a consideration of boron coordination number. The B(5) of 2,4-$C_2B_5H_7$ has a coordination number of 5, whereas B(2) of 1,10-$C_2B_8H_{10}$ has a coordination number of 6. A substitution reaction at a boron atom that has a higher coordination number might be less susceptible toward attack by an external reagent than a boron atom that has a lower coordination number.[1]

Acknowledgment. We wish to thank the National Science Foundation (Grant No. CHE-8315951) and the MARC-NIH program for partial support of this study. The ^{11}B NMR data were obtained by the use of a Bruker WM-500 instrument at the Southern California Regional NMR facility at the California Institute of Technology, funded by NSF Grant CHE-84-40137.

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Sulfur–Nitrogen-Bonded Metal Chelates. 16. Reactivities of Coordinated Nitriles in the Nickel(II) Complexes $[Ni(S\frown N\frown N)(NCR)](ClO_4)$ with Alcohols, Amines, and Different Nucleophiles. Synthesis, Characterization, and Stereochemistry of Imino–Ether, Amide, and Amidine Complexes

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Received July 22, 1986

The reactions of the nitrile complexes $[NiL(NCR)]ClO_4$ (HL^1 = methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate, HL^3 = methyl 2-((2-(diethylamino)ethyl)-amino)cyclopent-1-enedithiocarboxylate; R = Me, Et, Ph) with dry alcohols, wet alcohols, water, alkali, secondary aliphatic and heterocyclic amines, aliphatic primary amines, pyridine, PPh_3, $Ph_2P(CH_2)_2PPh_2$, and some anions (N_3^-, CN^-, NCO^-) have been investigated. Dry alcohols (R'OH) add on to the coordinated nitrile in the presence of excess of free nitrile to form imino–ether complexes, $[NiL(NH{=}C(OR')R)](ClO_4)$. The reaction becomes much faster when sodium alkoxide is used as a catalyst. If the alcohol used is wet, the product is an amido complex, $[NiL(NH_2COR)](ClO_4)$. Secondary amines (HNR'_2) react with the nitrile to form the amidine complexes $[NiL(NH{=}C(NR'_2)R)](ClO_4)$. With primary amines both addition to and substitution of the nitrile take place. With the remaining other nucleophiles displacement of the nitrile takes place. All of the reaction products have been isolated and characterized. The ^{1}H NMR spectra of the imino–ether and amidine complexes have revealed the presence of two (*E* and *Z*) isomeric species, whose distribution at ambient temperature has been determined.

Introduction

Augmented reactivities of coordinated molecules in metal complexes have wide implications in chemistry. Metal ions in complexes can have the effect of a "superacid" to polarize ligands and thus to render them susceptible to nucleophilic attack.[1] Such reactions are usually facilitated by the charge on cationic complexes, especially by the charge density of the metal ion. Aside from thermodynamic and kinetic factors, the stereochemical role of the metal ion and stabilization of the product molecule through complex formation often become important in deciding the course of a reaction.

Over the past 20 years considerable attention has been focused on the reactions based upon nucleophilic attack on coordinated nitriles[2] in metal complexes. These include reactions with alcohols to form imino–ethers[3–7] and with amines to form amidines[8–13] and base-catalyzed hydrolysis to imidates.[14–16] The nucleophilic attack of $[CH(PPh_2)X]^-$ (X = CO_2Et, CN)[17] and $[CH(COMe)(COR)]^-$ (R = Me, Ph)[18] anions on the nitrile carbon atom of $[Pt(NCPh)_2Cl_2]$ has also been reported. In all these reactions the product molecule remains bound to the metal center. However, in a few cases metal ion catalyzed hydrolysis of uncomplexed nitrile

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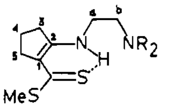
groups has also been found to take place.[19-21] Moreover, catalytic hydration of nitriles to the corresponding carboxamides in high turnover has been accomplished by using some metal complexes as homogeneous catalysts.[22-26]

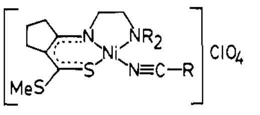
As expected, most of these studies have been concerned with kinetically robust (Co(III), Rh(III), IR(III), Ru(III)) systems or less labile square-planar complexes of platinum(II) and palladium(II). A comparative study of the base hydrolysis of $[M(NH_3)_5(NCPh)]^{3+}$ complexes showed[16] the following decreasing order of reaction rates: Co(III) > Rh(III) > Ir(III). This ordering follows the sequence of the charge densities of the metal ions. Although no such data are available for bivalent d^8 triads, one can expect that nickel(II) complexes will be most reactive, provided substitution of the nitrile(s) in highly labile nickel(II) systems can be prevented.

For quite some time, we have been investigating sulfur-nitrogen-bonded metal chelates.[27] More recently, we have reported the chemistry of nickel(II),[28] palladium(II),[29] and copper(II)[30] complexes of methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate (HL^1, **1a**), methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate (HL^2, **1b**), and methyl 2-((2-(diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate (HL^3, **1c**). We report here that despite the highly labile nature of the nitrile in $[NiL(NCR)]ClO_4$ complexes (**2**), facile addition of alcohols and amines take place on the carbon atom of the NCR group. The synthesis, characterization, and stereochemistry of the imino-ether, amide, and amidine complexes, as well as the products obtained by nucleophilic substitution of the nitrile in **2**, form the subject matter of the present communication. The kinetic and mechanistic aspects of these reactions will be reported[31] later.



(a): HL^1 ; R=H
(b): HL^2 ; R=Me
(c): HL^3 ; R=Et

(1)



(2)

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. MeOH, EtOH, and *n*-PrOH were made "superdry" by standard methods.[32] MeCN, EtCN, and PhCN were successively dried over CaH_2 and P_4O_{10}. The amines used were dried over KOH and distilled before use. The ligands HL^1 and HL^3 were prepared according to a previously described method.[29] HL^2, which is a new derivative, was obtained in the same way; mp 50 °C. $AgClO_4$ was prepared by dissolving an excess of "silver carbonate" (BDH) in dilute $HClO_4$. The filtered neutral solution was evaporated almost to dryness on a steam bath under diffused light. The product was dried over P_4O_{10} in vacuo. It was then twice recrystallized from boiling benzene.

