

order of thermal energies. Thus a Boltzmann distribution could exist between the two. In this way, one might explain the reported existence²⁴ of both singlet and triplet binuclear Mo(V) species in hydrochloric acid

solutions of Mo(V). Both would have the general constitution $[\text{Cl}_4\text{Mo}(\text{O})-\text{O}-\text{Mo}(\text{O})\text{Cl}_4]^{4-}$.

(24) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).

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Isotropic Proton Magnetic Resonance Shifts in π -Bonding Ligands Coordinated to Paramagnetic Nickel(II) and Cobalt(II) Acetylacetonates

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Isotropic proton magnetic resonance shifts due to contact and pseudo-contact interactions have been observed for protons in certain triarylphosphines and isonitrile molecules when these are placed in solution in CDCl_3 with the paramagnetic Ni(II) and Co(II) acetylacetonates. The alternation in sign of the observed shifts for adjacent protons on the phenyl rings is evidence for delocalization of spin density into the π -orbitals of these ligands when coordinated to both Co(II) and Ni(II) acetylacetonates. Evidence for a large upfield pseudo-contact shift in the cobalt systems is presented. Proton spin-spin coupling constants for the arylphosphines and isonitriles are given.

Introduction

This paper reports a high resolution proton magnetic resonance (p.m.r.) study of interactions in solution between π -bonding ligands and the paramagnetic chelates, cobalt(II) and nickel(II) acetylacetonate [bis(2,4-pentanediono)cobalt(II) and -nickel(II)], hereafter referred to as $\text{Co}(\text{AA})_2$ and $\text{Ni}(\text{AA})_2$. Large, concentration-dependent chemical shifts from the values in the diamagnetic ligands are observed for the proton resonances of certain triarylphosphines and isonitrile molecules when these are placed in chloroform solution with the paramagnetic complexes.

A great deal of extremely detailed and fundamental knowledge about the electronic structure of certain paramagnetic systems can be obtained from their p.m.r. spectra. The elegant work of Phillips and his co-workers¹⁻⁵ on the Ni(II)aminotroponeimines and related systems illustrates the potential of this technique. Most of the recent work in this field has been confined to systems containing Ni(II); however, recently several studies of systems containing Co(II) have appeared.⁶⁻⁹ Of particular interest to this work is the investigation by Happe and Ward⁵ of the p.m.r. spectra of pyridine-type bases complexed with $\text{Ni}(\text{AA})_2$ and $\text{Co}(\text{AA})_2$.

The theory of isotropic nuclear resonance shifts has been discussed at length by McConnell and Robertson.¹⁰ The conditions necessary for the observation of proton resonances in paramagnetic systems are by now well established.^{2,10,11} Either the electronic

spin-lattice relaxation time, T_1 , or a characteristic electronic exchange time, T_e , must be short compared with the isotropic hyperfine contact interaction constant, A_i , in order for resonances to be observed.

The contact interaction gives rise to a shift in resonance from the diamagnetic position due to the presence of unpaired spin density at the resonating nucleus. This spin density can be transmitted through the ligands by either σ - or π -orbitals. Another possible cause of an isotropic nuclear resonance shift is the pseudo-contact interaction which arises from anisotropy in the g -tensor of the paramagnetic complex. The pseudo-contact shift for a given proton depends on its geometrical position in the molecule.^{10,12,13}

The shifts observed in the Ni(II) aminotroponeimines have been satisfactorily explained by assuming that the unpaired electron spin density is distributed *via* the π -orbitals of these unsaturated ligands. Spin density in the σ -orbitals and the pseudo-contact interaction are apparently unimportant in these systems.¹⁻⁵ Happe and Ward interpreted the resonance shifts in pyridine-type ligands coordinated to $\text{Ni}(\text{AA})_2$ as being due to spin density being transferred *via* the σ -orbitals. In the case of the $\text{Co}(\text{AA})_2$ -pyridine-type base complexes, they found that a pseudo-contact interaction contributes significantly to the observed shifts as well.

The spectra of labile complexes, such as adducts of $\text{Co}(\text{AA})_2$ or $\text{Ni}(\text{AA})_2$, exhibit a time average spectrum.⁸ If the exchange of ligands between complexed and uncomplexed sites is rapid compared with the separation in resonance frequency for a given proton in the paramagnetic and diamagnetic environments, the various proton resonances will be shifted from their normal diamagnetic values by an amount proportional to the shifts in the complexes. Also, the more diamagnetic ligand is added to the system, the smaller become the observed shifts. Since the shifts we have observed are as large as 500 c.p.s., the rate at which this ligand exchange occurs must be in excess of 10^3 sec.^{-1} .

Noting that the results of Happe and Ward indicate that spin density is transferred only through the σ -

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

(2) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

(3) E. A. Lalancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *ibid.*, **84**, 3968 (1962).

(4) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **39**, 3513 (1963).

(5) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(6) C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963).

(7) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

(8) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(9) W. D. Horrocks, Jr., and G. N. LaMar, *J. Am. Chem. Soc.*, **85**, 3512 (1963).

(10) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(11) R. E. Richards, *Discussions Faraday Soc.*, **34**, 74 (1962).

(12) N. Bloembergen and W. C. Dickinson, *Phys. Rev.*, **79**, 179 (1950).

(13) W. C. Dickinson, *ibid.*, **81**, 717 (1951).

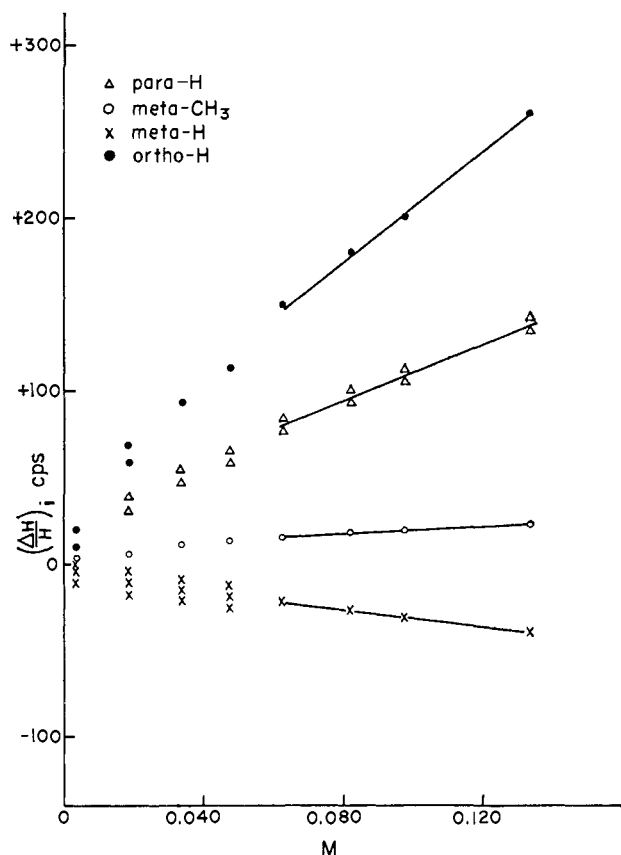


Fig. 1.—Plot of the isotropic p.m.r. shifts of tri-*m*-tolylphosphine (0.149 *M*) vs. concentration of $\text{Co}(\text{AA})_2$ in CDCl_3 solution.

