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Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of $L_nNi(CO)_{4-n}$ Derivatives

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^{13}C NMR spectra have been obtained for a series of $L_nNi(CO)_{4-n}$ derivatives (n = 0–3) where L = PR_3, PPh_2Y, $PPhY_2$, $P(OR')_3$, and PCl_3 (R = Me, Et, Bu, Ph; R' = Me, Et, *i*-Pr, Ph; Y = Cl, Me, OMe, OPh). The effect upon the carbonyl chemical shift of the replacement of X by Y substituents in $X_{3-n}Y_nPNi(CO)_3$ derivatives appears to be additive, as is the effect of the sequential replacement of carbonyl by phosphorus ligands. An excellent correlation is observed between the carbonyl chemical shifts and either the infrared stretching force constants or Kabachnik's σ parameters. These data are analyzed in terms of the electron donor–acceptor abilities of the ligands.

Introduction

The potential of ^{13}C NMR spectroscopy for the study of transition metal carbonyl complexes has only recently been realized, partially through the advent of Fourier transform pulsed NMR techniques and partially through the use of ^{13}C-enriched carbon monoxide.[1] Some of the earliest studies of transition metal carbonyl complexes suggested a linear correlation between the ^{13}C NMR carbonyl chemical shifts and the infrared stretching frequencies or force constants for the carbonyl mode. Such correlations have been observed for the equivalent carbonyls in η-$(C_5H_5)Fe(CO)_2X$,[2] η-$(C_5H_5)Mn(CO)_2L$,[3] and η-$(C_6H_5X)Cr(CO)_3$[4] derivatives. Gansow et al.[5] and Braterman et al.[6] have reported data which suggest that this correlation is valid for the cis carbonyls but not necessarily for the trans carbonyl in $LW(CO)_5$ derivatives. Similar results have been observed for $LM(CO)_5$ derivatives of Cr and Mo.[7,8] Mann[9] has reported data for a series of tungsten carbonyl derivatives which question the generality of this correlation. A linear correlation may not occur due to differences in the effects monitored by the two techniques or due to the approximations required for the calculation and interpretation of stretching force constants, such as the association of the k_1 stretching force constant with a purely trans carbonyl stretching mode in $LM(CO)_5$ derivatives.

We report herein the results of a study of the ^{13}C NMR spectra of a series of tetrahedral $L_nNi(CO)_{4-n}$ derivatives for which infrared data are available.[10]

Experimental Section

$PPh_2(OR)$ and $PPh(OR)_2$ derivatives (R = Me, Ph) were synthesized from the reaction of $PPh_2(NEt_2)$[11,12] and $PPh(NEt_2)_2$[12] with the corresponding alcohol[11,13] and were characterized by infrared and proton magnetic resonance spectroscopy. All other ligands were obtained from commercial sources. $Ni(CO)_4$ was purchased from Matheson Gas Products and used without further purification. Since attention must be paid to the extreme toxicity of tetracarbonylnickel(0), all manipulations were carried out via syringe in a well-ventilated hood. The $LNi(CO)_3$ complexes were prepared by the addition of a 2-ml aliquot of 4 *M* $Ni(CO)_4$ in $CDCl_3$ to an argon-purged 12-mm NMR sample tube containing 6 mmol of ligand dissolved in 2 ml of $CDCl_3$. The sample tubes were allowed to stand for approximately 10 min and then agitated for 15 min or until all CO evolution had ceased. $Me_3PNi(CO)_3$ was synthesized using $Me_3P{\cdot}AgNO_3$ as a source of trimethylphosphine. ^{13}C NMR spectra for these samples containing approximately 3:1 ratios of $LNi(CO)_3$ to $Ni(CO)_4$ were obtained on a Varian Associates XL-100-FT spectrometer operating at 25.16 MHz equipped with an internal deuterium lock, after which a 0.2-ml aliquot was removed, diluted with 15 ml of chloroform, and used for infrared spectroscopic characterization. The ^{13}C NMR chemical shifts were measured relative to the internal $Ni(CO)_4$ reference and are reported in ppm *downfield* from TMS using the conversion

$$\delta_{TMS} = \delta_{Ni(CO)_4} - 191.64 \text{ ppm}$$

Table I. ^{13}C NMR Chemical Shifts for $L_nNi(CO)_{4-n}$ Derivatives[a]

