reactions. Indeed, $Pt(dba)_2$ does catalyze the reaction of $Fe(CO)_5$ and $PPhMe_2$ to give $Fe(CO)_4(PPhMe_2)$ and the reaction of $CpFe(CO)_2I$ and $P(OMe)_3$ to give $CpFe(CO)[P(OMe_3](I)$. The reaction of $CpFe(CO)_2I$ and $Ph_2PCH_2CH_2PPh_2$(dppe) to produce CpFe(dppe)I in the presence of $Pt(dba)_2$ is complete within 1 h, and the isolated yield is 84%. Without $Pt(dba)_2$, the reaction is not complete (18% of $CpFe(CO)_2I$ remained unreacted) under the same conditions. There was no observed $Pt(dba)_2$ catalysis of the reactions of $Fe(CO)_5$ with dppe, $P(OMe)_3$, or 2,5-norbornadiene (NBD), which suggests that the method may be limited to monodentate phosphines.

Conclusion

There are several attractive features of the $Pt(PPh_3)_4$-catalyzed method of substituting a CO ligand in metal carbonyls by PPh_3: (a) The reaction cleanly provides monosubstituted products in high yields (70–98%). (b) The catalyst can be recovered almost quantitatively at the end of the experiment. (c) For clusters that tend to fragment under other conditions, the $Pt(PPh_3)_4$ method yields the intact clusters. (d) k_{CO} values are helpful for predicting metal carbonyl complexes to which the method can be applied. The substitution of one CO in $Fe(CO)_5$ and $CpFe(CO)_2I$ by PPh_3 and/or PMe_2Ph is also catalyzed by $Pt(dba)_2$, suggesting that $Pt(dba)_2$ may be used more generally to catalyze monodentate phosphine substitution of metal carbonyls.

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Registry No. dppe, 1663-45-2; NBD, 121-46-0; $W(CO)_6$, 14040-11-0; $Fe(CO)_5$, 13463-40-6; $CpFe(CO)_2I$, 12078-28-3; $Re(CO)_5CH_3$, 14524-92-6; $Re_2(CO)_{10}$, 14285-68-8; $Os_3(CO)_{12}$, 15696-40-9; $CpMn(CO)_3$, 12079-65-1; PPh_3, 603-35-0; $PPhMe_2$, 672-66-2; $P(OMe)_3$, 121-45-9; $Pt(PPh_3)_4$, 14221-02-4; $W(CO)_5(PPh_3)$, 15444-65-2; $Fe(CO)_4(PPh_3)$, 14649-69-5; $Fe(CO)_4(PPhMe_2)$, 37410-37-0; $CpFe(CO)(PPh_3)I$, 12099-18-2; CpFe(dppe)I, 55451-49-5; $CpFe(CO)[P(OMe)_3]I$, 31781-71-2; $Re(CO)_4(PPh_3)(CH_3)$, 56474-50-1; $Re_2(CO)_9(PPh_3)$, 27770-63-4; $Os_3(CO)_{11}(PPh_3)$, 30173-88-4; $Pt(dba)_2$, 33677-56-4.

Contribution from the Laboratoire de Chimie
de Coordination du CNRS, Unité No. 8241
liée par convention à l'Université
Paul Sabatier, 205 route de Narbonne,
31077 Toulouse Cedex, France

Reappraisal of the Amide Coordination Mode: Solution Properties of Nickel(II) and Copper(II) Complexes of Ligands Involving Simultaneously Enamine and Amide Groups

Jean-Pierre Costes* and Jean-Pierre Laurent

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Depending on experimental conditions, primary and secondary amide groups are known to bind copper(II) and nickel(II) ions with or without deprotonation.[1] It is generally accepted that, in the former case, coordination occurs through the nitrogen atom while, in the latter case, the carbonyl oxygen is the coordination site. This mode of bonding is largely supported by structural studies,[2,3] but there remains the possibility that the data obtained for solid samples may not be directly applicable to species in solution and that, in some instances, the intact amide nitrogen could serve as the coordinating site. Furthermore, it may be recognized that before considering the problem of the coordinating site (oxygen vs nitrogen), one has to demonstrate unambiguously whether the amide group is intact or not. This is not a trivial problem in the cases where the ligand bonded to the metal ions contains more than one type of ionizable proton.