orbital systems when nitrogen heterocyclic bases are coordinated to $\text{Co}(\text{AA})_2$ and $\text{Ni}(\text{AA})_2$, it is of interest to determine the behavior of ligands known to be capable of forming π -bonds.¹⁴ Recent p.m.r. results on bis-(triarylphosphine) complexes of the $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ halides indicate that spin density is transferred to the ligands by $d\pi-d\pi$ bonding in these tetrahedrally coordinated complexes.^{15,16} The nonlinearity of the C-N-C bond in isonitrile molecules coordinated to transition metals and the infrared spectra of these compounds have been interpreted in terms of $d\pi-d\pi$ bonding, with charge flowing from the metal to the ligand.¹⁷

Our results indicate that electron spin density is transferred from the metal to the π -electron systems of coordinated arylphosphines and isonitriles. This $d\pi-d\pi$ or $d\pi-p\pi$ bonding occurs in the $\text{Co}(\text{AA})_2$ systems and also, rather surprisingly (*vide infra*), in the $\text{Ni}(\text{AA})_2$ systems as well. Any spin density in the σ -orbital systems is apparently of minor importance. A pseudo-contact shift is found to be important in the $\text{Co}(\text{AA})_2$ adducts but is probably small or absent in the $\text{Ni}(\text{AA})_2$ systems. These latter conclusions are supported by the results for pyridine-type ligands.⁸

Experimental

Materials.— $\text{Ni}(\text{AA})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{AA})_2 \cdot 2\text{H}_2\text{O}$ were prepared by a method similar to the one described for the preparation of beryllium acetylacetonate.¹⁸ The anhydrous chelates were obtained by heating the hydrates *in vacuo* at 57° .¹⁹

(14) For a discussion of π -bonding in transition metal complexes see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 27.

(15) E. A. LaLancette and D. R. Eaton, to be published.

(16) G. N. LaMar, Ph.D. Thesis, Princeton University, 1964.

(17) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

(18) "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 17.

t-Butylisonitrile, *p*-tolylisonitrile, and *p*-phenylisonitrile were prepared and purified according to the procedures of Ugi and Meyr.²⁰

The tertiary phosphines were obtained from Eastman Organic Chemicals and were used without further purification.

Chloroform-*d* was obtained from the Sandoz Corp.

Tetramethylsilane (TMS) was obtained from Peninsular ChemResearch Inc., Gainesville, Florida.

Experimental Procedure.—Two procedures were followed depending on whether the added ligand was a phosphine or an isonitrile. These procedures are described below.

Procedure A. Phosphine Ligands.—A known amount of the phosphine was dissolved in the appropriate amount of a CDCl_3 -TMS mixture (TMS present at a concentration of ~1-2% by weight) to give a solution 0.149 *M* in the phosphine. Eight samples of $\text{M}(\text{AA})_2$ were accurately weighed out so that when 1 ml. of the phosphine- CDCl_3 -TMS solution was added to each sample, solutions from 0 to 0.14 *M* in $\text{M}(\text{AA})_2$ resulted.

Procedure B. Isonitrile Ligands.—Weighed samples of $\text{Ni}(\text{AA})_2$ or $\text{Co}(\text{AA})_2$ were dissolved in 1 ml. of CDCl_3 -TMS solution resulting in solutions from 0 to 0.14 *M* in $\text{M}(\text{AA})_2$, and 30 μl . of isonitrile was added by means of a microsyringe. The phenylisonitrile was added at 0° to decrease the rate of polymerization. *t*-Butylisonitrile and *p*-tolylisonitrile were added at room temperature. Each sample was run immediately after addition of the isonitrile. Spurious results were obtained if the samples were allowed to stand any length of time.

Bromobenzene, tri-*o*-tolylphosphine, triphenylarsine, triphenylamine, benzonitrile, and diphenyl sulfide did not exhibit significant isotropic p.m.r. shifts when placed in solution with the paramagnetic acetylacetonates.

All spectra were recorded on a Varian A-60 spectrometer with a probe temperature of 34° . The proton resonance shifts were measured relative to an internal TMS reference to eliminate bulk susceptibility effects. Absorption peaks were assigned to particular ligand protons on the basis of peak intensities and, when resolved, nuclear spin-spin splittings.

The proton resonance shifts referred to in this paper are shifts in the resonance frequencies from their normal values in the absence of the paramagnetic complexes, measured in c.p.s. at 60 Mc./sec.

$$\left(\frac{\Delta H}{H}\right) = \left(\frac{\Delta H}{H}\right)_{\text{in } \text{CDCl}_3}^{\text{complex measd}} - \left(\frac{\Delta H}{H}\right)_{\text{in } \text{CDCl}_3}^{\text{ligand}} \quad (1)$$

The values for the proton resonances of the ligands in CDCl_3 solution are given in Table I. The proton resonance frequencies of the diamagnetic complex, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}(\text{CO})_2$, were identical

TABLE I
PROTON RESONANCE FREQUENCIES FOR DIAMAGNETIC LIGANDS

Ligand	Ligand frequencies in CDCl_3 from TMS (c.p.s.)			Methyl
	<i>ortho</i>	<i>meta</i>	<i>para</i>	
$(\text{C}_6\text{H}_5)_3\text{P}$	-440.5	-443.9	-440.5
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	-435.5	-431.1	-141.2
$(m\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	-431.6	-436.1	-431.6	-139.4
$\text{C}_6\text{H}_5\text{NC}$	-445.4	-445.4	-445.4
$p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$	-435.2	-435.2	-143.1
				-89.1
$(\text{CH}_3)_3\text{CNC}^a$	-87.2
				-85.3

^a The observed triplet is due to long range N-H spin-spin coupling; see I. D. Kuntz, Jr., P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

with those of the free ligand measured in CDCl_3 . Negative shifts are shifts to lower applied fields. Shifts are reported for stated ligand and acetylacetonate concentrations which fall in the range over which the ratios of the shifts of the various protons remain constant.