Caution! Although we routinely prepared $AgClO_4$ in this way with no untoward incident, there is a reported case[33] of a violent explosion of benzene-recrystallized product during breaking of the lumps by gentle pressure.

Complexes. $[NiL(NCMe)](ClO_4)$ ($L = L^1-L^3$, I-III). $[NiLCl]^{28}$ (10 mmol) was partially dissolved in MeCN (50 mL), and dry $AgClO_4$ (2.08 g, 10 mmol) dissolved in MeCN (15 mL) was slowly added with stirring. AgCl precipitated, and the solution turned deep green. The mixture was stirred for 1 h and then filtered. The filtrate was concentrated to ca. 10 mL in a rotary evaporator and filtered, and the filtrate was kept in a refrigerator overnight. The green crystals deposited were collected by filtration and recrystallized by dissolving in a minimum volume of acetonitrile followed by overnight cooling at -5 °C; yield 90%.

$[NiL^1(NCR)](ClO_4)$ (R = Et, IV; R = Ph, V). These compounds were prepared in the same way as described above by using a mixture of 10 mL of EtCN/PhCN and 40 mL of $MeNO_2$. The compounds were recrystallized from nitromethane; yield 90%.

$[NiL(NH_2COR)](ClO_4)$ ($L = L^1-L^3$, R = Me, VI-VIII; $L = L^1$, R = Et, IX). About 0.5 g of $[NiL(NCR)](ClO_4)$ was dissolved in 20 mL of MeCN/EtCN to which were then added 60 mL of MeOH and 0.5 mL of water. The mixture was heated under reflux for 6 h, during which time the green solution changed to burgundy red. The solution was concentrated to ca. 5 mL and filtered, and the filtrate was kept in a refrigerator overnight. The brown crystals deposited were collected by filtration and recrystallized from a 4:1 MeOH-RCN mixture; yield 80%.

$[NiL(NH{=}C(OR')R)](ClO_4)$ ($L = L^1-L^3$, R = Me, Et, R' = Me, Et, X-XVII; $L = L^1$, L^3, R = Me, R' = *n*-Pr, XVIII, XIX). $[NiL(NCR)](ClO_4)$ (0.5 g) was dissolved in a mixture of *dry* RCN (20 mL) and *dry* R'OH (60 mL) and heated under reflux in the absence of moisture (2 h for MeOH, 8 h for EtOH, 14 h for *n*-PrOH). The cherry red solution was then concentrated to ca. 5 mL in a rotary evaporator and filtered, and the filtrate was kept in a $CaCl_2$ desiccator overnight. The reddish brown crystals deposited were collected by filtration and recrystallized from a 5:1 *dry* R'OH-RCN mixture; yield 80%.

$[NiL^1(NH{=}C(OMe)Ph)](ClO_4)$ (XX). Complex V (0.5 g) was dissolved in PhCN (5 mL), and *dry* MeOH (40 mL) containing 11.3 mg of NaOMe (20 mol % with respect to the complex) was added. The reaction mixture after 1-h reflux was evaporated to ca. 5 mL in a rotary evaporator and then kept in a $CaCl_2$ desiccator for 12 h. The reddish brown crystals deposited were collected by filtration and recrystallized from an 8:1 *dry* MeOH-PhCN mixture; yield 70%.

$[NiL(NH{=}C(R)Me)](ClO_4)$ ($L = L^1$, R = NMe_2, NEt_2, N-*n*-Pr_2, NC_4H_8 (pyrrolidinyl), NC_5H_{10} (piperidinyl), XXI-XXV; $L = L^2$, L^3, R = NMe_2, XXVI-XXVII; $L = L^1$, R = NHEt, XXVIII). To a MeCN solution (50 mL) of $[NiL(NCMe)](ClO_4)$ (2 mmol) was added the appropriate amine (2 mmol). The solution was kept at ambient temperature for about 12 h, after which it was concentrated to ca. 15 mL. The solution after filtration was allowed to evaporate slowly at ambient temperature. The reddish brown crystals deposited were collected by filtration and recrystallized from MeCN; yield 85%.

$[NiL^1(NH{=}C(NMe_2)Et)](ClO_4)$ (XXIX). Complex IV (0.43 g, 1 mmol) was dissolved in a mixture of EtCN (4 mL) and $MeNO_2$ (16 mL), to which Me_2NH (0.06 mL, 1 mmol) was added. Complex XXIX was isolated as above in 70% yield and recrystallized from $MeNO_2$.

$[NiL(H_2O)](ClO_4)$ ($L = L^1$, L^3; XXX, XXXI). $[NiL(NCMe)](ClO_4)$ (0.5 g) dissolved in a 1:1 mixture of MeCN and H_2O (40 mL) was refluxed for 1 h. The solution was filtered, and the brown crystals that deposited (90%) from the filtrate on standing for 12 h were recrystallized from a 1:3 MeCN-H_2O mixture.

$[NiL^1(PPh_3)](ClO_4)$ (XXXII), $[Ni_2L^1_2(dppe)](ClO_4)_2$ (XXXIII). To a MeCN solution (25 mL) of I (0.41 g, 1 mmol) was added PPh_3 (0.26 g, 1 mmol)/$Ph_2P(CH_2)_2PPh_2$ (dppe; 0.2 g, 0.5 mmol). After it was