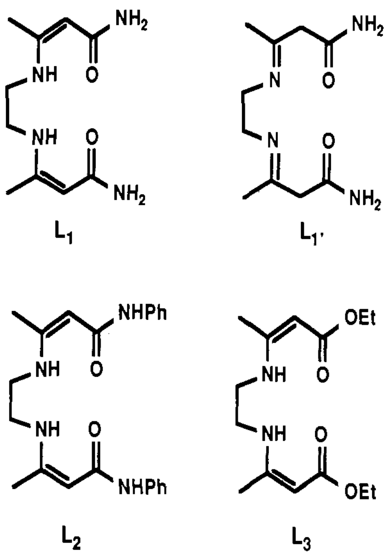

Figure 1. L_1, L_2, and L_3 ligands.

This happens for the complex $[CuL_1]^{2+}$ (Figure 1), L_1 being the Schiff base resulting from the condensation of 1 mol of 1,2-diaminoethane with 2 mol of acetoacetamide. It has been recently proposed,[4] on the basis of potentiometric, spectrophotometric, and ESR data, that the behavior of aqueous solutions of this complex may be depicted by an equilibrium involving the $[CuL_1]^{2+}$, $[Cu(L_1\text{-}H)]^+$ and $[Cu(L_1\text{-}2H)]$ species (L_1-H and L_1-2H representing respectively the mono- and dideprotonated forms of L_1). The point of importance is that, in the three species, the ligand is considered to be a diimino diamide (form $L_{1'}$ in Figure 1) which contains only one type of ionizable proton, viz., those of the amide groups. However, there is no reason to rule out the possibility for the ligand to be in another tautomeric form that can be described as a dienediamino diamide (form L_1 in Figure 1) with two types of ionizable proton.

In the present paper we intend to reappraise the behavior of the Cu^{2+}/L_1 system in solution through the isolation and characterization of the copper(II) complexes involving the ligand L_1 (or $L_{1'}$) in different states of deprotonation. This study includes the homologous nickel(II) complexes and also the copper(II) and nickel(II) complexes of two related ligands L_2 and L_3 (Figure 1).

Experimental Section

Ligand Preparation. The L_1 ligand, 3,8-dimethyl-4,7-diazadeca-2,8-diene-1,10-diamide, was synthesized from acetoacetamide and 1,2-diaminoethane as previously described.[4]

L_1. $^{13}C\{^1H\}$ NMR in DMSO: 15.8 (CH_3), 40.7 (CH_2), 82.8 (CH), 155.0 (CN), 169.5 ppm (CO).

L_2 and L_3 ligands were similarly obtained by respectively using acetoacetanilide and ethylacetoacetate instead of acetoacetamide.

L_2 (*N,N'*-Diphenyl-3,8-dimethyl-4,7-diazadeca-2,8-diene-1,10-diamide). Anal. Calcd for $C_{22}H_{26}N_4O_2$: C, 69.8; H, 6.9; N, 14.8. Found: C, 69.4; H, 7.0; N, 14.7. $^{13}C\{^1H\}$ NMR in $CDCl_3$: 19.4 (CH_3), 43.9 (CH_2), 85.8 (CH), 139.0 (CN), 119.8 (*o*), 128.8 ppm (*m*), 122.9 (*p*) (phenyl ring), 160.2 (CN), 169.0 ppm (CO).

L_3 (Diethyl 3,8-Dimethyl-4,7-diazadeca-2,8-diene-1,10-dioate). Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.1; H, 8.5; N, 9.9. Found: C, 58.8; H, 8.6; N, 9.7. $^{13}C\{^1H\}$ NMR in $CDCl_3$: 14.5 (CH_3CH_2), 19.1 (CH_3), 43.7 (CH_2), 58.3 (CH_3CH_2), 83.4 (CH), 161.1 (CN), 170.4 ppm (CO).

Complexes of L_1. $L_1Cu(NO_3)_2$. This compound was prepared as described previously.[4]

(L_1-2H)Cu. $L_1Cu(NO_3)_2$ (0.5 g) was dissolved in 50 mL of ethanol. NaOH (0.1 g) in 1 mL of water then was added dropwise, inducing the precipitation of gray precipitate with a quantitative yield. Anal. Calcd for $C_{10}H_{16}CuN_4O_2$: C, 41.7; H, 5.6; Cu, 22.1; N, 19.5. Found: C, 41.1; H, 5.5; Cu, 21.8; N, 19.5.