Results

The results are presented in Tables II and III. Figures 1 and 2 show typical plots of $(\Delta H/H)_i$ vs. chelate concentration for two of the systems studied.

(19) R. H. Holm and F. A. Cotton, *J. Phys. Chem.*, **65**, 321 (1961).

(20) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

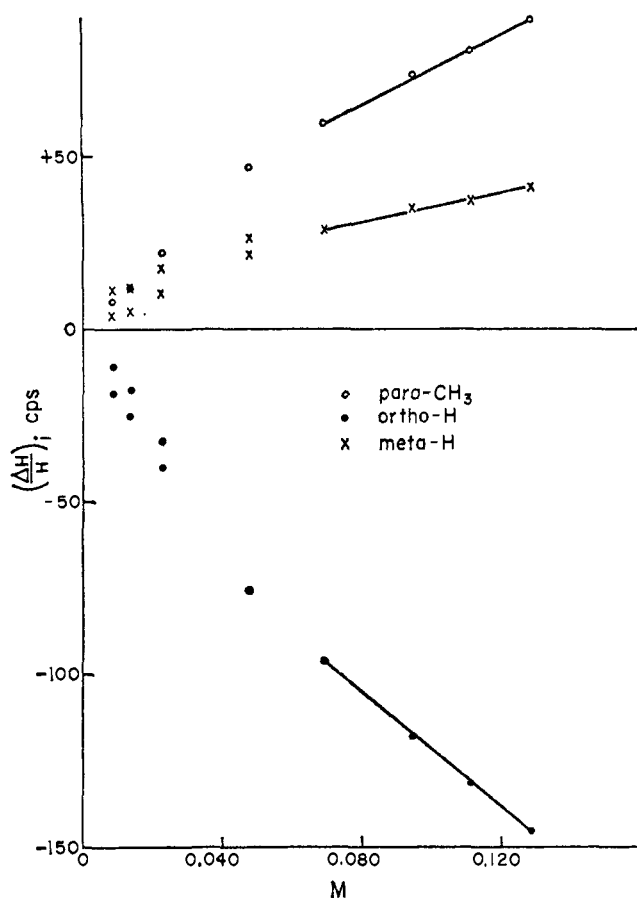


Fig. 2.—Plot of the isotropic p.m.r. shifts of *p*-tolylisonitrile (0.257 *M*) vs. concentration of Ni(AA)₂ in CDCl₃ solution.

The observed shifts are given for chelate concentrations in the region where $(\Delta H/H)_1$ vs. concentration is linear. Figures 3 and 4 show sample spectra for these

Ligand	Proton	Concn. of ligand, <i>M</i>	Shifts in c.p.s. at concn. of Ni(AA) ₂ , <i>M</i>		
			0.078	0.098	0.118
(C ₆ H ₅) ₃ P	<i>p</i>	0.149	45.0	53.0	61.0
	<i>m</i>		-43.0	-50.0	-56.5
	<i>o</i>		59.0	68.5	77.5
<i>p</i> -CH ₃ C ₆ H ₄) ₃ P	<i>p</i> -CH ₃	0.149	-64.5	-74.5	-85.0
	<i>o</i>		51.0	58.5	66.5
	<i>p</i>		55.0	64.5	74.0
<i>m</i> -CH ₃ C ₆ H ₄) ₃ P	<i>m</i>	0.149	-51.5	-60.5	-69.5
	<i>m</i> -CH ₃		22.0	25.0	28.5
	<i>o</i>		66.5	78.0	88.5
C ₆ H ₅ NC	<i>p</i>	0.299	-54.5	-63.0	-71.5
	<i>m</i>		20.0	24.0	28.0
	<i>o</i>		-90.5	-104.5	-118.5
<i>p</i> -CH ₃ C ₆ H ₄ NC	<i>p</i> -CH ₃	0.257	65.0	74.5	84.5
	<i>m</i>		31.0	35.0	39.0
	<i>o</i>		-104.5	-120.0	-136.5
(CH ₃) ₃ CNC	(CH ₃) ₃	0.266	-29.1	-34.2	-39.2

same two systems at a given chelate concentration. Dipolar broadening and spin-spin splitting are quite evident. The observed spin-spin coupling constants are listed in Table VII. Dipolar broadening ($1/r^6$ dependence) is greatest for the *ortho* resonances.

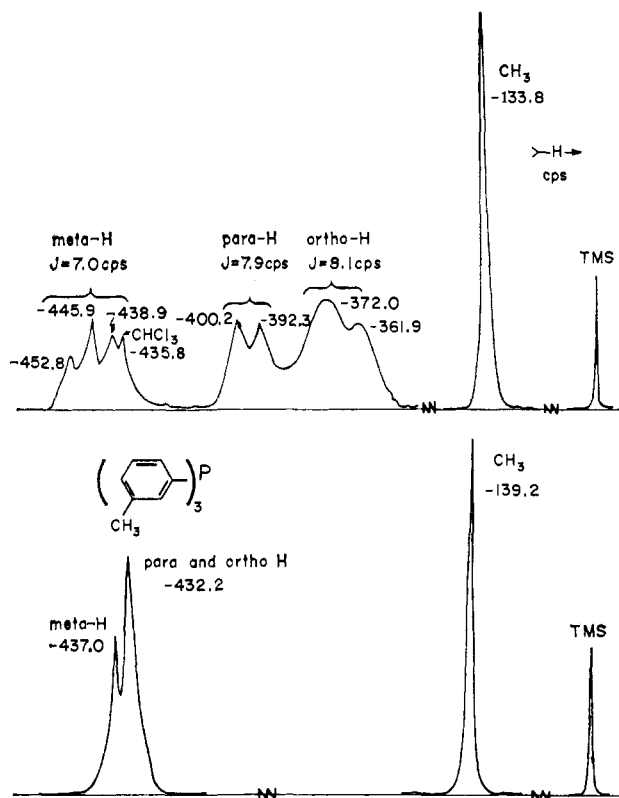


Fig. 3.—P.m.r. spectrum of tri-*m*-tolylphosphine (0.149 *M*) alone and in the presence of Co(AA)₂ (0.019 *M*) in CDCl₃ solution.

