Nuclear Magnetic Resonance Spectroscopy. The Use of Carbon-13 Isotropic Shifts as a Probe of Mechanisms of Spin Transmission in Metal Complexes. Some Pyridine-Type Bases and Triphenylphosphine Complexed to Nickel(II) and Cobalt(II) Acetylacetonates[1]

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Abstract: The theory of isotropic nmr chemical shifts produced by transition metal ions with unpaired electrons suggests that the relative signs and magnitudes of the proton and ^{13}C isotropic shifts should be directly related to the mode by which unpaired spin density is transmitted from the metal to the ligand. It has been concluded that the shifts observed in the ^{13}C and ^{1}H spectra of some pyridine-type bases and triphenylphosphine complexed to cobalt(II) and nickel(II) acetylacetonates are indicative of spin density in both the σ and π frameworks of the ligands. The ^{13}C isotropic shifts appear to be controlled mainly by contact interactions.

The magnetic interactions between unpaired electrons on transition metal ions and magnetic nuclei on ligands coordinated to these ions have been the subject of a number of recent nuclear magnetic resonance (nmr) studies, and a great deal of information has been deduced thereby concerning the manner of metal–ligand bonding.[2] However, to be most effective, it is necessary to be able to factor observed chemical shift changes into their contributing components. These are the contact shift σ_{con} resulting from the transmission of σ- and or π-type electrons, and the pseudocontact contribution σ_{pcon} from electron–nucleus dipolar interactions. Difficulties can arise in interpreting proton isotropic shifts in systems having large spin–orbit couplings because, in these cases, the pseudocontact contributions can be quite large.[3] In the case of six-coordinate cobalt(II) and nickel(II) complexes an attempt has been made to overcome this problem by assuming that the mechanisms by which the shifts are changed in the two types of complexes are the same, but that the observed shifts in the Ni(II) complex are caused only by contact interactions.[4] This approach has recently been criticized by Drago.[5] It is the purpose of this paper to discuss the applicability of ^{13}C isotropic shifts to this problem and to point out their general usefulness in probing the nature of metal–ligand interactions.

Although determination of high-resolution nmr spectra of ^{13}C in natural abundance in organic compounds is becoming routine,[6] some general comments are appropriate concerning the difficulties associated with applying the technique to paramagnetic transition metal complexes. Outside the general problem of solubility, the signal intensities will likely be reduced by line broadening associated with short ^{13}C relaxation times; however this will be offset by being able to use higher radiofrequency power levels. A more serious disadvantage will be the lack of Overhauser enhancement[7] of signal intensity associated with proton decoupling because, in paramagnetic systems, the dominant ^{13}C relaxation mechanism will probably not result from ^{1}H,^{13}C dipolar interactions. Of course, in some paramagnetic complexes ^{13}C–H coupling may not be observable but this will depend on the relative magnitudes of the coupling constants and proton relaxation rates. These difficulties are not prohibitive, for besides the ^{13}C isotropic shifts induced in some pyridine-type base and triphenylphosphine by nickel(II) and cobalt(II) acetylacetonates, Ni(AA)$_2$ and Co(AA)$_2$, respectively, which will form the topic of this paper,[8] we have observed eight of the possible nine carbon resonances in nickel(II) *N*,*N*′-di(*p*-tolyl)-aminotroponiminate.[9]

Theoretical Considerations

It is useful at this point to discuss the factors which may generally be responsible for ^{13}C isotropic shifts. The observed shift can be written as

$$\sigma_{\text{obsd}} = \sigma_{\text{con}}{}^{\pi} + \sigma_{\text{con}}{}^{\sigma} + \sigma_{\text{pcon}}{}^{\text{M}} + \sigma_{\text{pcon}}{}^{\text{L}} \qquad (1)$$

where $\sigma_{\text{con}}{}^{\pi}$ and $\sigma_{\text{con}}{}^{\sigma}$ are the contact shifts resulting from the transmission of π- and σ-type electrons, respectively. $\sigma_{\text{pcon}}{}^{\text{M}}$ and $\sigma_{\text{pcon}}{}^{\text{L}}$ are the metal- and ligand-centered pseudocontact shifts. If a^{N} is the

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[1] Supported by the National Science Foundation.

[2] For reviews see (a) E. de Boer and H. van Willingen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 2, 111 (1967); (b) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965).

[3] See C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., Chapter 7, for the variations of g_{xx}, g_{yy}, and g_{zz} with λ.

[4] (a) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964); (b) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965); (c) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966); (d) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[5] M. L. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2196 (1968).

[6] (a) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *ibid.*, **91**, 7445 (1969); (b) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965); (c) D. M. Grant and D. K. Dalling, *J. Amer. Chem. Soc.*, **89**, 6612 (1967); (d) E. Wenkert, A. O. Clouse, D. W. Cochran, and D. Doddrell, *ibid.*, **91**, 6879 (1969).

[7] K. F. Kuhlmann and D. M. Grant, *ibid.*, **90**, 7355 (1968).

[8] Professor R. S. Kurland and coworkers have observed ^{13}C isotropic shifts in Fe(CN)$_6{}^{3-}$ (private communication). See also A. Loewenstein, M. Shporer, and G. Navon, *J. Amer. Chem. Soc.*, **85**, 2855 (1963).