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Table I. ^{1}H NMR Data: Chemical Shifts in ppm, Multiplicities, and Relative Intensities

	L_1[a]	$(L_1\text{-}2H)Ni$[a]	$(L_1\text{-}4H)Ni^{2-}$[b]	L_2[c]	$(L_2\text{-}2H)Ni$[c]	L_3[c,h]	$(L_3\text{-}2H)Ni$[c,i]
CH_3	1.91 (s)[d] (3)[e]	1.81 (s) (3)	2.07 (s) (3)	1.91 (s) (3)	1.83 (s) (3)	1.89 (s) (3)	1.81 (s) (3)
CH_2	3.31 (m) (2)	2.84 (s) (2)	3.41 (s) (2)	3.35 (m) (2)	2.90 (s) (2)	3.33 (m) (2)	2.85 (s) (2)
CH	4.42 (s) (1)	5.13 (s) (1)	4.22 (s) (1) 5.22 (s) (1)[f]	4.43 (s) (1)	4.36 (s) (1)	4.47 (s) (1)	4.25 (s) (1)
NH_2 or NH (amide)	6.25 (s) (2)	5.83 (s) (1)	5.22 (s) (1) 4.22 (s) (1)[f]	6.63 (s) (1)	6.15 (s) (1)		
NH (imine)	9.22 (t) (1)			9.33 (t) (1)		8.63 (s)[g] (1)	

[a] Solvent: DMSO. [b] Solvent: H_2O. [c] Solvent: $CDCl_3$. [d] Multiplicity: s for singulet, d for doublet, t for triplet, q for quartet, m for multiplet. [e] Relative intensity with respect to the intensity of the CH signal. [f] Alternative attribution. [g] Broad. [h] Other signals: 1.21 (t) (3), 4.06 (q) (2). [i] Other signals: 1.17 (t) (3), 3.92 (q) (2).

$L_1Ni(NO_3)_2 \cdot 2H_2O$. The ligand L_1 (0.5 g) was suspended in 50 mL of acetone. An acetonic solution (30 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.64 g) then was added at once. The mixture was stirred at ambient temperature, and a violet precipitate appeared after 10 min and increased with time. One hour later, the product was isolated by filtration, washed with acetone and dried. The yield was nearly quantitative. Anal. Calcd for $C_{10}H_{18}N_6NiO_8 \cdot 2H_2O$: C, 27.0; H, 5.0; N, 18.9; Ni, 13.0. Found: C, 26.9; H, 5.0; N, 18.9; Ni, 12.9.

$(L_1\text{-}2H)Ni$. The neutral complex was obtained as the corresponding copper complex with the same yield. Anal. Calcd for $C_{10}H_{16}N_4NiO_2$: C, 42.5; H, 5.7; N, 19.9; Ni, 20.6. Found: C, 42.7; H, 5.8; N, 20.1; Ni, 20.4.

$(L_1\text{-}4H)NiNa_2 \cdot 2H_2O$. To $L_1Ni(NO_3)_2 \cdot 2H_2O$ (0.5 g) dissolved in 5 mL of water was added dropwise and quite slowly a 2.5 M NaOH solution. A first precipitate appeared, corresponding to the neutral species. It dissolved again in the solution and eventually from the solution a yellow precipitate appeared. It was filtered, washed with methanol and acetone, and dried. Yield: 60%. Anal. Calcd for $C_{10}H_{14}N_4Na_2NiO_2 \cdot 2H_2O$: C, 32.4; H, 7.0; N, 15.1; Ni, 15.7. Found: C, 32.5; H, 6.7; N, 15.0; Ni, 15.7.

Complexes of L_2. $L_2Cu(NO_3)_2$ and $L_2Ni(NO_3)_2 \cdot H_2O$ were obtained by using the same procedure as for $L_1Ni(NO_3)_2 \cdot 2H_2O$ and with a similar yield. Anal. Calcd for $C_{22}H_{26}CuN_6O_8$: C, 46.7; H, 4.6; Cu, 11.2; N, 14.8. Found: C, 46.4; H, 4.7; Cu, 11.1; N, 14.9.

Anal. Calcd for $C_{22}H_{26}N_6NiO_8 \cdot H_2O$: C, 45.7; H, 4.8; N, 14.5; Ni, 10.0. Found: C, 45.4; H, 5.0; N, 14.5; Ni, 9.8.

