under vacuum and stored in a desiccator under argon. Yield: 1.87 g (71.5%).

Diiodo[2,7-dimethyl-3–6-(1,1'-(2,2'-biimidazolo)-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene]nickel(II). A 1.03-g quantity of [Ni^{II}(trien)]ZnCl$_4$ (2.4 mmol) was dissolved in 25 mL of distilled H$_2$O and stirred at room temperature for 1 h. The solution was then adjusted to pH 5 with 0.1 M HClO$_4$. To the stirred solution was added a 0.545-g quantity of 1,1-diacetyl-2,2'-biimidazole (2.5 mmol) in 25 mL of 1,4-dioxane. The red-orange mixture was stirred for 36 h at room temperature. An excess of KI (1.16 g, 7.0 mmol) was added and stirring continued for an additional 6 h. The product was rotoevaporated under vacuum to near dryness to yield an orange, amorphous solid. The solid was redissolved in a minimum amount of 1:1 1,4-dioxane–water mixture, the resulting solution was filtered, and the solvent was removed by rotoevaporation to yield an orange product. Drying of the complex was completed in a desiccator under vacuum. Yield: 1.24 g (77.4%). Corresponding dichloro and dibromo complexes were obtained with the above procedure by substituting LiCl or KBr for KI, respectively. The [Ni(16N6)](ClO$_4$)$_2$ complex was prepared by using the above procedure with [Ni(trien)](ClO$_4$)$_2$ in nitromethane.

[2,7-Dimethyl-3–6-(1,1'-(2,2'-biimidazolo)-1,3,6,8,11,14-hexaaza-cyclohexadeca-1,7-diene]copper(II) Perchlorate. A 2.242-g (0.005-mol) quantity of [Cu(trien)](ClO$_4$)$_2$ was dissolved in 50 mL of 2-propanol. This solution was adjusted to pH 5 by addition of dilute perchloric acid. A 1.090-g (0.005-mol) quantity of 1,1'-diacetyl-2,2'-biimidazole, dissolved in 30 mL of 1,4-dioxane, was added with vigorous stirring. The

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reaction mixture was heated at reflux temperature for 24 h. This solution was then rotoevaporated under reduced pressure until the onset of the blue precipitate of the macrocycle. The product was collected and recrystallized from an isopropyl alcohol–dioxane mixture. Yield: 2.18 g (74.6%).

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Syntheses and Structural Studies of New Bicyclic 1,3-Diphenyl-1,3,2λ³,4λ³-diazadiphosphetidines

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Reactions of *cis*-[(C$_6$H$_5$N)PCl]$_2$ (1) with the difunctional reagents HO(CH$_2$)$_2$OH, H(CH$_3$)N(CH$_2$)$_2$N(CH$_3$)H, H(CH$_3$)N(CH$_2$)$_2$OH, and HO(CH$_2$)$_3$OH in the presence of triethylamine yield the new bicyclic 1,3,2λ³,4λ³-diazadiphosphetidines [(C$_6$H$_5$N)P]$_2$[-O(CH$_2$)$_2$O-] (2), [(C$_6$H$_5$N)P]$_2$[-(CH$_3$)N(CH$_2$)$_2$N(CH$_3$)-] (3), [(C$_6$H$_5$N)P]$_2$[-(CH$_3$)N(CH$_2$)$_2$O-] (4), and [(C$_6$H$_5$N)P]$_2$[-O(CH$_2$)$_3$O-] (5), respectively. The products have been characterized by elemental analyses and IR and NMR spectroscopic data. The structures of 4 and 5 have been determined by single-crystal X-ray analysis. Crystal data for 4: monoclinic, *P*2$_1$/*c*, *a* = 9.823 (2) Å, *b* = 8.608 (1) Å, *c* = 18.423 (3) Å, *β* = 90.55 (1)°, *Z* = 4. Crystal data for 5: monoclinic, *P*2$_1$/*c*, *a* = 9.727 (2) Å, *b* = 8.064 (2) Å, *c* = 19.702 (4) Å, *β* = 91.31 (1)°, *Z* = 4. The structures have been solved by direct methods and refined to *R* = 0.028 for 4 and *R* = 0.050 for 5. Compound 4 is the first example of an aminoalkoxy-1,3,2λ³,4λ³-diazadiphosphetidine. The P$_2$N$_2$ ring is slightly puckered in both 4 and 5 and the puckering occurs in a manner opposite to that observed for *cis*-[(RN)PX]$_2$ structures.