Ligand	$LNi(CO)_3$	$L_2Ni(CO)_2$	$L_3Ni(CO)$
PCl_3	-190.2_3 $(12._0)$[b]		
CO	-191.6_4	-191.6_4	-191.6_4
$PPhCl_2$	-192.3_3	-192.9_4	
$P(OPh)_3$	-193.3_3	-194.7_9	
PPh_2Cl	-194.1_3	-196.2_8	
$PPh(OPh)_2$	-194.1_8		
$P(OMe)_3$	-194.8_2	-197.9_9	-200.7_6
$PPh_2(OPh)$	-194.9_6		
$PPh(OMe)_2$	-195.1_2		
$P(OEt)_3$	-195.2_5	-198.3_7	-201.2_2
$P(O$-*i*-$Pr)_3$	-195.5_4	-198.9_4	
$PPh_2(OMe)$	-195.6_0		
$AsPh_3$	-195.8_0		
PPh_3	-195.9_4	-199.4[c]	
PPh_2Me	-196.1_7		
$P(p$-tol$)_3$	-196.2_1		
$PPhMe_2$	-196.4_0		
$SbPh_3$	-196.5_0		
PMe_3	-196.6_9		
PEt_3	-197.1_8	-202.1_1	
PBu_3	-197.3_3	-202.0_4	
$(Ph_2PCH_2)_2$		-200.7[c]	

[a] Chemical shifts in ppm *downfield* from TMS, in $CDCl_3$ solution. [b] $^2J_{^{31}P^{13}C}$ nuclear spin–spin coupling constant in Hz. [c] J. R. Wilkinson, A. R. Garber, and L. J. Todd, unpublished data; $CHCl_3$ solution; see ref 1.

The $L_2Ni(CO)_2$ derivatives were prepared by adding 6 mmol of ligand to the $LNi(CO)_3$ complexes prepared above and agitating until CO evolution had ceased; ^{13}C NMR spectra were then obtained for these 1:1 mixtures of $L_2Ni(CO)_2$ and $LNi(CO)_3$. ^{13}C NMR chemical shifts were measured relative to the internal $LNi(CO)_3$ resonance and are reported in ppm downfield from TMS. The $L_3Ni(CO)$ derivatives (L = $P(OMe)_3$, $P(OEt)_3$) were prepared from the reaction of $Ni(CO)_4$ with a fourfold excess of phosphite at elevated temperatures,[14] after which time sufficient $Ni(CO)_4$ was added to complex the unreacted phosphite and ^{13}C NMR spectra were obtained for these 1:1 mixtures of $L_3Ni(CO)$ and $LNi(CO)_3$. ^{13}C NMR chemical shifts were measured relative to the internal $LNi(CO)_3$ resonance. $LL'Ni(CO)_2$ derivatives were prepared by the reaction of 10-mmol quantities of both L and L' with 3 ml of 4 *M* $Ni(CO)_4$ in $CDCl_3$. ^{13}C NMR spectroscopy indicated the existence of a mixture of $LNi(CO)_3$, $L'Ni(CO)_3$, and $LL'Ni(CO)_2$. ^{13}C NMR chemical shifts were measured relative to the internal $LNi(CO)_3$ and $L'Ni(CO)_3$ resonances. The precision of duplicate measurements of all chemical shifts was within ±0.04 ppm.

Results

The ^{13}C NMR spectra of most $L_nNi(CO)_{4-n}$ derivatives exhibit a single sharp low-field resonance associated with the geometrically equivalent carbonyls, with no evidence of line broadening from unresolved coupling, and a pattern of resonances at high field analogous to those of the free ligand.[15] The ^{13}C NMR carbonyl chemical shifts are given in Table I. $^2J_{^{31}P^{13}C}$ nuclear spin–spin coupling has been observed in only one $LNi(CO)_3$ derivative, L = PCl_3, $^2J_{PMC}$ = $12._0$ Hz. In $LM(CO)_5$ derivatives $^2J_{^{31}P^{13}C}$ coupling has been observed