$(L_2\text{-}2H)Cu$ and $(L_2\text{-}2H)Ni$ were prepared by dissolution of the nondeprotonated precursors $L_2Cu(NO_3)_2$ and $L_2Ni(NO_3)_2 \cdot H_2O$ in a MeOH/water mixture followed by addition of an aqueous 2 M solution of NaOH. Neutral species precipitated and were filtered and dried. Yield: 90%. Anal. Calcd for $C_{22}H_{24}CuN_4O_2$: C, 60.1; H, 5.5; Cu, 14.4; N, 12.7. Found: C, 59.6; H, 5.7; Cu, 14.2; N, 12.8.

Anal. Calcd for $C_{22}H_{24}N_4NiO_2$: C, 60.8; H, 5.5; N, 12.9; Ni, 13.4. Found: C, 60.3; H, 5.4; N, 12.8; Ni, 13.2.

Complexes of L_3. $(L_3\text{-}2H)Cu$. To L_3 (1 g) in 50 mL of acetone was added with stirring $Cu(NO_3)_2 \cdot 3H_2O$ (0.85 g) dissolved in 40 mL of acetone. Then 1 mL of NEt_3 was added, and the solution turned purple. Ten minutes later, addition of water precipitated a purple compound, which was filtered. The solid product was dissolved in CH_2Cl_2. Slow evaporation of the solution gave the desired complex. Yield: 65%. Anal. Calcd for $C_{14}H_{22}CuN_2O_4$: C, 48.6; H, 6.4; Cu, 18.4; N, 8.1. Found: C, 48.5; H, 6.6; Cu, 18.1; N, 8.0.

A similar procedure yielded $(L_3\text{-}2H)Ni$. Anal. Calcd for $C_{14}H_{22}N_2NiO_4$: C, 49.4; H, 6.5; N, 8.2; Ni, 17.0. Found: C, 49.0; H, 6.6; N, 8.0; Ni, 16.8.

Physical Measurements. Microanalysis were performed by the Service Central du CNRS, Lyon, France. Infrared and electronic spectra were respectively obtained with a Perkin-Elmer PE-983 and a Cary 2390 spectrometer. ESR spectra were recorded with a Bruker 200 TT spectrometer in the X-band region at 9.4 GHz on liquid samples (water/MeOH (1/1) or CH_2Cl_2) at ambient temperature in round quartz sample tubes. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WH 90 spectrometer. All chemical shifts (^{1}H and ^{13}C) are given in ppm versus TMS, with DMSO, D_2O, or $CDCl_3$ used as solvent.

Results and Discussion

As described in the Experimental Section, 11 copper(II) and nickel(II) complexes have been prepared. From chemical analysis data and charge balance consideration, they can be described by the following crude formulation:

$$[L_1M]^{2+},\ [(L_1\text{-}2H)M],\ [(L_1\text{-}4H)Ni]^{2-}$$

$$[L_2M]^{2+},\ [(L_2\text{-}2H)M]$$

$$[(L_3\text{-}2H)M]$$

M being Cu^{2+} or Ni^{2+}.

Before considering in details the spectroscopic properties of these complexes, we would pay a particular attention to two points. First, deuteriation experiments performed on the cationic species $[L_1M]^{2+}$ yield products that display a single N–D absorption (2300 cm^{-1}) in their infrared spectra. This is not consistent with deuteriation occurring at the amide groups, which would result in the observation of two N–D absorptions separated by ca. 100 cm^{-1}.[5] Then reacting these deuteriated samples with NaOD yields neutral species that exhibit infrared spectra devoid of any N–D absorption and perfectly identical with those of $(L_1\text{-}2H)M$ complexes prepared from non-deuteriated $[L_1M]^{2+}$ species. This strongly suggests that the ligand actually reacts as a dienediamino diamide and that the protons lost in passing from the cationic complexes to the neutral ones belong to the enamine groups and not to the amide functions. This view is further supported by the fact that we succeeded in further deprotonating $(L_1\text{-}2H)Ni$ to obtain a $[(L_1\text{-}4H)Ni]^{2-}$ complex in which the amide groups are no longer intact.