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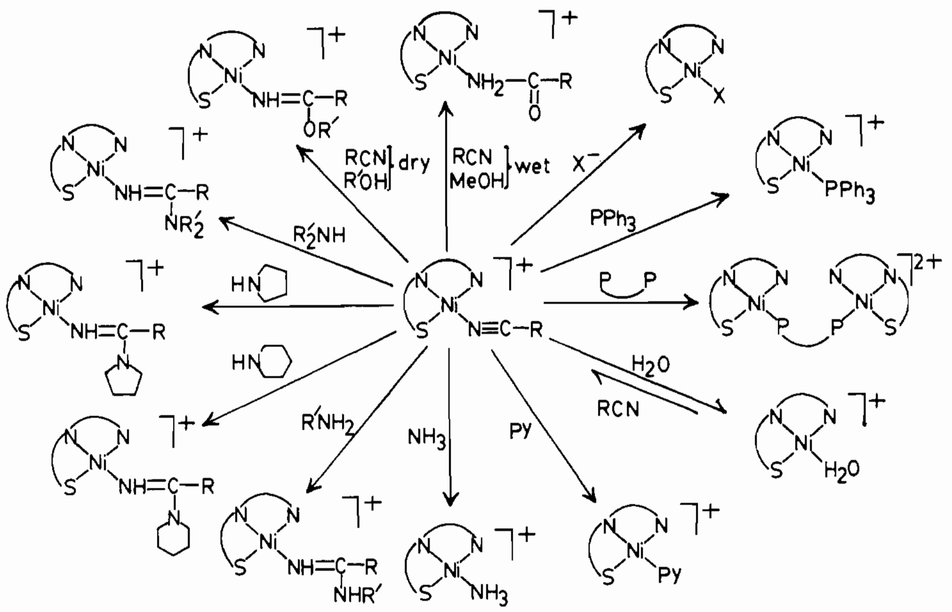
Scheme I



stirred for 1 h, the solution was evaporated almost to dryness on a rotary evaporator. The semisolid residue was dissolved in boiling MeOH (30 mL) and filtered hot. The filtrate gave large dark brown crystals on standing (90%).

$[NiL^1(py)](ClO_4)$ (XXXIV). A pyridine solution (10 mL) of I (0.5 g) gave this red complex on flooding with dry Et_2O.

$[NiL^1(NH_3)](ClO_4)$ (XXXV). This orange-red complex was prepared by passing NH_3 gas through a MeCN solution of I followed by precipitation with Et_2O.

[NiLX] ($L = L^1$–L^3; $X = N_3$, CN, NCO). These were obtained by treating the stoichiometric amount of an aqueous solution of NaX with a MeCN solution of $[NiL(NCMe)](ClO_4)$.

Caution! Although none of the perchlorate complexes detonated at ambient temperature on standing for several months, they exploded violently on heating.

Physical Measurements. Infrared spectra of KBr pellets or Nujol mulls were recorded on a Perkin-Elmer Model 783 spectrophotometer in the range 4000–200 cm^{-1}. Electronic spectra were recorded on a Pye-Unicam SP8-150 or a Cary 17D spectrophotometer. A Philips PR-9500 bridge was used for conductivity measurements. Magnetic measurements were carried out with a PAR Model 155 vibrating-sample magnetometer. ^1H NMR spectra were recorded in Varian XL-200 and Bruker WH270 spectrometers. The spectra were obtained with $CDCl_3$ or Me_2SO-d_6 solutions, and Me_4Si was used as the reference. Elemental analyses were performed on a Perkin-Elmer Model 240C elemental analyzer. Analytical data for some representative compounds (Table I) are available as supplementary material.

Results and Discussion

Synthesis and Reactivities. The reactions of the nitrile complexes $[NiL(NCR)](ClO_4)$ with *dry* alcohols, wet alcohols, amines, water, pyridine, ammonia, PPh_3, dppe, and some anions ($X^- = N_3$, CN, NCO) are outlined in Scheme I.

$[NiL(NCR)](ClO_4)$ ($L = L^1$–L^3; R = Me, Et) complexes in the presence of excess free RCN[34] react smoothly with dry alcohol, R'OH (R = Me, Et, *n*-Pr), to form the corresponding imino–ether complexes, $[NiL(NH{=}C(OR')R)](ClO_4)$ (X–XIX). The ease with which this reaction takes place depends upon the alcohol used: the reaction rate falls off rapidly with an increase in chain length of the alcohol. The reaction rate depends also upon the nitrile coordinated. For example, while MeCN and EtCN complexes react readily with MeOH, in the case of the PhCN complex the reaction is too slow even at the boiling temperature of the solvent. The rate of formation of the imino–ether complexes can be highly accelerated by using a strong base such as sodium alkoxide as a catalyst. In this way complex XX was prepared from V. The kinetic and mechanistic aspects of the imino–ether complex formation will be reported later.

In the above reaction, if the alcohol and nitrile used are not perfectly dry, then instead of the imino–ethers one obtains the corresponding amido complexes, $[NiL(NH_2COR)](ClO_4)$ ($L = L^1$–L^3, R = Me, Et, VI–IX). The amido complexes can also be prepard by recrystallizing the imino–ether complexes from solvents containing small amounts of water. Clearly, the hydration of a nitrile takes place via hydrolysis of the initially formed $NH{=}C(OR')R$ to $NH{=}C(OH)R$, which spontaneously reverts to the stable tautomeric form NH_2COR. The hydration of a nitrile does not take place, however, when $[NiL(NCR)](ClO_4)$ is reacted with water. In this case the substitution equilibrium

$$[NiL(NCR)]^+ \underset{RCN}{\overset{H_2O}{\rightleftharpoons}} [NiL(H_2O)]^+$$

is established.

The nitrile complexes react with aliphatic and heterocyclic secondary amines (R'_2NH) such as Me_2NH, Et_2NH, n-Pr_2NH, pyrrolidine, and piperidine to form amidine complexes, $[NiL(NH{=}C(NR'_2)R)](ClO_4)$ (XXI–XXIX). Because of the strong nucleophilicity of the amines the success of the amidine complex formation rests on keeping a high free nitrile to amine ratio. The situation becomes more delicate with primary aliphatic amines. For example, although $EtNH_2$ produces the desired amidine complex (XXVIII), $MeNH_2$ gives a mixture of amidine- and amine-substituted products.

Regarding reactivities of the remaining nucleophiles, the nitrile displacements occur in all cases.