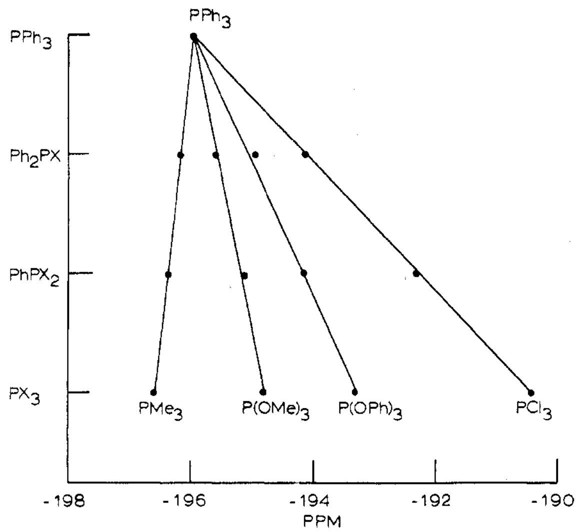

Figure 1. Effect of replacement of Ph by X on the ^{13}C NMR chemical shifts of $Ph_{3-n}X_nPNi(CO)_3$ derivatives. The precision of the carbonyl chemical shift measurements is approximated by the size of the circles.

to range from less than 1 Hz for the trans carbonyl resonance in $(PhO)_3PCr(CO)_5$ to 66 Hz for the cis carbonyl resonance in $Cl_3PMo(CO)_5$.[8] It is therefore of interest to note that the $^2J_{^{31}P^{31}P}$ coupling constant for *cis*-$Cr(CO)_4[P(OCH_2)_3CMe]_2$ is approximately 70 Hz[16] while the coupling constant for $Ni(CO)_2[P(OCH_2)_3CMe]_2$ is negligible.[17,18]

The data presented in Table I indicate that the sequential replacement of Ph by X substituents in $Ph_{3-n}X_nPNi(CO)_3$ derivatives results in incremental changes in the ^{13}C NMR carbonyl chemical shifts, as shown in Figure 1. It should therefore be possible to derive a set of substituent constants, χ_i, which characterize the contribution to the carbonyl chemical shift from substituent X_i on the phosphorus

$$\delta_{^{13}C}[(X_i)_3PNi(CO)_3] = -191.64 - 3\chi_i \text{ (ppm)}$$

Values of χ_i thus obtained correlate closely with parameters derived from the A_1 infrared stretching frequencies[10] and can be used to calculate the carbonyl chemical shifts of all derivatives in Table I

$$\delta_{^{13}C}[X_1X_2X_3PNi(CO)_3] = -191.64 - \sum_i^3 \chi_i \text{ (ppm)}$$

with an average deviation equal to the precision of the original chemical shift measurements, ±0.04 ppm.

There has been some interest in studies of filiation of carbonyl stretching frequencies and ^{31}P NMR chemical shifts in multiply substituted metal carbonyl complexes.[19,20] Examination of the data in Table I suggests that the effect of substitution of CO by X_3P is slightly less than additive. If we define Δ_j^k to be the difference between the chemical shifts of $(L_k)_jNi(CO)_{4-j}$ and $Ni(CO)_4$, then for any ligand k, Δ_2^k and Δ_3^k are respectively 5–8% and 5–10% less than 2 and 3 times Δ_1^k. A plot of the ^{13}C NMR carbonyl chemical shifts for $LNi(CO)_3$ derivatives vs. the carbonyl chemical shifts for $L_2Ni(CO)_2$ derivatives is shown in Figure 2. Examination of the data presented in Table II for $LL'Ni(CO)_2$ derivatives once again suggests that the perturbation of the carbonyl chemical shift is slightly less than additive. A plot of the experimental $LL'Ni(CO)_2$ carbonyl chemical shifts vs. those predicted on the basis of substituent additivity is shown in Figure 3.

Discussion

In $L_nM(CO)_m$ derivatives, an increase in the σ basicity or a decrease in the π acidity of the *ligand* leads to an increase