^{1}H and ^{13}C NMR Spectroscopy. The free ligands L_1, L_2, and L_3 display very characteristic spectra (Table I). For instance, five signals are observed in the ^{1}H spectrum of L_1, and on the basis of their chemical shifts, multiplicities and relative intensities, they can be unambiguously attributed. The observation of only one CH signal and one CH_2 signal is conclusive of the nature of the actual tautometric form as is the observation of two well-separated NH signals at 6.25 and 9.22 ppm. Furthermore, irradiation of the latter signal, which displays a triplet structure, causes the multiplet centered at 3.31 ppm (CH_2) to merge into a single signal. Therefore, the fine structure observed on both sets of signals results from a $^3J_{HH}$ coupling between the CH_2 and NH protons, which can be understood only within the framework of a dienediamino diamide structure. This structure is also supported by the observation of five signals in the ^{1}H-decoupled ^{13}C spectra. Owing to their multiplicities in the ^{1}H-coupled spectra, the attribution is straightforward, i.e. 15.8 (q, CH_3), 40.7 (t, CH_2), 82.8 (d, CH), 155.0 (s, CN), and 169.5 ppm (s, $CONH_2$). Obviously, a similar conclusion regarding the occurrence of an enamine-based structure can be drawn from the ^{1}H (Table I) and ^{13}C (cf. Experimental Section) spectra of L_2 and L_3.

Regarding the complexes, the NMR study is restricted to the ^{1}H resonance of the diamagnetic nickel complexes. From the data quoted in Table I, it is obvious that an enamine-type structure is the only one to occur in the four neutral complexes. Furthermore, the disappearance of the NH signal, which is located at 9.22 (L_1), 9.33 (L_2), and 8.63 ppm (L_3) in the spectra of the free ligands together with the simplification of the CH_2 multiplets into singlets provides definitive evidence that deprotonation concerns the enamine groups. Despite some uncertainty regarding the respective attributions of the signals that appear, in the $[(L_1\text{-}4H)Ni]^{2-}$ spectrum, at 4.22 and 5.22 ppm with equal intensities, there is no doubt that one is attributable to two CH protons and the other to two NH protons, showing that the amide groups are no longer intact.

ESR Spectroscopy. As previously reported, this spectroscopy offers in principle an easy means to determine the number of

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Table II. Optical Spectral Data and ESR Parameters

	$[L_1M]^{2+}$	$(L_1\text{-}2H)M$	$[(L_1\text{-}4H)M]^{2-}$	$[L_2M]^{2+}$	$(L_2\text{-}2H)M$	$(L_3\text{-}2H)M$
			M = Ni			
λ_{max},^{a} nm	820, 736, 570^a	440^a	432^c	820, 736, 564^a	590^d	596^d
			M = Cu			
λ_{max}, nm	626^a	524^a		630^a	550^d	550^d
g_{iso}^{b}	2.127^a	2.101^a		2.126^a	2.099^d	
A_{iso},^{b} G	74	75		75	92	
A_N,^{b} G	12.5	14.1		12.0	12.5	
no. of N-shf lines	5	9		5	5	

^{a}Solution in CH_3OH/H_2O (1/1). ^{b}Isotropic spectra related to solutions studied at 295 K. ^{c}Solution H_2O. ^{d}Solution in CH_2Cl_2.

nitrogen atoms adjacent to the copper ion through the observation of the superhyperfine (N-shf) lines.[6]

All the isotropic spectra (solutions studied at room temperature) considered in the present work (Table II) show the well-known hyperfine structure of four lines due to coupling of the electron with the nuclear spin ($I = {}^3/_2$) of the copper ion. In addition, interaction of the electron with the adjacent ^{14}N nuclei ($I = 1$) results in a superhyperfine structure clearly discernible on the high-field component of the hyperfine spectrum. In all complexes but one, five N-shf lines are observed with a separation of ca. 12.5 G, indicating that the environment of the copper ion is N_2O_2. In one case, namely $(L_1\text{-}2H)Cu$, the number of N-shf lines increases to nine in accordance with four nitrogen atoms surrounding the copper ion.

Electronic Spectroscopy. Considering the positions of the absorption maximum (λ_{max}) reported in Table II, it appears that similar trends are observed for the copper and nickel complexes. However, the spread of the observed λ_{max} values is markedly smaller in the former series than in the second one.