[9] D. Doddrell and J. D. Roberts, *ibid.*, **92**, 4484 (1970).

appropriate hyperfine coupling constant, then the contact contribution to the shift of nucleus N is given by the relationship[10]

$$\sigma_{\mathrm{con}}{}^{\mathrm{N}} = -a^{\mathrm{N}}(\gamma_{\mathrm{e}}/\gamma_{\mathrm{N}})\beta_{\mathrm{e}}g_{\mathrm{e}}S(S+1)/3kT \qquad (2)$$

from which it follows that

$$\sigma_{\mathrm{con}}{}^{\mathrm{C}_i}/\sigma_{\mathrm{con}}{}^{\mathrm{H}_i} = (a^{\mathrm{C}_i}\gamma_{\mathrm{H}})/(a^{\mathrm{H}_i}\gamma_{\mathrm{C}}) \qquad (3)$$

where C_i refers to carbon and H_i to hydrogen. For π-electron systems the proton hyperfine coupling constant has been correlated with the π spin density $\rho_{\mathrm{C}_i}{}^{\pi}$ on the carbon contiguous to the proton by eq 4.[11]

$$a^{\mathrm{H}_i} = Q^{\mathrm{H}}\rho_{\mathrm{C}_i}{}^{\pi} \approx -22.5\rho_{\mathrm{C}_i}{}^{\pi} \qquad (4)$$

This relation is assumed to arise as the result of π–σ exchange interactions. For carbons in the π framework, spin-polarization effects from the contiguous atoms are also important, and if $\rho_{\mathrm{X}}{}^{\pi}$ and $\rho_{\mathrm{Y}}{}^{\pi}$ are the π spin densities on the contiguous atoms X and Y, then it can be shown that[12]

$$a^{\mathrm{C}_i} = (S^{\mathrm{C}} + Q_{\mathrm{CH}}{}^{\mathrm{C}} + Q_{\mathrm{CX}}{}^{\mathrm{C}} + Q_{\mathrm{CY}}{}^{\mathrm{C}})\rho_{\mathrm{C}}{}^{\pi} + Q_{\mathrm{XC}}\rho_{\mathrm{X}}{}^{\pi} + Q_{\mathrm{YC}}{}^{\mathrm{C}}\rho_{\mathrm{Y}}{}^{\pi} \qquad (5)$$

where S^{C} is determined by the polarization of the 1s electrons and the 2s electrons by the Q's. If X and Y are carbons, as shown in **1**, then eq 5 reduces to[12]

$$a^{\mathrm{C}_2} = 35.6\rho_{\mathrm{C}_2}{}^{\pi} - 14.0(\rho_{\mathrm{C}_1}{}^{\pi} + \rho_{\mathrm{C}_3}{}^{\pi}) \qquad (6)$$

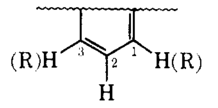
Combining eq 3, 4, and 6 yields

$$\sigma_{\mathrm{con}}{}^{\mathrm{C}_2}/\sigma_{\mathrm{con}}{}^{\mathrm{H}_2} = (\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}})(35.6\rho_{\mathrm{C}_2}{}^{\pi} - 14.0[\rho_{\mathrm{C}_1}{}^{\pi} + \rho_{\mathrm{C}_3}{}^{\pi}])/(-22.5\rho_{\mathrm{C}_2}{}^{\pi}) \qquad (7)$$

$$= -6.2 + 2.5(\rho_{\mathrm{C}_1}{}^{\pi} + \rho_{\mathrm{C}_3}{}^{\pi})/\rho_{\mathrm{C}_2}{}^{\pi} \qquad (8)$$

$$= -k_1 + k_2 f(\rho) \qquad (9)$$

Thus, if spin density in the π framework is the important mechanism controlling the shifts then $\sigma_{\mathrm{con}}{}^{\mathrm{C}_2}$ is of opposite sign to $\sigma_{\mathrm{con}}{}^{\mathrm{H}_2}$ because $f(\rho)$ is negative. This follows from the fact that $\rho_{\mathrm{C}_i}{}^{\pi}$ and $\rho_{\mathrm{C}_{i\pm1}}{}^{\pi}$ are of opposite sign.[2]



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To our knowledge, no correlations have been attempted relating electron–nuclear hyperfine coupling constants and delocalization of unpaired spin density *via* σ orbitals. In the absence of spin polarization effects, $\sigma_{\mathrm{con}}{}^{\mathrm{C}_2}$ and $\sigma_{\mathrm{con}}{}^{\mathrm{H}_2}$ will have the same sign and σ delocalization would be expected to drop off rapidly, resulting in an attenuation of the shifts as the carbons or protons are located further away from the complexing atom. Consequently, account need be taken of σ–σ configurational interactions probably only for those atoms in close proximity to the complexing atom.