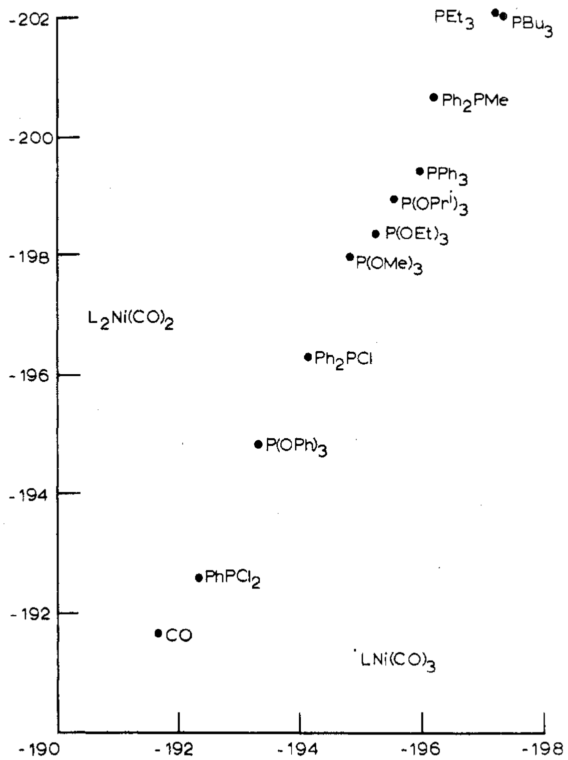

Figure 2. Plot of the ^{13}C NMR chemical shifts in ppm for the carbonyl resonance in $LNi(CO)_3$ derivatives vs. the ^{13}C NMR chemical shifts for the carbonyl resonance in $L_2Ni(CO)_2$ derivatives. $(Ph_2PCH_2CH_2PPh_2)Ni(CO)_2$ was taken to be the $L_2Ni(CO)_2$ analog of $(PPh_2Me)Ni(CO)_3$. The precision of the carbonyl chemical shift measurements is approximated by the size of the circles.

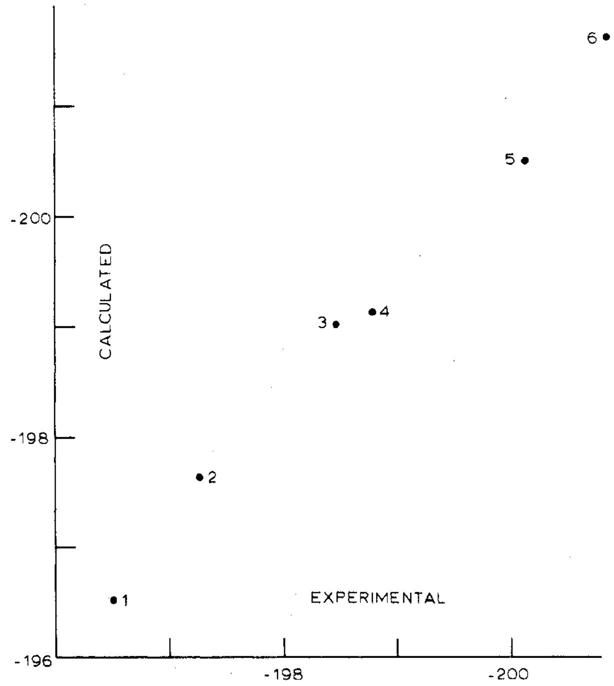

Figure 3. Plot of the experimental ^{13}C NMR chemical shifts in ppm for the carbonyl resonance in $L_xL_yNi(CO)_2$ derivatives vs. the chemical shifts calculated by adding the values of Δ_1^x and Δ_1^y for ligands x and y to the carbonyl chemical shift of $Ni(CO)_4$. The precision of the carbonyl chemical shift measurements is approximated by the size of the circles.

in electron density at the transition metal. This electron density may then be delocalized onto the carbonyls either via a decreased *carbonyl* σ basicity or by an increased transition

Table II. ^{13}C NMR Chemical Shifts for $LL'Ni(CO)_2$ Derivatives[a]

Complex	Exptl	Calcd
$[PPh_3][PBu_3]Ni(CO)_2$	-200.8_5 (3)[b]	-201.6_3
$[PBu_3][P(OMe)_3]Ni(CO)_2$	-200.1_5 (5)	-200.5_1
$[PPh_3][P(OMe)_3]Ni(CO)_2$	-198.7_9 (3)	-199.1_2
$[PBu_3][P(OPh)_3]Ni(CO)_2$	-198.4_8 (6)	-199.0_2
$[PPh_3][P(OPh)_3]Ni(CO)_2$	-197.2_8	-197.6_3
$[P(OPh)_3][P(OMe)_3]Ni(CO)_2$	-196.5_0	-196.5_1

[a] Chemical shifts in ppm *downfield* from TMS, in $CDCl_3$ solution. [b] $^2J_{^{13}C^{31}P}$ nuclear spin–spin coupling constants, in Hz.