Discussion

The nature of solutions of the acetylacetonates themselves and the probable structure of adducts formed on addition of other ligands must be considered. These systems are not simple. Graddon and

TABLE III
ISOTROPIC P.M.R. SHIFTS OF LIGANDS IN THE PRESENCE OF Co(AA)₂

Ligand	Proton	Concn. of ligand, <i>M</i>	Shifts in c.p.s. at concn. of Co(AA) ₂ , <i>M</i>		
			0.078	0.098	0.118
(C ₆ H ₅) ₃ P	<i>p</i>	0.149	87.0	102.0	117.5
	<i>m</i>		-23.0	-26.5	-30.0
	<i>o</i>		167.0	198.5	230.0
<i>p</i> -CH ₃ C ₆ H ₄) ₃ P	<i>p</i> -CH ₃	0.149	-64.0	-74.5	-85.0
	<i>o</i>		187.0	221.0	255.0
	<i>p</i>		93.5	109.0	125.0
<i>m</i> -CH ₃ C ₆ H ₄) ₃ P	<i>m</i>	0.149	-26.0	-31.0	-35.5
	<i>m</i> -CH ₃		16.5	19.0	21.0
	<i>o</i>		172.0	203.0	235.0
C ₆ H ₅ NC	<i>p</i>	0.299	31.0	39.0	47.0
	<i>m</i>		186.0	235.0	283.5
	<i>o</i>		244.0	308.0	372.5
<i>p</i> -CH ₃ C ₆ H ₄ NC	<i>p</i> -CH ₃	0.257	208.0	253.0	298.5
	<i>m</i>		221.0	269.5	318.0
	<i>o</i>		283.0	345.0	408.0
(CH ₃) ₃ CNC	(CH ₃) ₃	0.266	320.0	396.0	471.0

Watton²¹ determined the molecular weight of Ni(AA)₂ in benzene and their value indicates a trimer in solution. Cotton and Fackler²² obtained similar results which indicate that even at high temperatures [Ni(AA)₂]₃ is the principal species in solution. It is

(21) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).

(22) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

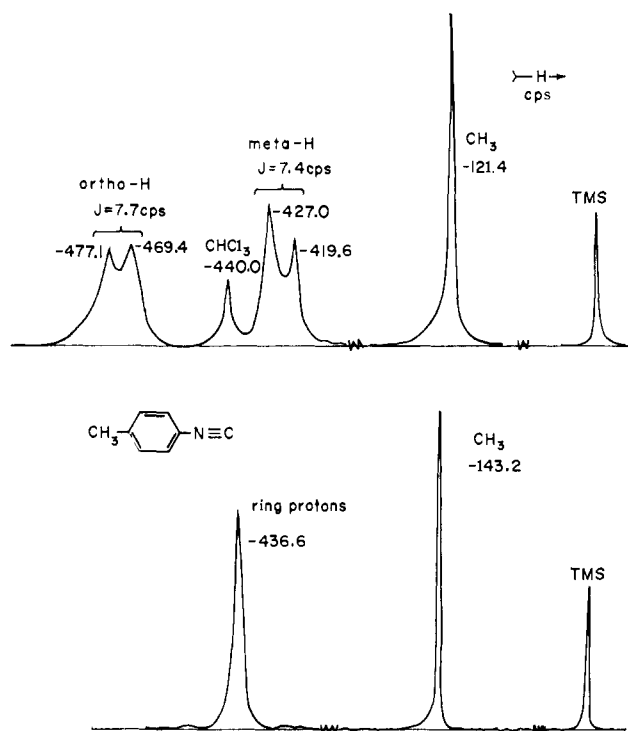


Fig. 4.—P.m.r. spectrum of *p*-tolylisonitrile (0.257 *M*) alone and in the presence of Ni(AA)₂ (0.022 *M*) in CDCl₃ solution.

postulated that the solution trimer is similar in structure to the trimer found in crystals of Ni(AA)₂ in which approximately octahedral coordination by oxygen atoms is achieved by each nickel atom.²³ Fackler²⁴ studied solutions obtained by addition of pyridine to Ni(AA)₂ in benzene. At low pyridine to Ni(AA)₂ concentration ratios, the principal species in solution appeared to be [Ni(AA)₂]₂pyridine. The reported dipyridinate, Ni(AA)₂2pyridine, did not become the dominant species until a large excess of pyridine was present. It is likely for the more weakly coordinating phosphine and isonitrile ligands that the principal adduct species is [Ni(AA)₂]₂ligand at the concentrations studied in the present work. The approximate local symmetry at the ligand-coordinated nickel in the above complex is C_{4v}, but if the whole structure is taken into account the symmetry is much lower.

The magnetic properties, electronic spectra, and molecular weight of Co(AA)₂ in solution have been studied by Cotton and co-workers.^{25,26} Their results indicate that there is a temperature and concentration dependent equilibrium between monomers, dimers, and higher polymers in solutions of Co(AA)₂ in several solvents. Judging from these data it is not unreasonable to expect that in a chloroform solution ~0.1 *M* in Co(AA)₂ the principal species is the dimer [Co(AA)₂]₂. Although Cotton and Soderberg²⁶ state that speculation about the structure of the associated species is hazardous, they consider it plausible for the dimer to be built up of two Co(AA)₂ units in which four oxygen atoms form a more or less square array about each cobalt atom. Two of these combine so that the CoO₄ planes lie parallel to one another, but off-set so that an oxygen in each plane occupies a fifth coordination

position of the cobalt atom in the other plane. A recent study²⁷ of the reaction of pyridine with Co(AA)₂ in benzene solution indicates that an equilibrium exists between [Co(AA)₂]₂pyridine, Co(AA)₂pyridine, and Co(AA)₂2pyridine, depending on the pyridine concentration. In the concentration ranges studied in this paper, complexes of the former two types predominate. These complexes would have at maximum C_{4v} symmetry at the cobalt atom and probably less.

That arylphosphines and isonitriles coordinate to Co(AA)₂ and Ni(AA)₂ in chloroform-*d* solution is evident from the large proton resonance shifts observed. As mentioned in the Experimental section, a number of other molecules, when placed in a similar situation, failed to exhibit any resonance shift. Of particular interest is the fact that tri-*o*-tolylphosphine failed to coordinate while the *m*- and *p*-tolyl compounds did. This is undoubtedly due to the steric effect of the *o*-methyl groups. Molecular models show that these groups protrude considerably in the direction of the phosphorus lone-pair and would be expected to inhibit coordination.