For octahedrally coordinated complexes having axial symmetry the metal-centered pseudocontact shift is given by[10] eq 10 where G_{N} is the usual geometric factor $(3\cos^2\theta_{\mathrm{N}} - 1)/r_{\mathrm{N}}{}^3$, and F is some function of the components of the g tensor depending on the relative magnitudes of the electron relaxation time, the tumbling time of the complex in solution, and the Zeeman anisotropy energy.[13] It follows from eq 10 that

$$\sigma_{\mathrm{pcon}}{}^{\mathrm{M,N}} = -\beta_{\mathrm{e}}{}^2S(S+1) \times (g_{\|} - g_{\perp})F(g_{\|}, g_{\perp})G_{\mathrm{N}}/3kT \qquad (10)$$

$$\sigma_{\mathrm{pcon}}{}^{\mathrm{M,C}_i}/\sigma_{\mathrm{pcon}}{}^{\mathrm{M,H}_i} = G_{\mathrm{C}_i}/G_{\mathrm{H}_i} \qquad (11)$$

Thus, it appears that the relative magnitudes of the C-2 and H-2 (see **1**) isotropic shifts will be comparable for a predominant pseudocontact effect, but that the shift of C-2 will be much greater if a contact mechanism is dominant. A more detailed discussion of why the ligand-centered pseudocontact effect is not important will be given later in this paper.

We have used these ideas to try to elucidate the mechanisms of spin transmission into some pyridine-type bases and triphenylphosphine complexed to $\mathrm{Ni(AA)_2}$ and $\mathrm{Co(AA)_2}$. However, before discussing the results we will comment on the signs of the various possible contributors to the total isotropic shift of a pyridine-type base octahedrally coordinated to Ni(II) or Co(II).

(a) Direct Introduction of Spin Density into the π Framework. Happe and Ward[4d] have concluded that the observed proton isotropic shifts in such systems are indicative of only σ delocalization of unpaired spin density;[14] however, the appearance of π spin density in the ligands of octahedral nickel complexes has been noted.[15] For this reason, it is useful to consider the signs of the resultant ^{13}C and proton isotropic shifts, if spin density were considered to be introduced into the π orbitals of a pyridine-type base due to complexation with either $\mathrm{Co(AA)_2}$ or $\mathrm{Ni(AA)_2}$. It is easy to see how π spin density could arise with cobalt complexes, by direct delocalization of the unpaired t_{2g} electron from d_π–p_π overlap, but Ni(II) has only e_g type electrons (of σ symmetry) available and some indirect mechanism would need to be invoked to explain unpaired spin density in the π orbitals of the ligand. Of the mechanisms postulated, such as (a) expected by consideration of σ–π configuration interactions[4d] or (b) distortion from rigorous octahedral symmetry,[15a–c] LaMar[15d] has concluded that the most likely one would involve some degree of unpairing of the t_{2g} electrons resulting in π-type electrons being available for transmission onto the ligand. In the case of both metals, positive (α) spin density would be placed at the pyridine nitrogen and would alternate around the ring. Thus, the α-carbon would exhibit a positive (upfield) contact shift while the α-proton a negative (downfield) contact

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[10] (a) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); (b) eq 2 and eq 10 to be discussed later are only valid for systems having a first-order contribution to their magnetic moments and no thermally populated excited Kramer doublets. However, eq 3 and 11 are generally applicable and we feel that this justifies the qualitative discussion in the rest of the paper.

[11] (a) H. M. McConnell, *ibid.*, **28**, 1188 (1958); (b) H. M. McConnell, *Proc. Nat. Acad. Sci. U. S.*, **43**, 721 (1957); (c) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

[12] M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

[13] J. P. Jesson, *ibid.*, **47**, 579, 582 (1967).

[14] They also suggested that spin density may be introduced into the ligand π orbitals by an indirect mechanism in order to account for positive methyl-proton shifts in α- and γ-picoline.

[15] (a) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965); (b) J. D. Thwaites and L. Sacconi, *ibid.*, **5**, 1029 (1966); (c) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964); (d) G. N. La Mar, *Mol. Phys.*, **12**, 427 (1967); (e) M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 5963 (1969); (f) B. B. Wayland, R. S. Drago, and H. F. Henneike, *ibid.*, **88**, 2455 (1966); (g) R. E. Cramer and R. S. Drago, *ibid.*, **92**, 66 (1970).

Table I. Predicted Signs of the Carbon-13 Isotropic Shifts of a Pyridine-Type Base Complexed to $Co(AA)_2$ or $Ni(AA)_2$

Resonance[a]	Component of total shift $\sigma_{\mathrm{con}}{}^{\pi}$	$\sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}}$	$\sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}}$
α-C	+	−	+
β-C	−	−	+
γ-C	+	−	0
α-*C*H$_3$	−	−	+
β-*C*H$_3$	+	−	0
γ-*C*H$_3$	−	−	0

[a] Only the predicted signs of the ^{13}C isotropic shifts are given since the proton signs are easily determined from these (see text).

shift.[16] The predicted results for the other ring positions are shown in Table I under $\sigma_{\mathrm{con}}{}^{\pi}$.

(b) Direct introduction of spin density into the σ framework will result from overlap from the unpaired e_g electrons with the nitrogen lone pair. Negative (β) spin density will flow to the metal leaving an excess of positive (α) spin density on the nitrogen with a similar mechanism causing a buildup of positive spin density further around the ring. At this point it is convenient to divide the total σ ^{13}C isotropic shift, $\sigma_{\mathrm{con}}{}^{\sigma}$, into two components

$$\sigma_{\mathrm{con}}{}^{\sigma} = \sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}} + \sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}} \qquad (12)$$

where $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}}$ results from spin density at the carbon under consideration, and $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}}$ from spin polarization effects from the contiguous atoms. Whereas a contiguous atom should produce a contact shift of the *same* sign for π spin density, $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}}$ will be of opposite sign to $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}}$. Thus, $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}}$ will be negative for the α-carbon and α-proton of the pyridine ring, but $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}}$ will be positive for both. The predicted signs for the other ring positions are given in Table I.