metal→carbonyl π back-donation. There has been considerable controversy over the relative importance of the σ basicity and/or π acidity of various ligands and their effect upon the infrared spectra of transition metal carbonyl complexes. The Darensbourgs[21] have provided an alternative to the contentious separation of these effects; they argued that an increase in the positive character of the carbonyl carbon, whether the result of an increase in the σ basicity or a decrease in the π acidity of the carbonyl, leads to an increase in the infrared stretching force constant for the carbonyl mode. These arguments suggest that a linear correlation should exist between the ^{13}C NMR carbonyl chemical shifts and the infrared stretching force constants, such that an increase in the magnitude of k_{CO} would be reflected by a *deshielding* of the carbonyl resonance. In all derivatives studied to date, the opposite effect is observed, such that increasing values of k_{CO} are associated with increasingly *shielded* carbonyl resonances.[4]

Thus we may safely conclude that changes in the ^{13}C NMR carbonyl chemical shift within a series of closely related derivatives are not dominated by the effect of either local diamagnetic screening[22] or the $\langle 1/r^3 \rangle_{2p}$ dependence of the local paramagnetic screening.[23] An analysis of the ^{13}C NMR spectra of a series of $LCr(CO)_5$, η-$(C_6H_5X)Cr(CO)_3$, and η-$(C_5H_5)M(CO)_3$ derivatives (M = Cr^-, Mn^0, and Fe^+)[4] has suggested that the carbonyl chemical shift in $L_nM(CO)_m$ is proportional to the electron donor–acceptor character of L, *such that the carbonyl resonance is deshielded with increasing electron density at the transition metal*, possibly due to a decrease in the separation of the ground state and the lowest lying excited states with increasing transition metal→carbonyl π back-donation.[24]

A plot of the ^{13}C NMR carbonyl chemical shifts, in ppm downfield from TMS, vs. the infrared stretching force constants for the carbonyl mode, in mdyn/Å, is shown in Figure 4 for 17 of the 21 $LNi(CO)_3$ derivatives in Table I. The force constants were calculated via the Cotton–Kraihanzel approximations,[25] under an assumed C_{3v} symmetry, from infrared stretching frequencies (CH_2Cl_2 solution) reported by Tolman.[10] Bigorgne and coworkers[26–28] have reported infrared data in hexadecane solution for $LNi(CO)_3$ derivatives where L = PCl_3, $AsPh_3$, and $SbPh_3$. The C–K force constants for these derivatives are 17.19, 16.54, and 16.61 mdyn/Å, in close agreement with values of 17.2, 16.5, and 16.4 mdyn/Å obtained by extrapolation of the correlation depicted in Figure 4. A normal-coordinate analysis by Jones et al.[29] afforded force constants for $Ni(CO)_4$ in the gas phase and CCl_4 solution of 17.85 and 17.69 mdyn/Å, while C–K force constant calculations suggest a value of 17.42 mdyn/Å. These data are not in particularly close agreement with the value of 17.0 mdyn/Å obtained from extrapolation of the correlation in Figure 4.

Examination of the data presented in Table I suggests that the order of increasing electron density at the transition metal in $LNi(CO)_3$ derivatives is $PCl_3 < P(OPh)_3 < P(OR)_3 < PPh_3 < PR_3$, in accord with the order of decreasing electron-withdrawing character for the substituents on phosphorus.[30] It is questionable to use substituent parameters defined for aromatic carbon compounds to characterize the electron density in phosphorus ligands, and it is therefore of interest to examine the correlation between the carbonyl chemical shifts and the σ parameters obtained from studies of the pK_a's of phosphinic acids.[31] A plot of the ^{13}C NMR carbonyl chemical shifts in $LNi(CO)_3$ derivatives vs. Kabachnik's σ is shown in Figure 5. The linearity of this correlation may be somewhat exaggerated by the assumption of a σ = 0.48 for $P(OPh)_3$. This