Isotropic proton resonance shifts can arise from two causes, the contact and pseudo-contact interactions which we will consider briefly. The contact interaction shift is described by eq. 2.^{10,28}

$$\left(\frac{\Delta H}{H}\right)_i = -A_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} \quad (2)$$

where A_i is the isotropic hyperfine contact interaction constant for the *i*th proton, g is the spectroscopic splitting factor, β is the Bohr magneton, γ_e and γ_H are the gyromagnetic ratios for the electron and proton, respectively, and S is the total spin quantum number [$S = 1$ for Ni(II) and $S = 3/2$ for Co(II)]. The other symbols have their usual meaning. A_i is a measure of the amount of unpaired spin density at the *i*th proton. The σ - and π -mechanisms for transferring spin density are considered below.

σ -Model.—If unpaired spin density resides in metal orbitals of σ -symmetry and is transferred to the σ -orbitals of the ligands, the magnetic field at the protons is reinforced by the electron spin magnetic field, and the proton resonances are all shifted to lower applied fields. These shifts attenuate rapidly as the number of bonds between a given proton and the metal increases. The spectra of pyridine-type bases coordinated to Ni(AA)₂⁸ are explicable on this basis. The resonance of a proton attached to a carbon three bonds removed from the metal is shifted downfield only about 30% of the resonance shift experienced by a proton attached to a carbon two bonds removed from the metal.⁸

π -Model.—If the metal atom has orbitals of π -symmetry containing unpaired electrons, their spin density may be transferred into the ligand π -systems by $d\pi-d\pi$ or $d\pi-p\pi$ bonding. In cases such as the Ni(II) aminotroponimineates where this is the dominant mechanism, positive spin density is placed at every other atom in the π -system. Negative spin density is induced by spin correlation at the remaining carbons. For a single unpaired electron delocalized in the π -

(23) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

(24) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962).

(25) F. A. Cotton and R. H. Holm, *ibid.*, **82**, 2979 (1960).

(26) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

(27) J. P. Fackler, Jr., *ibid.*, **2**, 266 (1963).

(28) R. E. Robertson in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 10.

orbitals of an aromatic system, McConnell^{29,30} obtained eq. 3 for the relation between A_i and the unpaired spin density on the i th carbon atom, ρ_i :

$$A_i = Q_{CH}\rho_i \quad (3)$$

For systems with more than one unpaired electron, this equation can be generalized to²⁸

$$A_i = \frac{Q_{CH}\rho_i}{2S} \quad (4)$$

Q_{CH} is a negative constant approximately equal to -22.5 gauss, the value obtained for the benzene negative ion.³¹ An analogous expression for the hyperfine interaction of a methyl group may be written, but where the proportionality constant Q_{CH_3} is positive and has been found to vary considerably in magnitude ($\sim +5$ to $\sim +30$ gauss).^{2,3,16,32} It is clear from eq. 1, 2, and 3 that a positive spin density (electron spin in direction of applied magnetic field) at a given carbon atom gives rise to an upfield resonance shift of an attached hydrogen and a downfield shift of an attached methyl group.

The other isotropic shift mechanism, the pseudo-contact interaction, may be important if there is an anisotropy in the g -tensor of the paramagnetic complex. Shifts due to this cause are described by eq. 5¹⁰ for axially symmetric molecules.

$$\left(\frac{\Delta H}{H}\right)_i = -\frac{\beta^2 S(S+1)}{27kT}(g_{11} + 2g_1)(g_{11} - g_1) \times \frac{(3 \cos^2 \chi_i - 1)}{r_i^3} \quad (5)$$

Here χ_i is the angle between the ligand field axis of the complex and the radius vector from the metal atom to the i th proton, r_i is the distance between the i th proton and the paramagnetic nucleus, and g_{11} and g_1 are the g -factors parallel and perpendicular to the ligand field axis, respectively.

In order to assess the relative importance of the contact and pseudo-contact interactions, we calculated the ratios of the expected pseudo-contact shifts for the various protons on the ligands. The labile nature of the complexes of course precludes any determination of the actual resonance shifts for the coordinated ligands. It is clear that for a given system, the ratios of shifts due to a pseudo-contact interaction alone will be given by⁸

$$\left(\frac{\Delta H}{H}\right)_i : \left(\frac{\Delta H}{H}\right)_j : \left(\frac{\Delta H}{H}\right)_k : \dots = \frac{3 \cos^2 \chi_i - 1}{r_i^3} : \frac{3 \cos^2 \chi_j - 1}{r_j^3} : \frac{3 \cos^2 \chi_k - 1}{r_k^3} \quad (6)$$

In order to determine the role of pseudo-contact shifts in our systems, we calculated the average value of $(3 \cos^2 \chi - 1/r_3)$ for each of the ligand protons. This involved averaging over all possible orientations of the phenyl rings rotating about an axis through the P-C bond in the phosphines. The integrals converged quite

slowly and the computations were carried out on an IBM 7094 computer employing intervals of 1° of arc.¹⁶ For the m -methyl protons, a double integration was performed, both the phenyl ring and the methyl group being rotated. The metal-phosphorus or metal-carbon bond serves to define the ligand field axis in these systems. Deviations from axial symmetry were ignored. The bond lengths and angles used in estimating the geometric factors listed in Table VI are given in Table IV. The most uncertain bond length is the metal-ligand distance. In the case of phosphine ligands, the geometric factor is particularly sensitive to the M-P distance. Several reasonable M-P distances were tried. Since $(3 \cos^2 \chi - 1/r^3)_{av}$ was found to be positive for all the phosphine and isonitrile protons (Table VI), any pseudo-contact term will shift all resonances either to high or low fields depending on the relative magnitudes of g_{11} and g_1 . The direction of shift for possible combinations of contact and pseudo-contact interaction are listed in Table V.

TABLE IV
STRUCTURAL PARAMETERS USED IN CALCULATING GEOMETRIC FACTORS

Triarylphosphines ^a		Arylisonitriles ^a	
Bond	Distance, Å., or angle, deg.	Bond	Distance, Å., or angle, deg.
M-P	2.35	M-C	1.85
P-C	1.90	C-N	1.18
C-C	1.397	N-C	1.42
C-H	1.089	\angle C-N-C	180°
C-CH ₃	1.52		
\angle M-P-C	109° 28'		

^a The same phenyl ring parameters were used for the phosphines and isonitriles with normal 120° angles.