Characterization. All of the complexes under consideration are diamagnetic in nature. Their electrical conductivities in MeCN show that, except for XXXIII, the complexes are 1:1 electrolytes[35] (Λ_M = 130–150 Ω^{-1} cm^2 mol^{-1}). The molar conductivity of XXXIII (250 Ω^{-1} cm^2 mol^{-1}) is typical of those of 1:2 electrolytes.[35]

The IR spectra of the complexes, especially those of amido (VI–IX), imino–ether (X–XX), and amidine (XXI–XXIX) complexes have been useful to characterize them. All of the complexes exhibit three characteristic bands due to the principal ligand moiety (L^1–L^3) at 1560 ± 10, 1460 ± 5, and 1280 ± 5 cm^{-1}. Complexes derived from L^1 show three more bands between 3300 and 3100 cm^{-1} with decreasing intensities due to the N–H stretchings of the terminal NH_2 group. The ν(C≡N) vibration of the precursor nitrile complexes (I–V) appears at 2270 ± 10 cm^{-1}. This band is observed at a higher frequency (+40 to +20 cm^{-1}) relative to that of the free nitrile and may be related to the usually considered criterion of end-on nitrile bonding.[2a,36,37] IR

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[34] It has been observed that, in the absence of free RCN, $[NiL^1(NCR)](ClO_4)$ dimerizes in R'OH.

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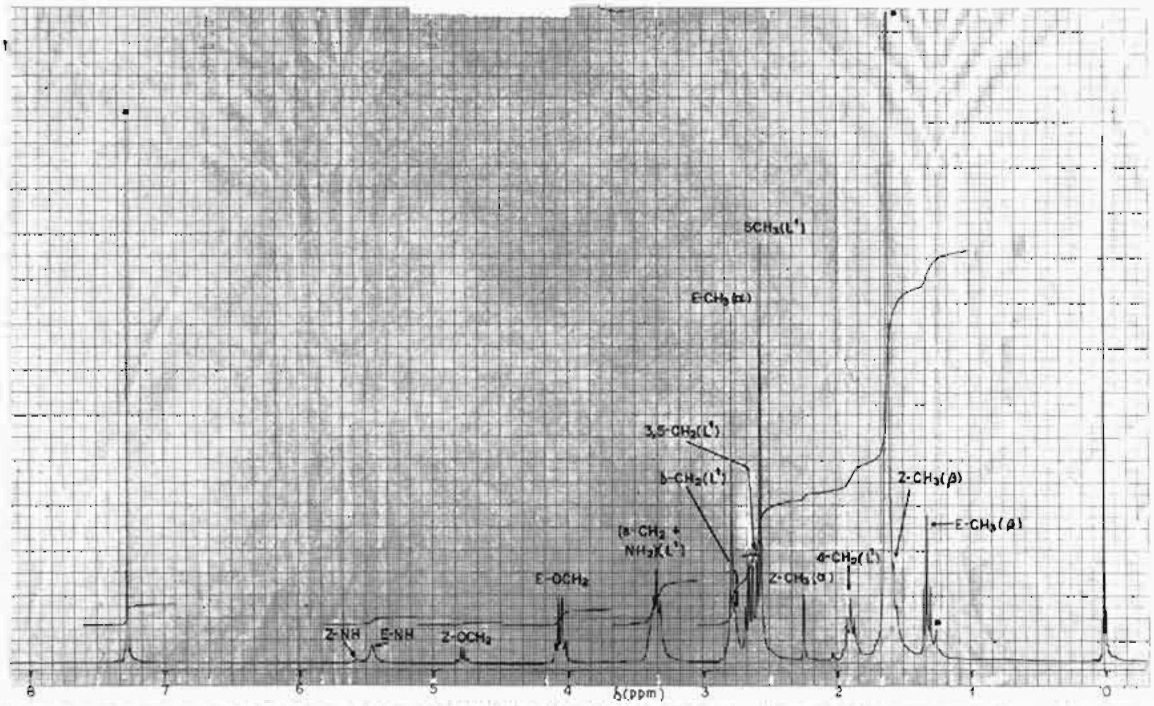

Figure 1. ^{1}H NMR spectrum of $[NiL^1(NH{=}C(OCH_2CH^{\beta}_3)CH^{\alpha}_3)]ClO_4$ (XIV) in $CDCl_3$ at 15 °C. Signals marked with an asterisk are due to the solvent.

data that are diagnostic of the coordinating groups are available as supplementary material (Table II) for some typcial complexes.

Amido complexes (VI–IX) are characterized by two N—H stretchings at about 3450 and 3350 cm^{-1}. They also exhibit a strong band at 1650 cm^{-1} and a band of medium intensity at 1610 cm^{-1}, which may be attributed[38] to the so-called amide I and amide II vibrations, respectively. Imino–ether complexes (X–XX) can be easily distinguished from the amido complexes, particularly by considering those compounds that are derived from L^2 or L^3. In these complexes a single N—H stretching is observed at about 3320 cm^{-1}, which is clearly indicative of the presence of the NH═C(OR′)R moiety. Moreover, these compounds exhibit a strong band due to C═N stretching at about 1640 cm^{-1} and a band of much weaker intensity at ca. 1595 cm^{-1} due to N—H bending. Similarly, amidine complexes (XXI–XXIX) show a ν(N—H) vibration between 3370 and 3310 cm^{-1}. In these compounds the C═N stretching and N—H bending overlap to a single band at 1600 cm^{-1}. The appearance of the ν(C═N) vibration at a lower frequency is not without precedence; it has been noted to lie between 1600 and 1575 cm^{-1} in many other amidine complexes.[2b,3,6]

In the visible region all of the complexes exhibit a single absorption band (or a shoulder) in the range 16 000–19 000 cm^{-1}, whose molar absorptivity lies between 60 and 150 M^{-1} cm^{-1}. This band can be considered as due to the $^1A_{2g} \rightarrow {}^1A_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) transition of nickel(II) in a square-planar environment,[39] although it is possible that an apically elongated square-pyramidal geometry arises due to weak solvent interaction. The energies due to the d–d transition for various $[NiLB]^+$ species (Table II) depict the following spectrochemical series for B: amide > amidine > imino–ether > PPh$_3$ > py > amine > H$_2$O > RCN.