(c) Delocalization of Spin Density onto a Ring Methyl Group. In the case of σ delocalization, $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{I}}$ will be of the same sign for both the protons and carbon of the methyl group. Similarly for $\sigma_{\mathrm{con}}{}^{\sigma \mathrm{II}}$, however, at least for the β- or γ-methyl groups, it would be expected that this latter term would have little bearing on the magnitude and sign of the observed shift due to their distant proximity to the complexing atom. For π delocalization, consider the molecular fragment shown in **2**. Let $\rho_{\mathrm{C_1}}{}^{\pi}$ be the π spin density in the p_{π} orbital centered on C-1. Then the hyperfine coupling constant for the protons of the methyl group can be approximated by[16,17]

$$a^{\mathrm{C}H_3} = Q_{\mathrm{CH_3}}{}^{\mathrm{H}}\rho_{\mathrm{C_1}}{}^{\pi} \approx +27.0\rho_{\mathrm{C_1}}{}^{\pi} \qquad (13)$$

In this case, the spin density arrives at the proton by direct hyperconjugative mechanism. The dominant mechanism of introducing spin density onto the carbon of the methyl group will be through π–σ spin polarization, and thus the hyperfine coupling constant can be approximated by

$$a^{\mathrm{CH_3}} \approx Q_{\mathrm{CC}}{}^{\mathrm{C}}\rho_{\mathrm{C_1}}{}^{\pi} \approx -14.0\rho_{\mathrm{C_1}}{}^{\pi} \qquad (14)$$

Thus, it follows that

$$(a^{\mathrm{CH_3}}/a^{\mathrm{C}H_3}) \approx -{}^{1}/_{2} \qquad (15)$$

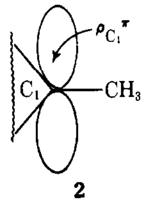
The absolute value of this result has recently been confirmed experimentally by esr measurements on the ethyl radical,[18] and theoretically from SCF calculations.[19] The sign dependency of the ratio has also

$$|(a^{\mathrm{CH_3}}/a^{\mathrm{C}H_3})|_{\mathrm{exp}} = 0.506,\ (a^{\mathrm{CH_3}}/a^{\mathrm{C}H_3})_{\mathrm{theor}} = -0.45$$

been confirmed by nmr measurements on the carbon[9] and protons[20] of the methyl group in nickel(II) *N*,*N′*-di(*p*-tolyl)aminotroponiminate. From eq 15 it follows that

$$\sigma_{\mathrm{con}}{}^{\mathrm{CH_3}}/\sigma_{\mathrm{con}}{}^{\mathrm{C}H_3} \approx -{}^{1}/_{2}(\gamma^{\mathrm{H}}/\gamma^{\mathrm{C}}) \approx -2 \qquad (16)$$

It is thus expected that this result will be a sensitive test of a dominant π spin-delocalization mechanism. The predicted signs for the methyl group at various ring positions of a pyridine-type base are given in Table I.



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Experimental Section

Carbon-13 spectra were determined as described previously[21] using the DFS-60 spectrometer under conditions of complete noise decoupling. Proton spectra were determined on a Varian A-60 instrument. The pyridine bases and triphenylphosphine were obtained from Aldrich, while the anhydrous metal acetylacetonates were products of Alfa Inorganics. The shifts were determined on saturated solutions of the acetylacetonates dissolved in the pyridine base containing 15% cyclohexane as internal reference. Chloroform containing cyclohexane was used as solvent for triphenylphosphine. The normalized value of the shift of nucleus N, R_{N}, is given by eq 17 where σ^{N} is the induced isotropic shift in parts per million

$$R_{\mathrm{N}} = 1000\sigma^{\mathrm{N}}/|\sigma_{\alpha}{}^{\mathrm{C}}| \qquad (17)$$

of nucleus N, and $|\sigma^{\mathrm{C}}{}_{\alpha}|$ is the absolute value of the induced isotropic shift of the α-carbon in parts per million. That is, $\sigma_{\mathrm{N}} = \delta_{\mathrm{comp}}{}^{\mathrm{N}} - \delta_{\mathrm{free}}{}^{\mathrm{N}}$, where $\delta_{\mathrm{comp}}{}^{\mathrm{N}}$ is the chemical shift induced by dissolution of the complex in the ligand and $\delta_{\mathrm{free}}{}^{\mathrm{N}}$ is the chemical shift for the ligand itself in cyclohexane. For compounds having two different α-carbons, the one having the largest positive (upfield) shift is set equal to 1000. The normalized values given in Table II were determined in concentration regions where R_{N} is constant. This was checked by changing the concentration only for pyridine and triphenylphosphine. The comparison of results using this approach is only valid in the fast exchange limit between complexed and uncomplexed adduct. The constancy of R_{N} is evidence for, but not proof of, the occurrence of fast exchange. It should also be noted that the ^{13}C isotropic shifts are expected to be very temperature dependent. Although no attempts were made to regulate the temperature of the samples, we feel that the temperature differences between samples are not more than ±2°.