TABLE V
CONTACT AND PSEUDO-CONTACT INTERACTIONS FOR COORDINATED LIGANDS

Proton	Predicted contact shifts ^a				Predicted pseudo-contact shifts ^a	
	R ₃ P	RNC	R ₃ P	RNC ^b	Relative g factors	All ring protons
<i>para</i>	-	-	+	-	$g_{11} = g_1$	0
<i>meta</i>	-	-	-	+	$g_{11} < g_1$	+
<i>ortho</i>	-	-	+	-	$g_{11} > g_1$	-

^a + = upfield shift, - = downfield shift, 0 = no shift. ^b R = phenyl.

Ni(AA)₂ Complexes.—The alternation in the direction of shift for the *ortho*, *meta*, and *para* protons evident in the isotropic shift data listed in Table II for the various ligands coordinated to Ni(AA)₂ indicates that spin density is delocalized into the π -orbitals of these ligands. The π -contact interaction is the dominant factor in these compounds in contrast to the behavior of pyridine-type ligands⁸ where all protons are shifted downfield due to σ -spin density. That any σ -contribution must be relatively minor in the phosphine ligands is further emphasized by the fact that the *ortho* proton resonance is shifted further upfield than the *para*. A σ -contribution would tend to shift the *ortho* proton downfield a great deal more than the *para* proton. It is important to note that whereas the π -mechanism is expected to shift the *ortho* and *para* proton resonances upfield and the *meta* resonance downfield in phosphine ligands, the reverse is true for the phenyl protons of the isonitriles since the aromatic ring is one atom further removed. The experimental data agree with these pre-

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(30) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(31) S. I. Weissman, T. R. Tuttle, and E. deBoer, *J. Phys. Chem.*, **61**, 28 (1957).

(32) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

TABLE VI

Co(AA) ₂ complex	Position	$\left\langle \frac{3 \cos^2 \chi_i - 1}{r_i^3} \right\rangle$	IS ^a	PS ^b	CS ^c	Ratio	Co ratio, obsd.	Co ratio, cor.	Ni ratio, obsd.
(C ₆ H ₅) ₃ P	<i>p</i>	0.000433	87.0	38.0	49.0	<i>p/o</i>	0.521	0.793	0.763
	<i>m</i>	0.000249	-23.0	21.8	-44.8	<i>p/m</i>	-3.78	-1.094	-1.045
	<i>o</i>	0.00120	167.0	105.2	61.8	<i>m/o</i>	-0.138	-0.725	-0.738
<i>m</i> -CH ₃ C ₆ H ₄) ₂ P	<i>p</i>	0.000433	93.5	39.3	54.2	<i>p/o</i>	0.544	0.859	0.827
	<i>m</i>	0.000249	-26.0	22.5	-48.5	<i>p/m</i>	-3.60	-1.118	-1.068
	<i>m</i> -CH ₃	0.000757	16.5	68.7	-52.2	<i>m/o</i>	-0.151	-0.769	-0.774
<i>p</i> -CH ₃ C ₆ H ₄) ₂ P	<i>o</i>	0.00120	172.0	108.9	63.1				
	<i>p</i> -CH ₃	0.000583	-64.0	6.1	-70.1	CH ₃ / <i>o</i>	-0.342	-1.111	-1.265
	<i>m</i>	0.000249	-30.5	25.8	-56.3	CH ₃ / <i>m</i>	2.098	1.245	1.418
C ₆ H ₅ NC	<i>o</i>	0.00120	187.0	123.9	63.1	<i>m/o</i>	-0.163	-0.892	-0.892
	<i>p</i>	0.00348	31.0	123.2	-92.2	<i>p/o</i>	0.127	0.606	0.602
	<i>m</i>	0.00432	186.0	152.8	33.2	<i>p/m</i>	0.167	-2.777	-2.725
<i>p</i> -CH ₃ C ₆ H ₄ NC	<i>o</i>	0.01118	244.0	396.0	-152.0	<i>m/o</i>	0.762	-0.218	-0.221
	<i>p</i> -CH ₃	0.0054	208.0	101.2	106.8	CH ₃ / <i>o</i>	0.735	-0.656	-0.622
	<i>m</i>	0.00432	221.0	172.1	48.9	CH ₃ / <i>m</i>	0.941	2.184	2.097
<i>o</i>	0.01118	283.0	445.9	-162.9	<i>m/o</i>	0.781	-0.300	-0.297	

^a Isotropic shift for metal(AA)₂ concentration of 0.078 M. ^b Pseudo-contact shift. ^c Contact shift.

dictions. For the arylphosphine ligands the proton nearest the paramagnetic center (*ortho*) is attached to a carbon three chemical bonds removed from the central metal atom, while in the isonitriles the *ortho* carbon is four bonds removed. This may account somewhat for the lack of σ -spin density in these systems compared to pyridine since σ -spin density falls off rapidly as the number of bonds between the proton and the metal increases. That spin density can arrive on the ligands by π -bonding with Ni(II) is itself surprising. The d⁸ electron configuration of Ni(II) in a ligand field of O_h, D_{3h}, or C_{4v} symmetry places the unpaired electrons in orbitals of σ -symmetry only, and no spin density would be expected to arrive on the ligands from π -bonding with the nickel. The experimental fact that spin density does occur in the π -orbitals of ligands coordinated to Ni(AA)₂ may be taken as evidence that the actual complex formed has a symmetry low enough that the unpaired electrons on the nickel may enter orbitals capable of π -bonding to the ligands. It should be remembered that only an extremely small fraction of an unpaired electron is necessary on a ligand to produce large observable isotropic resonance shifts.

Co(AA)₂ Complexes.—The isotropic shift data for the phosphine ligands listed in Table III show the alternate upfield, downfield shift for the phenyl protons indicative of a π -contact interaction; however, comparing the shifts with the corresponding Ni(AA)₂ data, it is noted that there is an upfield bias, especially for the *ortho* proton resonances. The data for the isonitriles are especially telling in that all the observed shifts are upfield. The only mechanism capable of producing these results is a π -contact interaction in conjunction with a pseudo-contact interaction with $g_{11} < g_1$ (Table V). A similar pseudo-contact effect was observed by Happe and Ward⁸ for pyridine-type bases complexed with Co(AA)₂.