The chemical shifts observed in the ^{1}H NMR spectra of a few representative complexes for the principal ligand L^1 or L^2 are given in Table III (supplementary material). The chemical shifts pertaining to imino–ether and amidine moieties in these complexes are discussed in the next part in the context of their stereochemistry. It may be pointed out[40] that, on complex formation, the NH$_2$ or NMe$_2$ resonances of the free ligands (HL^1 or HL^2) undergo significant shifts to lower fields, and due to delocalization of the double bonds in the metal chelates some shielding of the 3,5-CH$_2$ protons of the cyclopentene ring occurs. Another notable feature[41] is that both SCH$_3$ and NH$_2$ resonances of L^1 are appreciably shifted to higher fields in the complexes $[NiL^1(PPh_3)](ClO_4)$ and $[Ni_2L^1_2(dppe)](ClO_4)_2$ compared to those of the other compounds. This is most likely due to the proximity anisotropic shielding effect of the aryl phosphines. Similar shielding effects due to tertiary phosphines have been reported[42,43] in a number of platinum(II) and palladium(II) complexes.

Stereochemistry. The ^{1}H NMR spectra of imino–ether and amidine complexes have been quite helpful to understand their stereochemistry. Unfortunately, these compounds have poor solubilities in CDCl$_3$ and CD$_2$Cl$_2$, and therefore, important information that one could expect to obtain from measurements at subambient temperatures are not available. The complexes are more soluble in Me$_2$SO-d_6, but here again, the signals due to CD$_3$SOCH$_3$ and DOH often interfere with the integration of peak areas. Moreover, when it is kept in mind that the imino–ether complexes are moisture-sensitive, their partial hydrolysis in Me$_2$SO-d_6 is possible. We, therefore, have investigated ^{1}H NMR spectra of the imino–ether complexes in CDCl$_3$ at 25 °C. For amidine complexes, since hydrolysis does not present a problem, the spectra were recorded either in CDCl$_3$ (when solubility permitted) or in Me$_2$SO-d_6.

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(36) Byler, D. M.; Shriver, D. F. *Inorg. Chem.* **1973**, *12*, 1412–1416; **1974**, *13*, 2697–2705.

(37) (a) Purcell, K. F.; Drago, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 919–924. (b) Purcell, K. F. *Ibid.* **1967**, *89*, 247–250.

(38) (a) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975. (b) Dyer, J. R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New Delhi, India, 1978.

(39) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

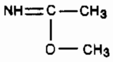
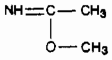
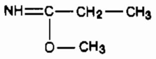
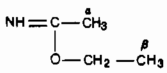
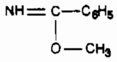
(40) For example, the NH$_2$ resonance of HL^1 observed at about 1.1 ppm is shifted to 3.4 ppm in the complexes, whereas the 3,5-CH$_2$ resonance of HL^1 at ca. 2.8 ppm is observed at about 2.6 ppm in the complexes.

(41) The NH$_2$ resonance observed at about 2.9 ppm in both PPh$_3$ and dppe complexes can be compared with the chemical shift 3.4 ppm observed for other complexes. Similarly, the SCH$_3$ resonance observed at 2.1 ppm in PPh$_3$ and dppe complexes is significantly shielded compared to that observed at 2.55 ppm in other compounds.

(42) Baba, S.; Ogura, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 665–668.

(43) (a) Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 1732–1738. (b) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *Ibid.* **1970**, 1653–1658.

Table IV. ^{1}H NMR Spectral Data for the Imino–Ether Moiety of the Corresponding Complexes

imino–ether	compd	chem shifts, ppm *Z* isomer	chem shifts, ppm *E* isomer	*E*:*Z* (25 °C)
 $\mathrm{NH{=}C(CH_3){-}O{-}CH_3}$	X	2.08 s (*e*-CH_3), 4.37 s (*a*-OCH_3), 5.6 br (NH)	2.79 s (*a*-CH_3), 3.81 s (*e*-OCH_3), 5.5 br (NH)	3:1
 $\mathrm{NH{=}C(CH_3){-}O{-}CH_3}$	X1	2.19 s (*e*-CH_3), 3.52 s (*a*-OCH_3), 3.9 br (NH)	2.58 s (*a*-CH_3), 3.49 s (*e*-OCH_3), 3.7 br (NH)	3:2
 $\mathrm{NH{=}C(CH_2{-}CH_3){-}O{-}CH_3}$	X111	1.14 t (*e*-CH_3), 4.71 s (*a*-OCH_3), 5.7 br (NH)	1.38 t (*a*-CH_3), 3.81 s (*e*-OCH_3), 5.6 br (NH)	3:1
 $\mathrm{NH{=}C(\overset{\alpha}{C}H_3){-}O{-}CH_2{-}\overset{\beta}{C}H_3}$	XIV	1.58 t (*a*-CH^{β}_3), 2.23 s (*e*-CH^{α}_3), 4.89 q (*a*-OCH_2), 5.7 br (NH)	1933 t (*e*-CN^{β}_3), 2.81 s (*a*-CH^{α}_3), 4.06 q (*e*-OCH_2), 5.4 br (NH)	3:1 4:1 (15 °C)
 $\mathrm{NH{=}C(C_6H_5){-}O{-}CH_3}$	XX	5.42 s (*a*-OCH_3), 6.6 br (NH), 7.74 m (*e*-C_6H_5 + $^3/_5$ *a*-C_6H_5)	4.06 s (*e*-OCH_3), 5.9 br (NH), 9.28 d ($^2/_5$ *a*-C_6H_5)	7:3