Results

Table II gives the experimental and normalized values of the shifts induced in the carbons and protons of the pyridine-type bases and triphenylphosphine by $Ni(AA)_2$ and $Co(AA)_2$. The ^{13}C spectra were assigned by off-resonance decoupling experiments[6] and/or by lowering the concentration of the metal chelates. This was necessary because, with pyridine in particular, the

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[16] A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

[17] D. B. Chesnut, *J. Chem. Phys.*, 29, 43 (1958).

[18] (a) R. W. Fessenden and R. H. Schuler, *ibid.*, 43, 2704 (1965); (b) R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).

[19] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

[20] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 37, 347 (1962).

[21] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 89, 2967 (1967).

Table II. Experimental and Normalized Proton and Carbon-13 Isotropic Shifts of Some Ligands Complexed to Co(AA)$_2$ and Ni(AA)$_2$

		Ni(AA)$_2$			Co(AA)$_2$	
Ligand	Resonances[a]	$\delta_{\text{free}}^{\text{N}\,b}$	$\delta_{\text{camp}}^{\text{N}\,b}$	R_{N}	$\delta_{\text{comp}}^{\text{N}\,b}$	R_{N}
Pyridine	α-H	−7.5	−10.8	−943	−12.8	−165
	β-H	−6.0	−7.0	−286	−6.8	−25
	γ-H	−6.4	−6.7	−86	−4.9	+47
	α-C	−122.8	−119.3	(+1000)	−90.6	(+1000)
	β-C	−96.4	−109.3	−3686	−133.5	−1150
	γ-C	−108.5	−107.2	+371	−98.4	+314
α-Picoline	α-H	−7.3	−8.5	−293	−8.6	−156
	β-H	−5.6	−6.2	−146	−5.8	−24
	β'-H	−5.7	−6.0	−73	−5.9	−24
	γ-H	−6.1	−6.2	−24	−5.8	+37
	α'-CH_3	−1.1	−0.9	+48	−0.3	+98
	α-C	−122.8	−118.7	(+1000)	−114.0	(+1000)
	α'-C	−131.2	−133.2	−488	−130.2	+122
	β-C	−95.8	−102.6	−1659	−102.8	−854
	β'-C	−93.6	−98.2	−1122	−97.6	−488
	γ-C	−108.7	−108.3	+98	−106.6	+256
	α'-CH$_3$	+2.8	+0.4	−585	+0.6	−268
β-Picoline	α-H	−6.9	−8.2	−930	−8.8	−167
	α'-H	−6.9	−8.2	−930	−8.8	−167
	β-H	−5.6	−6.1	−360	−6.0	−35
	γ-H	−5.6	−6.2	−214	−5.3	+54
	β'-CH_3	−0.7	−0.8	−72	−0.4	+26
	α-C	−123.5	−122.1	(+1000)	−112.3	+983
	α'-C	−120.3	−118.9	(+1000)	−108.9	(+1000)
	β-C	−96.0	−100.5	−3214	−109.6	−1193
	β'-C	−106.1	−110.3	−3000	−119.0	−1131
	γ-C	−108.9	−108.3	+430	−105.1	+334
	β'-CH$_3$	+9.1	+8.5	−430	+7.8	−114
γ-Picoline	α-H	−7.0	−8.1	−394	−8.5	−375
	β-H	−5.6	−5.8	−71	−5.9	−75
	γ-CH_3	−0.7	−0.6	+36	−0.3	+100
	α-C	−122.2	−119.4	(+1000)	−188.2	(+1000)
	β-C	−97.1	−102.5	−1930	−103.1	−1500
	γ-C	−119.6	−119.1	+180	−118.5	+275
	γ-CH$_3$	+6.7	+6.3	−144	+6.4	−75
2,4-Lutidine	α-H	−7.0	−7.9	−450	−7.5	−95
	β-H	−5.4	−5.5	−50	−5.4	~0
	β'-H	−5.5	−5.7	−100	−5.5	~0
	α'-CH_3	−1.0	−1.0	~0	−0.8	~+40
	γ-CH_3	−0.7	−0.7	~0	−0.5	~+40
	α-C	−122.0	−120.0	(+1000)	−116.3	(+1000)
	α'-C	−130.0	−131.1	−550	−130.6	−113
	β-C	−96.6	−99.7	−1550	−101.4	−905
	β'-C	−94.5	−96.9	−1200	−97.4	−548
	γ-C	−119.6	−119.1	+250	−117.6	+376
	α'-CH$_3$	+3.0	+1.7	−650	+1.9	−208
	γ-CH$_3$	+6.7	+6.2	−250	+6.7	~0
2,6-Lutidine	β-H	−5.1			−5.2	−53
	γ-H	−5.6	No apparent δ complexation		−5.3	+158
	α-CH_3	−0.7			−0.9	−105
	α-C	−130.1			−132.0	(−1000)
	β-C	−92.5			−95.0	−1320
	γ-C	−109.0			−108.1	+48
	α-CH$_3$	+2.9			−0.2	−1632
Triphenylphosphine	*o*-H	−5.8	−5.7	+28	−5.0	+110
	m-H	−5.9	−6.1	−56	−6.0	−14
	p-H	−5.8	−5.7	+28	−5.4	+55
	1-C	−110.7	−114.3	−1125	?	?
	o-C	−107.0	−110.2	(−1000)	−114.3	(−1000)
	m-C	−101.6	−101.5	+28	−100.8	+109
	p-C	−101.6	−102.5	−281	−103.3	−234