Those authors⁸ were able to separate the contact and pseudo-contact shifts in their systems on the basis that the resonance shift of the most distant proton in the 4-phenylpyridine complex was due entirely to a pseudo-contact interaction. They reasoned that since the spin density was delocalized in the σ -system of these ligands and was observed to fall off rapidly with the number of bonds, there would be no spin density at the *para* hydrogen of the 4-phenylpyridine complex. The

pseudo-contact shift at this position was then scaled by the calculated geometric factors to obtain the relative pseudo-contact shifts for the other positions. This procedure will not work in systems such as ours where the spin density is delocalized in π -orbitals. We followed a procedure similar to that used to estimate the pseudo-contact contribution to the resonance shifts in some tetrahedral triarylphosphine complexes of the Co(II) halides.^{16,33} The ground state of Ni(II) in an octahedral field is an orbitally nondegenerate ³A_{2g} state, and such a state would not be expected to exhibit significant *g*-value anisotropy even in fields of lower symmetry.³⁴ Co(II) on the other hand has a ⁴T_{1g} ground state in octahedral symmetry, and small distortions will lift this degeneracy and give rise to a considerable anisotropy in the *g*-values.³⁴ We therefore consider the observed isotropic shifts in the Ni(AA)₂ complexes to be caused by the contact interaction alone, while the shifts in the Co(AA)₂ systems arise from both contact and pseudo-contact interactions. The basic assumption in our method is that the spin density, which is primarily in the ligand π -orbital systems, will distribute itself in a manner which is independent of the metal to which it is coordinated; that is, that the ratios of the spin densities at the various carbon atoms (*ortho*, *meta*, *para*) will be the same for the Co(II) and Ni(II) systems, and hence the ratios of the isotropic shifts due to the *contact* interaction will be the same in these two cases. The ratios of the observed isotropic shifts of the various protons in the Co(AA)₂ and Ni(AA)₂ complexes are given in Table VI; the discrepancy between the observed cobalt and nickel ratios is readily apparent. We are able to obtain agreement in the contact shift ratios between cobalt and nickel by subtracting a pseudo-contact contribution from the observed Co(AA)₂ shifts. The pseudo-contact shifts are related to each other by the calculated geometric ratios. The observed Co(AA)₂ isotropic shifts (IS), the necessary pseudo-contact shift correction (PS), and the actual contact shifts (CS) for the cobalt complexes are given in Table VI. The ratios of the corrected cobalt contact shifts and the observed nickel contact shifts are shown in the last two columns of Table VI. The agreement is

(33) G. N. Lamar and W. D. Horrocks, Jr., *J. Chem. Phys.*, to be published.

(34) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, Cambridge, England, 1961, Chapter 12.

satisfactory. The success of this calculation depends upon the constancy in the distribution of spin density and not upon the absolute magnitude of the spin density reaching a given ligand. In these labile systems the observed shifts reflect a weighted average of proton resonances in complexed and uncomplexed ligands. The observed shifts depend upon unknown complex formation constants and so a direct comparison of observed shifts is meaningless in terms of absolute spin density values. Our treatment of the data indicates that the difference between the observed isotropic shift ratios in the cobalt and nickel systems is due to a pseudo-contact contribution to the cobalt shifts although a small nickel pseudo-contact shift is not impossible.

One further line of evidence points to the fact that the pseudo-contact shift is large and positive for cobalt. Although Q_{CH_3} is not a constant (*vide supra*), it should not vary for a given ligand, and identical results should be obtained for the cobalt and nickel systems. We calculate the value of Q_{CH_3} from our observed isotropic shifts for coordinated *p*-tolylisonitrile by assuming that the entire observed shift is due to a π -contact mechanism, and that the ratio of spin densities at the *para* and *meta* positions, p/m , remains unchanged upon substitution of a methyl group for a hydrogen. For the Co(AA)₂ adduct we find $Q_{\text{CH}_3} = -127.5$. This is clearly an impossible result. By using the corrected contact shift given in Table VI, the much more reasonable value of $Q_{\text{CH}_3} = 17.6$ is obtained. The observed Ni(AA)₂·*p*-tolylisonitrile complex isotropic shift leads to a Q_{CH_3} of 17.3, in excellent agreement with the corrected cobalt value. The fact that the same Co(AA)₂ pseudo-contact contribution which corrected the contact shift ratios also yields identical Q_{CH_3} values for the cobalt and nickel complexes gives us some confidence in the validity of our pseudo-contact correction.

The situation in the methyl-substituted phosphine complexes is less satisfactory. The same pseudo-contact correction which matches the contact shift ratios does not exactly correct the Q_{CH_3} values in the cobalt compounds to those in the nickel complexes. For instance, assuming the spin density ratio p/m is the same for the phenyl and *p*-tolyl compounds, it is found that $Q_{\text{CH}_3} = 30.4$ from the observed nickel shifts and Q_{CH_3} is improved from 12.5 for the uncorrected cobalt data to 25.7 with correction for the pseudo-contact interaction in the Co(AA)₂ complexes. Considering the uncertainty in the evaluation of the geometric factors and the assumptions involved in our Q_{CH_3} calculation, better agreement is perhaps not to be expected. The values of Q_{CH_3} that we obtain may be altered somewhat by postulating a small pseudo-contact shift in the Ni(AA)₂ complexes, as well as the large shift due to the same mechanism in the Co(AA)₂ adducts. Our results by no means rule out a small pseudo-contact shift in the nickel systems, but since the actual Q_{CH_3} values are unknown, speculation of this sort is probably unwarranted. It should be noted here that the agreement between the contact shift ratios of the Co(AA)₂ systems corrected for pseudo-contact interaction and the observed Ni(AA)₂ ratios is worst for the methyl resonances in the phosphines. This is not surprising when it is recalled that these triarylphosphine ligands subtend a large solid angle, and the protons of these ligands rotate in and out of regions where $(3 \cos^2 \chi - 1)$ is negative.

This causes the average value of certain of the geometric factors, particularly those of the methyl groups, to be extremely sensitive to the structural parameters employed. The Co-P-C angle and the Co-P distance are particularly important but are uncertain to a considerable degree.¹⁶ By altering these parameters a small amount, a good fit for the methyl resonances and the Q_{CH_3} values could no doubt be obtained with no sacrifice of the phenyl proton agreement. The protons in the arylisonitriles, which subtend a smaller solid angle, are always in a region where $(3 \cos^2 \chi - 1)$ is positive, and the geometric factors are much less sensitive to the structural parameters. A nonlinear model of the isonitrile ligands with a C-N-C angle of 173°³⁵ yields geometric factors varying only slightly from those for the linear model. The actual values of the structural parameters employed are given in Table IV. The metal-carbon distance in the isonitrile complexes was taken the same as the Fe-C distance in an isonitrile complex of Fe(II) whose structure is known.³⁵ The metal-phosphorus distance is less certain³⁶ and values of 2.25, 2.30, 2.35, and 2.38 Å. were tried.¹⁶ The 2.35 Å. distance gives the best fit, but reasonable agreement between contact shift ratios may be obtained using other values of this parameter.