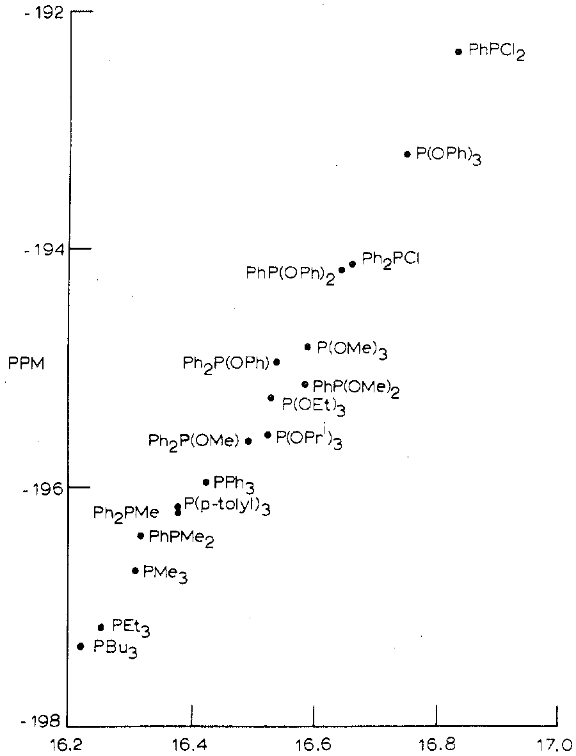

Figure 4. Plot of the ^{13}C NMR chemical shifts in ppm for the carbonyl resonance in $LNi(CO)_3$ derivatives vs. the infrared stretching force constants in mdyn/A for the carbonyl mode. The precision of the carbonyl chemical shift measurements is approximately twice the size of the circles.

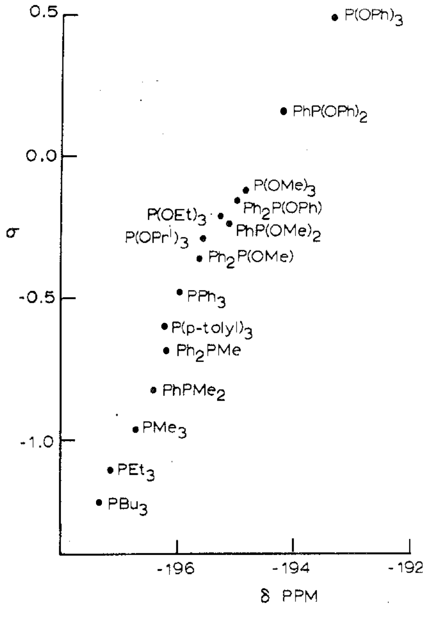

Figure 5. Plot of the ^{13}C NMR chemical shifts in ppm for the carbonyl resonance in $LNi(CO)_3$ derivatives vs. Kabachnik's σ. Values of σ for $PR_2(OR)$ and $PR(OR)_2$ ligands were calculated as the weighted averages of values for PR_3 and $P(OR)_3$. A value of σ equal to 0.48 was assumed for $P(OPh)_3$. The precision of the carbonyl chemical shift measurements is approximated by the size of the circles.

assumption is supported by the fact that it yields values of σ for $PPh_2(OPh)$ and $PPh(OPh)_2$ which also correlate quite closely with the carbonyl chemical shifts.

It is tempting to suggest that the extent of transition metal→carbonyl π back-donation is therefore dependent predominantly upon the σ basicity of the phosphorus ligand. While this may indeed be true, we must conclude that an increased electron density at the phosphorus may be reflected at the transition metal via either an increased σ basicity or a decreased π acidity of the phosphorus ligand. The data in Table I may thus be interpreted in terms of a relative order of the electron donor:acceptor ratios for various ligands toward $Ni(CO)_3$.