[a] For the methylpyridines, the α'- or β'-carbon is that bearing the methyl group. In the case of triphenylphosphine C-1 is the directly bonded carbon. It is estimated that the error in the R_{N} values is 10%, mainly caused by rounding errors in the σ^{N} values. In some cases, the ^{13}C signal-to-noise was not sufficient to obtain σ^{C} values more accurate than ±0.3 ppm. [b] In parts per million relative to the ^{13}C or proton resonances of internal cyclohexane.

ordering of the peaks changed completely at high chelate concentrations. The usual appearance of the ^{13}C spectrum of pyridine[22] is, from downfield, α, γ, β, but at high chelate concentrations becomes β, γ, α.

The appearance of the ^{13}C spectrum of triphenylphosphine complexed to the chelates showed an interesting change compared to the normal spectrum, namely that of chemically induced phosphorus "decoupling";[23] however the directly bonded carbon could

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(22) P. C. Lauterbur, *J. Chem. Phys.*, 43, 360 (1965).

only be observed, in the case of $Co(AA)_2$, at low chelate concentrations.

Discussion

It seems apparent from the data in Table II that the ^{13}C isotropic shifts are not dominated by a metal-centered pseudocontact interaction. In most cases they are more than any order of magnitude larger than the corresponding proton-contact shift. Because the binding constants of the ligands to the two chelates are undoubtedly not equal, no direct atom-to-atom comparison can be made; however the variations between positions in the same ligand can be compared. Table III contains calculated relative magnitudes of the ^{13}C isotropic shifts for the various ring positions of pyridine and triphenylphosphine. These ratios reflect the spin distribution in the two ring systems, and thus the delocalization mechanisms. It is likey that the mechanisms of spin delocalization in the two adducts are *not* the same. For example, there is a reduction of a factor of −9.9 between the β-C and γ-C of pyridine in the case of $Ni(AA)_2$ but only a factor of −3.7 in the case of $Co(AA)_2$. It would be tempting to suppose that the upfield shift of the γ-C of pyridine complexed to $Co(AA)_2$ was due mainly to a metal-centered pseudocontact effect; however, there is more than a factor of eight between the isotropic chemical shifts of the γ-H and γ-C which is too great to attribute to differences in geometric factors. The different mechanisms of spin transmission are also apparent when the relative magnitudes of the carbon and proton isotropic shifts are compared for the triphenylphosphine adducts. In most cases, the ratios for the same sets of carbon atoms differ by over a factor of two between the two chelates. It is convenient at this point to discuss the isotropic shifts of the different positions in the pyridine-type bases.

Table III. Relative Magnitudes of Carbon-13 Isotropic Shifts for the Various Ring Positions of Pyridine and Triphenylphosphine

Ligand	$\sigma_{obsd}^{C_i}/\sigma_{obsd}^{C_j}$	$Ni(AA)_2$	$Co(AA)_2$
Pyridine	α-C, β-C	−0.3	−0.9
	α-C, γ-C	+2.7	+3.2
	β-C, γ-C	−9.9	−3.7
Triphenylphosphine	*o*-C, *m*-C	−32.0	−9.1
	o-C, *p*-C	+3.6	+4.3
	m-C, *p*-C	−0.1	−0.5

γ-Carbon and -Proton. For all of the bases studied, the γ-carbon is shielded by complexation to either chelate, whereas the γ-proton is deshielded in the case of $Ni(AA)_2$ but shielded in the case of $Co(AA)_2$. The relative magnitudes for pyridine are given in Table IV. Because any $\sigma_{con}^{\sigma II}$ contribution can probably be safely neglected for this position, the surprising conclusion emerges that the dominant contribution to the shifts of the carbons at this position is σ_{con}^{π} and *not* $\sigma_{con}^{\sigma I}$ (see Table I). The $\sigma_{obsd}^{\gamma\text{-}C}/\sigma_{obsd}^{\gamma\text{-}H}$ value for pyridine of −4.3 is close to that predicted by eq 8 if the contribution from $f(\rho)$ is considered small. The γ-H shifts are, in the case of $Co(AA)_2$, undoubtedly influenced by a $\sigma_{pcon}^{M,\gamma\text{-}H}$ contribution.

Table IV. Relative Magnitudes of Proton and Carbon-13 Isotropic Shifts for Pyridine and Triphenylphosphine

Ligand	$\sigma_{obsd}^{C_i}/\sigma_{obsd}^{H_i}$	$Ni(AA)_2$	$Co(AA)_2$
Pyridine	α-C, α-H	−1.1	−6.1
	β-C, β-H	+12.9	+46.4
	γ-C, γ-H	−4.3	+6.7
Triphenylphosphine	*o*-C, *o*-H	−32.0	−9.1
	m-C, *m*-H	−0.5	−8.0
	p-C, *p*-H	−9.0	−4.3