The large isotropic proton resonance shifts allow us to observe nuclear spin-spin splitting in the simple, first-order, spectra of the coordinated phosphines and isonitriles. These observed coupling constants are listed in Table VII and the experimental points in Fig. 1 and 2 indicate the concentration ranges where this splitting is observable in these typical cases. Our results agree

TABLE VII
NUCLEAR SPIN-SPIN COUPLING CONSTANTS

Ligand	Acetyl-acetone	Coupling constants, c.p.s. ^a	
		J_{om}^b	J_{mp}^b
Triphenylphosphine	Ni	7.2 ± 0.5	7.2 ± 0.5
	Co	6.8 ± 0.5	7.2 ± 0.5
Tri- <i>p</i> -tolylphosphine	Ni	7.7 ± 0.5	...
	Co	7.4 ± 0.5	...
Tri- <i>m</i> -tolylphosphine	Ni	7.4 ± 0.5	7.1 ± 0.5
	Co	6.8 ± 0.5	6.8 ± 0.5
Phenylisonitrile	Ni	7.2 ± 0.5	6.8 ± 0.5
	Co	7.3 ± 0.5	7.0 ± 0.5
<i>p</i> -Tolylisonitrile	Ni	7.4 ± 0.5	...
	Co	6.9 ± 0.5	...

^a Average values. ^b J_{om} refers to the *ortho-meta* coupling constant, J_{mp} refers to the *meta-para* coupling constant.

well with the coupling constant values obtained for some diamagnetic mono- and disubstituted benzene derivatives,^{37,38} and with the spin-spin coupling found in certain paramagnetic Ni(II) aminotroponeimines.⁴

Perhaps the most interesting information obtainable from a study of this type is the distribution of spin density in the coordinated ligands. For systems where the isotropic shift arises only from a π -type contact interaction, the ratios of the observed proton resonance

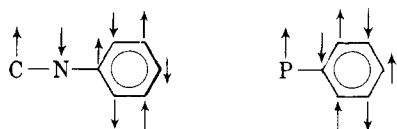
(35) Values for the metal-carbon, carbon-nitrogen, and nitrogen-carbon distances in the isonitrile complexes were taken from the data for hexamethylisocyanido ferrous chloride of H. M. Powell and G. W. R. Bartindale. *J. Chem. Soc.*, 799 (1945).

(36) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi. *ibid.*, 3625 (1963). The metal-phosphorus distance given in this reference appears to be in error. The phosphorus-carbon distance was calculated from the final atomic parameters given in this reference and found to be 1.90 Å.

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(38) D. M. Grant, R. E. Hirst, and H. S. Gutowsky. *J. Chem. Phys.*, **38**, 470 (1963).

shifts are the ratios of the spin densities at the various carbon atoms. For triphenylphosphine coordinated to $\text{Ni}(\text{AA})_2$ the spin-density ratios are *ortho:meta:para* = +1.000: -0.730: +0.763, while for phenylisonitrile coordinated to the same paramagnetic complex, the corresponding spin-density ratios are -1.000: +0.221: -0.603. A comparison of phenylisonitrile with a phosphorus-phenyl fragment of triphenylphosphine, with positive spin density placed on the coordinated atom in each case, shows immediately why the signs of the spin densities are opposite on the phenyl rings of these two compounds if there is an alternation in sign of the spin densities in a π -conjugated system.



Spin-density distributions on phenyl groups derived from p.m.r.^{1,2} and e.s.r.^{39,40,41} studies show extremely wide variations depending on the environment of the phenyl ring. In most, but not all, cases the spin density at the *para* position is larger than at the *meta*. It is interesting to note that for a phenyl ring bonded to a sulfur atom the *para* spin density is less than the *ortho* spin density.¹ Spin density arrives at the *meta* positions in the phosphines by spin correlation and so is opposite in sign to the *ortho* and *para* spin density; *meta* spin density varies in magnitude, but since it arises from a correlation effect, it is always considerably less than the sum of the *ortho* and *para* spin densities. The magnitude of the *meta* spin density ranges from about equal to less than a tenth of that of the *ortho*.

The coordinated isonitriles are interesting in that they are systems in which positive spin density is placed at the *meta* position of the phenyl ring. The magnitude of the correlated negative spin density at the *ortho* and *para* positions suggests the probability of a fairly sizable positive spin density on the phenyl carbon-

bonded to the N-C group. Comparison of the spin-density distribution in coordinated molecules and in the corresponding radical anions may lead to some interesting conclusions. Unfortunately, the e.s.r. spectrum of the anion radical of the triphenylphosphine is not well understood,⁴² and there are no reported studies of anion radicals of arylisonitriles.

In conclusion, then, it appears that both $\text{Co}(\text{AA})_2$ and $\text{Ni}(\text{AA})_2$ transfer spin density to the π -orbitals of coordinated isonitriles and phosphines. $\text{Co}(\text{AA})_2$ has an unpaired electron in a d-orbital capable of π -bonding with the ligand in complexes of C_{4v} or higher symmetry while $\text{Ni}(\text{AA})_2$ does not. The actual symmetry of the complexes may be quite low since π spin density is transferred from $\text{Ni}(\text{AA})_2$. The ability to delocalize spin density into a ligand π -system is a function of the ligand rather than the complex to which it is coordinated. Pyridine-type bases accept spin density into their σ -orbital systems when they are coordinated to the acetylacetonates⁸ and also in tetrahedral complexes with the nickel halides.¹⁵ Triphenylphosphine on the other hand receives spin density into its π -system in the analogous situations.^{15,16,33} As was the case with pyridine-type base adducts, a sizable upfield pseudocontact shift is evident for arylphosphine and isonitrile complexes of $\text{Co}(\text{AA})_2$ implying that $g_{11} < g_1$. It is interesting that the observed failure of pyridine-type ligands to accept spin density into their π -orbital systems is consistent with some infrared studies of π -bonding in transition metal carbonyl and nitrosyl compounds.⁴³ The nitrogen heterocyclic chelate molecule, *o*-phenanthroline, was found to be a poor recipient of π -electron density from a transition metal atom while arylphosphines and isonitriles were observed to be relatively good π -electron acceptors.

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(43) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).