Registry No. $[PCl_3]Ni(CO)_3$, 18474-97-0; $Ni(CO)_4$, 13463-39-3; $[PPhCl_2]Ni(CO)_3$, 18474-95-8; $[PPhCl_2]_2Ni(CO)_2$, 55333-53-4; $[P(OPh)_3]Ni(CO)_3$, 18474-92-5; $[P(OPh)_3]_2Ni(CO)_2$, 14653-44-2; $[PPh_2Cl]Ni(CO)_3$, 18559-01-8; $[PPh_2Cl]_2Ni(CO)_2$, 35824-48-7; $[PPh(OPh)_2]Ni(CO)_3$, 55333-54-5; $[P(OMe)_3]Ni(CO)_3$, 17099-58-0; $[P(OMe)_3]_2Ni(CO)_2$, 16787-28-3; $[P(OMe)_3]_3Ni(CO)$, 17084-87-6; $[PPh_2(OPh)]Ni(CO)_3$, 55333-39-6; $[PPh(OMe)_2]Ni(CO)_3$, 55333-40-9; $[P(OEt)_3]Ni(CO)_3$, 18558-97-9; $[P(OEt)_3]_2Ni(CO)_2$, 16787-36-3; $[P(OEt)_3]_3Ni(CO)$, 25945-15-7; $[P(O\text{-}i\text{-}Pr)_3]Ni(CO)_3$, 55333-41-0; $[P(O\text{-}i\text{-}Pr)_3]_2Ni(CO)_2$, 55333-42-1; $[PPh_2(OMe)]Ni(CO)_3$, 55333-43-2; $[AsPh_3]Ni(CO)_3$, 37757-32-7; $[PPh_3]Ni(CO)_3$, 14917-13-6; $[PPh_3]_2Ni(CO)_2$, 13007-90-4; $[PPh_2Me]Ni(CO)_3$, 55333-44-3; $[P(p\text{-tol})_3]Ni(CO)_3$, 52729-09-6; $[PPhMe_2]Ni(CO)_3$, 55333-45-4; $[SbPh_3]Ni(CO)_3$, 52151-12-9; $[PMe_3]Ni(CO)_3$, 16406-99-8; $[PEt_3]Ni(CO)_3$, 18555-45-8; $[PEt_3]_2Ni(CO)_2$, 16787-33-0; $[PBu_3]Ni(CO)_3$, 15698-54-1; $[PBu_3]_2Ni(CO)_2$, 20658-46-2; $[Ph_2PCH_2CH_2PPh_2]Ni(CO)_2$, 15793-01-8; $[PPh_3][PBu_3]Ni(CO)_2$, 55333-46-5; $[PBu_3][P(OMe)_3]Ni(CO)_2$, 55333-47-6; $[PPh_3][P(OMe)_3]Ni(CO)_2$, 55333-48-7; $[PBu_3][P(OPh)_3]Ni(CO)_2$, 55400-72-1; $[PPh_3][P(OPh)_3]Ni(CO)_2$, 55333-49-8; $[P(OPh)_3][P(OMe)_3]Ni(CO)_2$, 55333-50-1; ^{13}C, 14762-74-4.

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Kinetics of Nickel(II) Complexation Reactions in Nonaqueous Solvents. II. Ammonium Salt of 2,2'-Nitrilodi-1,3-indandione (Ruhemann's Purple) and 4-(2-Pyridylazo)resorcinol (PAR)

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The kinetics of the reactions of nickel(II) with the ammonium salt of 2,2'-nitrilodi-1,3-indandione, Ruhemann's Purple (NH_4RP), in pyridine and with 4-(2-pyridylazo)resorcinol (PAR) in 0.0125 *M* pyridine in nitromethane have been investigated. For the Ni^{II}–NH_4RP reaction the mechanism is assumed to be

$$\mathrm{NH_4RP} \overset{K_2}{\rightleftharpoons} \mathrm{NH_4^+} + \mathrm{RP^-}$$

$$\mathrm{Ni^{2+}} + \mathrm{RP^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{NiRP^+}$$

The rate constants K_2k_2 and k_{-2} at 25° and their Arrhenius activation energies, E_a, are 2.1×10^4 sec^{-1}, 19.6 ± 0.2 kcal/mol, and 15.8 sec^{-1}, 13.3 ± 0.4 kcal/mol, respectively. For the Ni^{II}–PAR reaction the mechanism is assumed to be

$$\mathrm{Ni^{2+}} + \mathrm{H_{-1}PAR^-} \xrightarrow{k_4} \mathrm{NiH_{-1}PAR^+}$$

The rate constant k_4 at 25° and E_a are 1.4×10^5 M^{-1} sec^{-1} and 13.5 ± 0.5 kcal/mol, respectively.

The kinetics of nickel(II) complexation reactions have been widely studied.[1,2] Most of these kinetic studies have dealt with reactions in water. For those reactions which are not sterically controlled, the available data are consistent with the Eigen–Wilkins mechanisms.[1,2] A restrictive Eigen–Wilkins mechanism requires that the second-order rate constants for metal ion complexation reactions be equal to an ion-pairing constant multiplied by the rate constant for solvent exchange at the metal center. The rate-determining step is the elimination of a solvent molecule from the primary coordination sphere of