β-Carbon and -Proton. In all cases the β-carbons are deshielded with the β-protons exhibiting much smaller deshielding effects. However, the striking difference between the two chelates is the magnitude of the $\sigma_{obsd}^{\alpha\text{-}C}/\sigma_{obsd}^{\beta\text{-}C}$ ratios. This difference is plausibly attributed to the α-C showing a larger positive shift in the case of $Co(AA)_2$ than for $Ni(AA)_2$. This could arise by either a σ_{con}^{π} or $\sigma_{con}^{\sigma II}$ mechanism; however the σ_{con}^{π} effect is considered more likely. Evidence for a σ_{con}^{π} contribution to the $Ni(AA)_2$ shifts is apparent from an inspection of the magnitudes of the β-H shifts. Although they are in the right direction for positive spin density resulting from σ delocalization, the $\sigma_{obsd}^{\beta\text{-}C}/\sigma_{obsd}^{\beta\text{-}H}$ ratio is too large for this to be the only effect. Any $\sigma_{con}^{\sigma I}$ effect would be reduced by negative spin density arriving at the proton from the p_π orbital centered at the β-C giving rise to a positive σ_{con}^{π} shift, and a smaller overall shift. In the cases of the $Co(AA)_2$ adducts, the β-C shifts are influenced by $\sigma_{pcon}^{M,\beta\text{-}H}$ contributions.

α-Carbon and -Proton. It is readily apparent that no one contribution can be invoked to explain these shifts. This is the only position for the $Ni(AA)_2$ adducts, which would be expected to have an isotropic *g* tensor and thus no $\sigma_{pcon}^{M,N}$ shift, where the α-H and α-C shifts are of equivalent magnitude. However, the important feature of the carbon shifts is that they are positive (negative spin density), except for 2,6-lutidine, and thus σ delocalization is not important unless it be supposed that $\sigma_{con}^{\sigma II} \gg \sigma_{con}^{\sigma I}$ for this position, but this seems unlikely. The interesting feature of the α-carbon shifts is the effects of α-methyl substitution on their sign and magnitude. Methyl substitution reduces the magnitude of the upfield α-C shift, in the case of $Co(AA)_2$, but changes its sign in the case of $Ni(AA)_2$ (see Table II). It is unlikely that this is caused solely by the electronic influence of the methyl group and it would appear that steric effects on the manner of metal–ligand bonding are as, or more, important. It is possible that the metal orbitals are interacting directly with the $N\text{–}C_\alpha$ bonding electrons causing the greatest influence on the $C_\alpha\text{–}C_\beta$ side of the pyridine ring and smaller effects on the $C_{\alpha'}\text{–}C_{\beta'}\text{–}$ side, or methyl side. Drago[15g] has suggested that molecular orbital calculation should be used for interpretations of isotropic shifts. It would appear that they would be extremely useful in this instance; however some knowledge of the geometry of the complex would be required such as might be obtained by X-ray diffraction.

The negative α-carbon shift of 2,6-lutidine and the smaller magnitude of the β- and γ-carbon shifts imply that the isotropic shifts of the carbons in this ligand are controlled by σ unpaired spin density. This is not surprising because $d_\pi\text{–}p_\pi$ overlap between the cobalt and nitrogen would be much smaller for this ligand

(23) L. S. Frankel, *J. Mol. Spectrosc.*, 29, 273 (1969).

because of the steric effects of the methyl groups. The sign reversal of the α-carbon shift between this ligand and those lacking α-methyl groups is good evidence for some $\sigma_{\mathrm{con}}{}^{\pi}$ shift in the latter produced by d_{π}–p_{π} bonding.

Methyl Carbons and Protons. The methyl carbon isotropic shifts are almost an order of magnitude larger than the methyl proton shifts and thus are useful in probing the manner of unpaired spin delocalization. Whereas the $\alpha\text{-}C\mathrm{H}_3$ and $\alpha\text{-}\mathrm{C}H_3$ shifts are of the correct signs for π delocalization in the $\mathrm{Ni(AA)_2}$ adduct, the $\sigma_{\mathrm{obsd}}{}^{\alpha\text{-}C\mathrm{H}_3}/\sigma_{\mathrm{obsd}}{}^{\alpha\text{-}\mathrm{C}H_3}$ ratio is much larger than that predicted by eq 16 and probably implies that the dominant delocalization process at this position is that involving the σ framework. This is consistent with the suggestion proposed to account for the effect on the α-carbon isotropic shifts by α-methyl substitution. Similar comments are appropriate for the β position. However, $\sigma_{\mathrm{obsd}}{}^{\gamma\text{-}C\mathrm{H}_3}/\sigma_{\mathrm{obsd}}{}^{\gamma\text{-}\mathrm{C}H_3}$ is on the order of -3.0 which is in good agreement with that predicted by eq 16 which assumes that the unpaired spin density is due solely to π delocalization. Unfortunately, in the case of the $\mathrm{Co(AA)_2}$ adduct $\sigma_{\mathrm{con}}{}^{\gamma\text{-}\mathrm{H}}$ cannot be estimated because of the uncertainty from any $\sigma_{\mathrm{pcon}}{}^{\mathrm{M},\gamma\text{-}\mathrm{H}}$ contributions. However, $\sigma_{\mathrm{con}}{}^{\gamma\text{-}\mathrm{C}}$ and $\sigma_{\mathrm{con}}{}^{\gamma\text{-}C\mathrm{H}_3}$ are of opposite sign for this chelate as required by a π mechanism. Any contribution from unpaired spin density in the σ framework would be largely attenuated at the γ position allowing $\sigma_{\mathrm{con}}{}^{\pi}$ to be dominant.