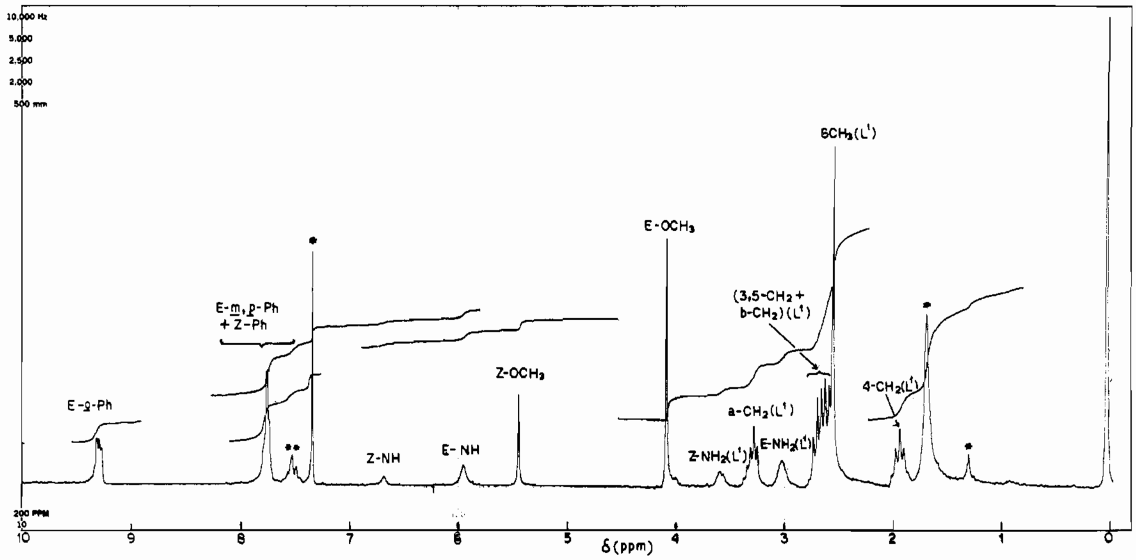
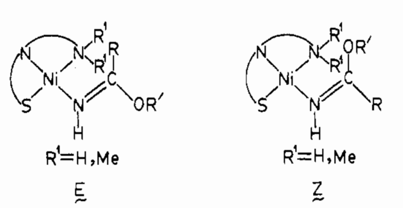


Figure 2. ^{1}H NMR spectrum of $[NiL^1(NH{=}C(OCH_3)C_6H_5)]ClO_4$ (XX) in $CDCl_3$ at 25 °C. Signals marked with an asterisk are due to the solvent, and those marked with two asterisks are due to the presence of traces of adsorbed PhCN in the complex.

The ^{1}H NMR spectral data related to the imino–ether moieties of complexes X, XI, XIII, XIV, and XX are given in Table IV. The typical spectral features of these complexes are illustrated in Figures 1 (XIV) and 2 (XX). In all these complexes the observed resonances can be explained by taking into consideration the presence of two isomeric species, which we designate as *E* and *Z* isomers (shown in **3**). In the *E* isomer, the alkyl group is axially disposed, but the O–alkyl group is equatorial to the metal chelate plane. The reverse situation arises in the case of the *Z* isomer. Construction of molecular models shows that the axially oriented group can approach above and close to the coordination plane where paramagnetic anisotropy of the nickel(II) ion is pronounced.[44] On the other hand, the equatorial group, being farthest from the metal center, remains unperturbed. The net effect is, in the *E* isomer the axial alkyl group is deshielded, whereas the equatorial O–alkyl group is shielded compared to the corresponding groups in the *Z* isomer. Consider the complex $[NiL^1(NH{=}C(OCH_3)CH_3)]$ (X), which exhibits four singlets at 2.08, 2.79, 3.81, and 4.37 ppm and two broad resonances at 5.5 and 5.6 ppm. The singlets at 2.08 and 2.79 ppm can be recognized as *e*-CH_3 and *a*-CH_3 (*e* = equatorial, *a* = axial), and their intensity ratio is 1:3. The other two singlets appearing at 3.81 and 4.37 ppm with the intensity ratio 3:1 are due to *e*-OCH_3 and *a*-OCH_3,



(3)

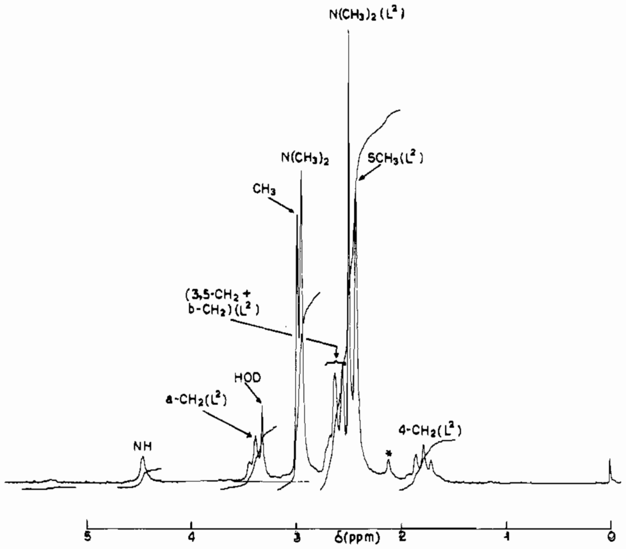


Figure 3. ^{1}H NMR spectrum of $[NiL^2(NH{=}C(N(CH_3)_2)CH_3)]ClO_4$ (XXVI) in Me_2SO-d_6 at 25 °C. Signals marked with an asterisk are due to the solvent.

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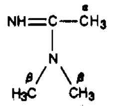
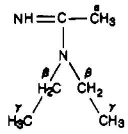
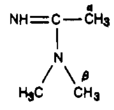
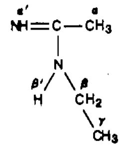
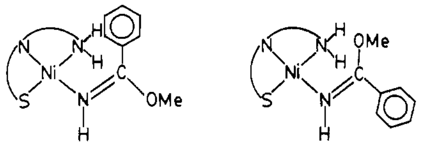
(44) (a) Miller, R. G.; Stauffer, R. D.; Fahey, D. R.; Parnell, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 1511–1521. (b) Fahey, D. R. *J. Organomet. Chem.* **1973**, *57*, 385–388.