Among the three neutral copper complexes, the same value (550 mm) is observed for $(L_2\text{-}2H)Cu$ and $(L_3\text{-}2H)Cu$ whereas $(L_1\text{-}2H)Cu$ displays a lower value (524 nm). This is in accordance with the change in the coordination sphere established by ESR data (from N_2O_2 in the former complexes to N_4 in the latter one) and the generally accepted assumption that a shift of the absorption maximum toward shorter wavelengths is associated with an increase in the number of the nitrogen atoms adjacent to the metal center.[7] The high values of ca. 630 nm characterizing the cationic complexes likely reflect a tetragonal deformation.[8]

Regarding the nickel complexes, identical spectra, characteristic of an octahedral geometry, are obtained for the cationic complexes. This contrasts with the behavior of the related neutral complexes, which display very different values of the absorption maximum. In addition, we must note that similar values of λ_{max} are observed for $(L_1\text{-}2H)Ni$ and $[(L_1\text{-}4H)Ni]^{2-}$ on the one hand and $(L_2\text{-}2H)Ni$ and $(L_3\text{-}2H)Ni$ on the other hand. Recalling that in this last complex the environment of the nickel can be nothing but N_2O_2 and that deprotonation of the amide groups likely favors a N_4 environment in $[(L_1\text{-}4H)Ni]^{2-}$, we think that, as is the case for the related copper complexes, the shift of λ_{max} from 590 nm in $(L_2\text{-}2H)Ni$ to 440 nm in $(L_1\text{-}2H)Ni$ reflects a change of the coordination mode from N_2O_2 to N_4.

Conclusion

The ESR and visible spectroscopic data herein obtained for $[L_1Cu]^{2+}$ and $(L_1\text{-}2H)Cu$ are almost identical with those previously reported by Lim and McCool[4] for the isolated cationic complex and the nonisolated neutral species, respectively. However, comparative scrutiny of the chemical behavior and spectroscopic data relating to the whole set of copper and nickel complexes prepared from L_1, L_2, and L_3 affords converging arguments to demonstrate that, in all cases, (i) not only the ligand L_3 but also L_1 and L_2 are in the enamine form and (ii) the first step of the deprotonation process concerns the protons of the enamine functions and not those of the amide groups.

Therefore, the presence of four nitrogen atoms adjacent to the metal ion in the $(L_1\text{-}2H)M$ complexes (M = Cu, Ni) implies that the nitrogen atoms of the intact primary amide groups are able to coordinate the metal ion at least in solution.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Pillaring of Layered Zirconium and Titanium Phosphates

A. Clearfield* and B. D. Roberts

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In the preceding two decades, a new class of two-dimensional porous materials has been synthesized from smectite clay minerals.[1] This was accomplished by swelling the clays and inserting large species between the layers to keep them apart. Smectite clays are able to swell in water because of their low layer charge and, thus, easily intercalate organic guest molecules or large inorganic polymers.[2] In general, the organically pillared structures suffer from the thermal instability of the organic component, which limits their use in catalysis. Since a major motive for the preparation of these materials is to provide new catalytically active large-pore structures, robust pillars are required. Therefore, attention was focused on the use of the aluminum Keggin ion, $[Al_{13}O_4(OH)_{24}\cdot 12H_2O]^{7+}$, or the zirconium tetramer, $[Zr(OH)_2\cdot 4H_2O]_4^{8+}$, as pillars.[3–5] Ideally, the inserted inorganic species will be arranged so as to leave large spaces, of the order of 10–12 Å, between them. They have therefore been viewed as pillars propping open the layers so as to provide porosity for sorption or enhanced catalytic activity. From its early beginnings, a considerable literature has developed, details of which are given in recent reviews.[2,6,7] However, there are a large number of clays and nonsilicious layered compounds that do not swell in water and therefore are not accessible to pillaring by conventional methods. We were interested in pillaring such compounds, and in developing several methods applicable to large classes of layered materials so as to produce potential sorbents and catalysts with a range of acidic and shape-selective properties. In this note we describe a method of accomplishing this goal with zirconium and titanium phosphates. It entails first intercalating an amine between the layers and then exchanging the cationic pillar for the interlamellar alkylammonium ion. We had earlier shown that large charged complexes could be incorporated between the layers in this manner.[8]

Experimental Section

α-Zirconium (α-ZrP) and α-titanium phosphates (α-TiP), $M(HPO_4)_2\cdot H_2O$, and γ-zirconium (γ-ZrP) and γ-titanium phosphates (γ-TiP), $M(HPO_4)_2\cdot 2H_2O$, were prepared in the usual way.[9,10] Butylamine

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* To whom correspondence should be addressed.