Conclusion

It is apparent that ^{13}C isotropic shift studies will be extremely useful in probing the nature of metal–ligand bonding. Although only qualitative comparisons were made for the cases studied here it seems that no simple pictures of spin delocalization can be invoked to explain the observed shifts. Shifts resulting from both σ and π delocalization are readily apparent in the pyridine-type bases and triphenylphosphine. When these conclusions are combined with those deduced from our previous study[9] involving the ^{13}C spectrum of Ni(II) *N*,*N'*-di(*p*-tolyl)aminotroponiminate it is seen that mixed delocalization processes are probably quite common even in systems for which a "simple crystal field theory" approach predicts unpaired electrons of only π or σ symmetry available for transmission onto the ligand. Hence, calculated values for unpaired spin density on the ligands of complexes from the McConnell relationship, which assumes a pure π delocalization of spin density, should be looked upon with caution. Our conclusions follow closely those deduced recently by Drago[15g] for nickel(II) complexes of pyridine-type bases from molecular orbital calculations.

Investigation of ^{13}C isotropic shifts of other complexes will probably be relatively easy to carry out by high-resolution natural-abundance ^{13}C nmr where the proton-contact shifts do not exceed a span of 120 ppm and have line widths less than about 100–120 Hz and the compounds are reasonably soluble (1 *M*). In these circumstances time averaging over 100–600 scans will be required to achieve reasonable signal-to-noise ratios. Natural-abundance ^{13}C spectra should be possible on more complex systems but with a greater degree of difficulty.

Ligand-Centered Pseudocontact Shifts. Because the symmetry at the ligand site is not octahedral but tetragonal, it is possible for through space dipolar coupling between the unpaired spin density at the ligand site and the magnetic moment of the nucleus not to average to zero. This gives rise to a pseudocontact shift.[11c] Kurland and McGarvey[24] have shown that this shift $\sigma_{\mathrm{pcon}}{}^{\mathrm{L,N}}$ can be approximated by

$$\sigma_{\mathrm{pcon}}{}^{\mathrm{L,N}} = k'f^2\langle r^{-3}\rangle_{\mathrm{N}}H(\lambda)/T \tag{18}$$

where f is a measure of the admixture of the ligand and metal orbitals, $\langle r^{-3}\rangle_{\mathrm{N}}$ is the mean of the inverse of the cube of the distance from the ligand site to the nucleus N, H(λ) is some function involving the spin orbit coupling constant, and k' is a constant. Consider the molecular fragment **1**; then

$$\sigma_{\mathrm{pcon}}{}^{\mathrm{L,C_2}}/\sigma_{\mathrm{pcon}}{}^{\mathrm{L,H_2}} = \langle r^{-3}\rangle_{2\mathrm{p}}/\langle r^{-3}\rangle_{\mathrm{CH}} \tag{19}$$

where $\langle r^{-3}\rangle_{2\mathrm{p}}$ is the mean of $1/r^3$ for a carbon 2p orbital, and $\langle r^{-3}\rangle_{\mathrm{CH}}$ is the cube of the inverse of the CH bond length. Reasonable values of these parameters are: $\langle r^{-3}\rangle_{2\mathrm{p}} = 10 \times 10^{24}\ \mathrm{cm^{-3}}$ and $\langle r^{-3}\rangle_{\mathrm{CH}} = 10^{24}\ \mathrm{cm^{-3}}$. Hence

$$\sigma_{\mathrm{pcon}}{}^{\mathrm{L,C_2}} \approx 10\sigma_{\mathrm{pcon}}{}^{\mathrm{L,H_2}} \tag{20}$$

McConnell and Chesnut[11c] have concluded that $\sigma_{\mathrm{pcon}}{}^{\mathrm{L,H}}/\sigma_{\mathrm{con}}{}^{\mathrm{H}}$ is on the order of 10^{-3} for the methyl radical; hence it is apparent that $\sigma_{\mathrm{pcon}}{}^{\mathrm{L,C_2}}$ will also be negligible in comparison to $\sigma_{\mathrm{con}}{}^{\mathrm{C_2}}$ when it is remembered that $\sigma_{\mathrm{con}}{}^{\mathrm{C_2}}/\sigma_{\mathrm{con}}{}^{\mathrm{H_2}}$ is already on the order of ten.[25] Thus, any inconsistent trends in the carbon isotropic shifts for the ligand discussed above cannot be attributed to large $\sigma_{\mathrm{pcon}}{}^{\mathrm{L,C}}$ contributions but must be due to $\sigma_{\mathrm{con}}{}^{\mathrm{C}}$ effects. These remarks should not be taken as general, because it is likely that $\sigma_{\mathrm{pcon}}{}^{\mathrm{L}}$ effects may be important in other systems, as pointed out by Kurland and McGarvey for ^{14}N and perhaps ^{13}C in $\mathrm{Fe(CN)_6}^{-}$.[3,24]

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(24) We thank Professors R. J. Kurland and B. R. McGarvey for a preprint of their work.

(25) It should be noted that the methyl radical does not have a zero-order spin–orbit interaction such as is present in Co(II); however, we feel that a value of $\sigma_{\mathrm{pcon}}{}^{\mathrm{L,H}}/\sigma_{\mathrm{con}}{}^{\mathrm{H}}$ of 10^{-3} is at least a reasonable approximation for positions at the ligand site.