Introduction

There has been considerable interest in the cis–trans isomerization of 1,3,2λ³,4λ³-diazadiphosphetidines,[2–10] and some generalizations have been made concerning the factors that determine the relative proportions of the two isomers Ia and Ib. The ^{31}P
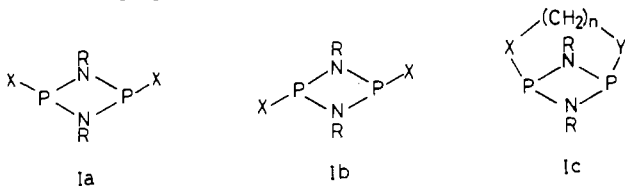

NMR chemical shifts of the two geometrical isomers (Ia, cis, and Ib, trans) differ by 50–90 ppm. Our previous work[10] and that of others[3–7] have clearly demonstrated that for both *N*-alkyl- and *N*-aryl-substituted diazadiphosphetidines, the low-field ^{31}P chemical shift corresponds to the trans isomer and the high-field shift corresponds to the cis counterpart.

The ^{31}P chemical shifts of bicyclic derivatives Ic[7,8,11] obtained from the reaction of *N*-tert-butylchlorodiazadiphosphetidine (Ia, R = t-C$_4$H$_9$, X = Cl) with difunctional reagents lie inbetween the values for the cis and trans isomers even though in these compounds the atoms of the bridging group attached to the phosphorus must have a mutual cis orientation with respect to the P–N ring. Structural studies, which may provide a clue to the origin of these shifts have not been carried out on these compounds. We now report the synthesis of a series of bicyclic compounds (2–5) derived from the *N*(ring)-phenyldiazadiphosphetidine, [(PhN)PCl]$_2$ (1), their spectroscopic characterization, and the X-ray crystal structure analysis of two of these derivatives, 4 and 5.[12] The structural features are compared with those available for geometrical isomers of diazadiphosphetidines and also the related *ansa*-cyclotriphosphazenes and trans-annular bridged cyclotetraphosphazenes.

Results and Discussion

Syntheses and NMR Spectra. The reactions of *cis*-[(C$_6$H$_5$N)PCl]$_2$ (1)[3,13] with the diols HO(CH$_2$)$_n$OH (*n* = 2 or

3), the diamine H(CH$_3$)N(CH$_2$)$_2$N(CH$_3$)H and the amino alcohol H(CH$_3$)N(CH$_2$)$_2$OH afford bicyclic 1,3-diphenyl-1,3,2λ³,4λ³-diazadiphosphetidines 2–5. Triethylamine is used as a hydrogen
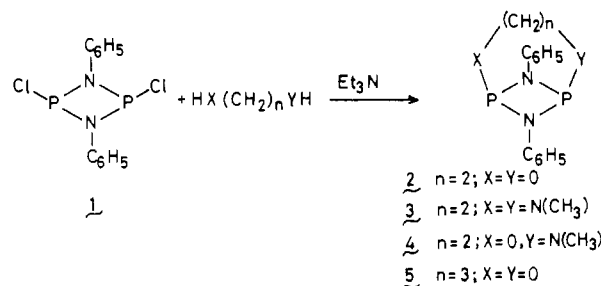
chloride acceptor in all of the reactions except in the reaction with the diamine, where the reactant diamine itself functions as a scavenger of hydrogen chloride.

The reaction conditions vary depending on the nature of di-

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