Table V. ^1H NMR Spectral Data for the Amidine Moiety of the Corresponding Complexes

amidine	compd	chem shifts, ppm		E:Z (25 °C)
		Z isomer	E isomer	
	XXI[a]	2.10 s (e-CH^{α}_3), 2.97 s (a-CH^{β}_3 + e-CH^{β}_3), 3.2 br (NH)	2.66 s (a-CH^{α}_3), 2.97 s (e-CH^{β}_3 + a-CH^{β}_3), 3.2 br (NH)	10:1
	XXII[a]	1.34 t (a-CH^{γ}_3 + e-CH^{γ}_3), 2.40 s (e-CH^{α}_3), 3.1 br (NH), 3.50 m (a-CH^{β}_2 + e-CH^{β}_2)	1.14 t (e-CH^{γ}_3 + a-CH^{γ}_3), 2.96 s (a-CH^{α}_3), 3.1 br (NH), 3.50 m (e-CH^{β}_2 + a-CH^{β}_2)	
	XXVI[b]		2.95 s (e-CH^{β}_3 + a-CH^{β}_3), 2.99 s (a-CH^{α}_3), 4.45 br (NH)	single isomer
	XXVIII[b]	1.57 t (a-CH^{γ}_3), 2.60 s (e-CH^{α}_3), 3.0 br ($NH^{\alpha'}$), 7.2 br (e-$NH^{\beta'}$)	1.04 t (e-CH^{γ}_3), 2.94 s (a-CH^{α}_3), 4.1 br ($NH^{\alpha'}$), 7.8 br (a-$NH^{\beta'}$)	8:7

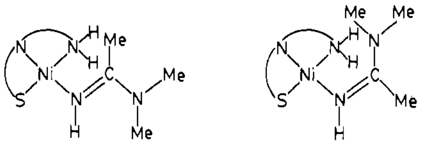
[a] In $CDCl_3$. [b] In Me_2SO-d_6.

respectively. The result indicates that the E and Z isomers are present in the ratio 3:1. It may be noted that the NH proton of the imino–ether becomes magnetically nonequivalent in the two isomers. The question why the E isomer is more abundant than the Z isomer may be answered by considering the fact that the CH_3 group will be sterically less interacting with the NH_2 group of L^1 than the OCH_3 group. In contrast to the case for X, the ratio of E to Z isomer is 3:2 in $[NiL^2(NH{=}C(OMe)Me)](ClO_4)$ (XI). Here, we note that the terminal NMe_2 group of L^2 interacts with both the CH_3 and OCH_3 groups of the imino–ether; as a result, the relative concentrations of E and Z isomers are not much different. On the other hand, similar to the situation for X, the E to Z ratios in both $[NiL^1(NH{=}C(OCH_3)C_2H_5)](ClO_4)$ (XIII) and $[NiL^1(NH{=}C(OC_2H_5)CH_3)](ClO_4)$ (XIV) are 3:1 at 25 °C. It is interesting to note that the spectrum of XIV recorded at 15 °C (Figure 1) gives a clear indication that when the temperature is lowered, the ratio of E to Z isomer changes to 4:1. This observation is consistent with the presence of a rotational barrier in the molecule. The spectrum of $[NiL^1(NH{=}C(OCH_3)C_6H_5)](ClO_4)$ (XX) shown in Figure 2 deserves some comments. In this compound the areas of the singlets due to e-OCH_3 (4.06 ppm) and a-OCH_3 (5.42 ppm), as well as the NH resonances at 5.9 and 6.6 ppm, indicate that the E and Z isomers (shown in **4**) are present in the ratio 7:3. On this basis one should expect that the resonances due to the axially and equatorially oriented phenyl rings will also exhibit the same intensity ratio. However, Figure 2 shows that the phenyl resonance observed at higher field (7.74 ppm) is more intense than the one observed at lower field (9.28 ppm) by a factor of 18/7. Such a reversal of E to Z ratio based on phenyl protons can be rationalized in the following way. If we consider that the C–C_6H_5 bond is rotating freely, then in the E isomer only the ortho protons are under the influence of the paramagnetic anisotropic effect of the nickel(II) ion, while the protons in the meta and para positions, being remote from the metal center, are expected to have approximately the same chemical shifts as in the equatorially oriented phenyl ring. Since the observed E to Z ratio is 7:3, the protons in the equatorially and axially oriented phenyl rings can be apportioned as follows: e-phenyl, (3/10) × 5 + (7/10) × 3; a-phenyl, (7/10) × 2. In other words, the ratio of e-C_6H_5 and a-C_6H_5 is 18:7. Thus, close agreement between the observed and calculated ratios substantiates the assumption made.

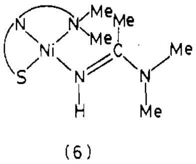


(4)

The ^1H NMR spectral data of amidine complexes (XXI, XXII, XXVI, XXVII; due to the amidine moiety) are set out in Table V. The spectrum of $[NiL^1(NH{=}C(NMe_2)CH_3)](ClO_4)$ (XXI) in $CDCl_3$ indicates that the E form is 10 times more abundant than the Z form. Such a high E to Z ratio in this compound can be expected on steric grounds. One can visualize that in the Z isomer (shown in **5**) the NMe_2 group of the amidine moiety cannot approach the metal center due to its steric involvement with the NH_2 group of L^1; as a result, the conformation of the molecule is such that both methyl groups of NMe_2 are away from the paramagnetic influence of the metal ion. Inasmuch as the chemical shifts of the NMe_2 group are identical in both E and Z isomers, the relative concentrations of the two isomers in this compound have been determined by comparing the intensities of a-CH_3 and e-CH_3 signals. Similarly, the data for $[NiL^1(NH{=}C(NEt_2)CH_3)](ClO_4)$ (XXII) indicate the presence of two isomers, but their ratio could not be determined because the proton integration of the amidine moiety was invalidated by the overlapping resonances of L^1. The spectrum of $[NiL^2(NH{=}C(NMe_2)CH_3)](ClO_4)$ (XXVI) shown in Figure 3 indicates the presence of a single isomer. In this compound, due to the steric interaction between the NMe_2 group of L^2 and C–CH_3 or NMe_2 groups of the amidine moiety, the conformation of XXVI can be neither E nor Z, but a staggered one (**6**), in which both the C–CH_3 and NMe_2 groups of the amidine are away from the NMe_2 group of L^2. Finally, we note that, in $[NiL^1(NH{=}C(NHEt)CH_3)]$-



(5)



(6)

(ClO_4) (XXVIII), both *E* and *Z* isomers are present in almost equal amounts (*E*:*Z* = 8:7).

The occurrence of different isomers in the complexes under consideration can be attributed to the restricted rotation of the N═C bond. In addition, one may consider several other factors: (1) The isomers may result from the mode of attack by, for example, the alcohol on the coordinated nitrile, that is, one side or the other. (2) Inversion may occur at the coordinated nitrogen site. (3) The rotation about the Ni–N bond may be contributing to the isomeric distribution. Factor 1 seems to be unlikely, because there is no obvious reason for preferential attack on a particular side. The possibility of factor (2) cannot be ruled out, although such inversion at the nitrogen center is without precedence in imino–ether, amidine, and imidate complexes. Factor 3 might play an important role, as hindered rotation of the nitrogen–metal bond has been reported in some imino–ether[7] and amidine[13] complexes. The dynamics of internal rotation in the present complexes could not be investigated due to the already mentioned solubility problem.

Acknowledgment. We are grateful to Professor U. R. Ghatak and Dr. R. V. Venkateswaran of the Department of Organic Chemistry of this institute, and the sophisticated instruments facility at the Indian Institute of Science, Bangalore, for recording ^{1}H NMR spectra.

Supplementary Material Available: Listings of analytical data (Table I), infrared and visible spectral data (Table II), and ^{1}H NMR for the principal ligand moiety in the imino–ether and amidine complexes (Table III) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Cattedra di Chimica Industriale, Dipartimento di Chimica Organica, Università di Firenze,
I-50121 Firenze, Italy, and Istituto di Chimica Generale ed Inorganica, Centro di Studio per la
Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Interaction between $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ in Solution: Synthesis and Characterization of $[P(n\text{-}Bu)_3](CO)_2Ru(\mu\text{-}OH)(\mu\text{-}CH_3COO\text{-}O)(\mu\text{-}CH_3COO\text{-}O,O')Ru(CO)(CH_3COO)[P(n\text{-}Bu)_3]$

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Received April 7, 1986

The title compound, obtained by reaction of $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ with $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ at 120 °C in *n*-heptane solution, has been characterized by standard analytical procedures, IR and NMR spectrometry, and X-ray diffraction. The formation of intermediates such as $Ru(CO)_2(CH_3COO\text{-}O,O')(CH_3COO)[P(n\text{-}Bu)_3]$ is suggested, and the reactivity of the system is discussed. Crystal data for the title compound $C_{33}H_{64}O_{10}P_2Ru_2$: space group *Pbca*, $a = 32.473$ (10) Å, $b = 15.342$ (5) Å, $c = 17.401$ (6) Å, $V = 8669$ (5) Å^3, $Z = 8$, $D_{calcd} = 1.356$ g cm^{-3}, $F(000) = 3680$, Mo Kα_1 radiation, $\lambda = 0.709\,300$ Å for the determination of lattice parameters. The structure, determined by Patterson and Fourier methods and refined by least squares to $R_F(4193/546) = 0.0697$, consists of neutral complex molecules in which two octahedral metal centers are joined together by three oxygen bridges: μ-hydroxo [Ru–O = 2.071 (6), 2.104 (6) Å; Ru–O–Ru = 104.2 (2)°], μ-acetato-*O* [Ru–O = 2.147 (6), 2.196 (6) Å; Ru–O–Ru = 98.6 (3)°], and μ-acetato-*O,O′* [Ru–O = 2.102 (6), 2.065 (7) Å, Ru–O–C = 132.3 (6), 128.2 (6)°], with an intermetallic contact Ru···Ru = 3.294 (2) Å. Coordination is completed to octahedral by a phosphorus atom of a phosphine [Ru–P = 2.316 (3) Å] and two carbonyls [Ru–C = 1.890 (8) Å, average] about one ruthenium atom and by a phosphorus atom [Ru–P = 2.262 (3) Å] of the second phosphine, one carbonyl [Ru–C = 1.823 (11) Å], and one oxygen [Ru–O = 2.092 (7) Å] of a terminal monodentate acetate group about the second ruthenium atom. The two octahedra share the O[μ-hydroxo]···O[μ-acetato-*O*] edge, and the angular deformations in them are roughly symmetrical with respect to this edge.

Introduction

In the hydrogenation of carboxylic acids, carried out in the presence of phosphine-substituted ruthenium carbonyls, the evolving catalytic system gives rise to the formation of phosphine-substituted ruthenium carbonyl carboxylates.[1,2] Complexes such as $Ru(CO)_2(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ (I), $Ru_2(CO)_4(CH_3COO)_2[P(n\text{-}Bu)_3]_2$ (II), and $Ru_4(CO)_8(CH_3COO)_4[P(n\text{-}Bu)_3]_2$ (III) have been detected in the crude mixture of the acetic acid hydrogenation by using $H_4Ru_4(CO)_8[P(n\text{-}Bu)_3]_4$ as catalytic precursor.

In order to understand the role of these compounds in the hydrogenation process, we studied the reactivity of ruthenium carbonyl carboxylates under comparable reaction conditions, in particular the interaction between I and III. The reaction was monitored by infrared spectroscopy using an IR pressure cell with heating facilities.

The constitution and structure of the new dinuclear product IV obtained in this reaction has been unequivocally defined by X-ray crystal structure analysis.

Table I. IR and ^{1}H NMR Data for $Ru_2(CO)_3(CH_3COO)_3(OH)[P(n\text{-}Bu)_3]_2$ (IV)

IR,[a] cm^{-1}	ν_{CO}	2060 (s), 1991 (vs), 1942 (vs), 1900 (vw)
	ν_{COO}	1678 (m), 1592 (m), 1561 (m), 1470 (w), 1425 (mw)
	others	1392 (mw), 1360 (w), 1338 (w), 1271 (m)
^{1}H NMR,[b] δ		0.80–1.15 (t, 18 H, CH_3CH$_2$), 1.15–2.05 (m, 36 H, $-CH_2CH_2CH_2$P), 1.82 (s, 3 H, CH_3COO), 1.88 (s, 3 H, CH_3COO-*O*), 2.37 (s, 3 H, CH_3COO-*O,O′*), 7.34 (s, 1 H, OH)

[a] C_6D_{12} as solvent. [b] Tetramethylsilane was used as internal standard, CD_2Cl_2 as solvent.

Results

(a) Spectroscopic Analyses. In the 0–50 °C temperature range a reversible interaction between I and III has been observed in *n*-heptane solution.[3] Above 50 °C, this system reacts, giving rise

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