# Nuclear Magnetic Resonance Contact Shifts in Bis(triphenylphosphine)nickel(II) Halides. Evidence for dπ–dπ Bonding between Nickel and Phosphorus

By E. A. LaLancette and D. R. Eaton

Proton n.m.r. spectra of dihalonickel(II) triphenylphosphine complexes (I) have been examined. All the compounds are paramagnetic and show contact interaction shifts. The shifts of the phenyl ring protons in the triphenylphosphine compounds are consistent with the view that the unpaired electrons of the nickel atom have been partially delocalized to the π-system of the ligand. This result provides evidence for dπ–dπ bonding between Ni and P in these complexes. The rate of ligand exchange of the complexes with triphenylphosphine is in the order Cl > Br > I.
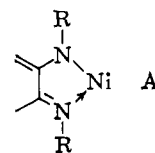
Since first invoked by Syrkin and Dyatkina[1] to explain bond strengths in trialkylphosphineplatinous complexes, the concept of dπ–dπ bonding has been repeatedly postulated in rationalizing various experimental observations: e.g., the stability of $(PF_3)_2$-$PtCl_2$,[2] $Ni(PF_3)_4$,[3] and trimethylgallium coordination compounds[4]; the cis-trans equilibria of trialkylphosphine-, trialkylarsine-, and trialkylstibineplatinous dihalide complexes[5]; and the magnetic moment of various tris-o-phenylenebis(dimethylarsine) transition metal complexes.[6]

This postulate has also been discussed theoretically by Jaffé[7] and by Craig, Maccoll, Nyholm, Orgel, and Sutton.[8] As of 1954, however, the latter authors[8] concluded: "there is at present a relative lack of direct physical evidence for such dπ–dπ bonding." More recently,[9] it has been observed that nuclear spin coupling constants between platinum and phosphorus suggest the occurrence of dπ–dπ bonding in $(R_3P)_2$-$PtX_2$ compounds.

Measurements of n.m.r. contact shifts in paramagnetic Ni(II) coordination compounds[10] have been recently employed to estimate the extent of dπ–pπ bonding between nickel and a conjugated ligand. In this paper, we report n.m.r. evidence for dπ–dπ bonding in the ground state of tetrahedral[11] bis(triphenylphosphine)nickel(II) halides.

The observation of n.m.r. contact shifts of protons attached to the ligands of paramagnetic chelates proves the presence of unpaired spin on the ligand. Insofar as the physical process by which the spin is delocalized corresponds to the physical process for double bond formation, the observation of contact shifts provides evidence for such bonding. This is the case for the bonding situation A, which occurs in the nickel(II) aminotroponeimineates previously studied.

Spin is transferred to the ligand π-system by partial donation of an electron from the nitrogen lone pair to a Ni dπ-orbital, and this corresponds exactly to partial double bond formation. The amount of spin delocaliza-



tion is, therefore, a direct measure of the amount of double bonding. In the bonding situation B the phosphorus atom has no lone pairs available for such donation, but spin can be transferred to the ligand π-system via the empty d-orbitals of the phosphorus atom.
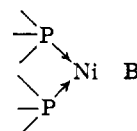


The amount of spin in the ligand π-system is, therefore, a measure of the extent of donation from the half-filled Ni dπ-orbitals, whereas the π-bonding is usually envisaged as involving a filled Ni d-orbital and an empty P d-orbital. The $d^8$-configuration of Ni in a tetrahedral ligand field has both filled and half-filled dπ-bonding orbitals. The two processes of π-spin transfer and of π-bonding are not, therefore, identical but are sufficiently closely related that the observation of the former may be taken as good qualitative evidence for the existence of the latter.[12]

## Experimental

**General.**—N.m.r. spectra were obtained with a Varian HR 60 instrument. Deuteriochloroform was used as solvent and tetramethylsilane as internal calibrant. Frequency calibration was effected by the usual audiofrequency modulation technique. The melting points were determined with a Mel-Temp apparatus and are uncorrected.

**Preparation of Phosphine Complexes.**—Bis(triphenylphosphine)dichloronickel(II) (Ia) was prepared following Cotton and

(1) (a) Ya. K. Syrkin and M. E. Dyatkina, J. Gen. Chem. USSR, **16**, 345 (1946); (b) Ya. K. Syrkin, Bull. acad. sci. URSS, Classe sci. chim., 61 (1948).

(2) (a) J. Chatt, Nature, **165**, 637 (1950); (b) J. Chatt and A. A. Williams, J. Chem. Soc., 3061 (1951).

(3) G. Wilkinson, J. Am. Chem. Soc., **73**, 5501 (1951).

(4) G. E. Coates, J. Chem. Soc., 2003 (1951).

(5) J. Chatt and R. G. Wilkins, ibid., 4300 (1952); 525 (1956).

(6) F. H. Burstall and R. S. Nyholm, ibid., 3570 (1952), and earlier papers.

(7) H. H. Jaffé, J. Phys. Chem., **58**, 185 (1954).

(8) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, J. Chem. Soc., 332 (1954).

(9) A. Pidcock, R. E. Richards, and L. M. Venanzi, Proc. Chem. Soc., 184 (1962).

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

(11) (a) L. M. Venanzi, J. Chem. Soc., 719 (1958); (b) Carton, Henn, Powell, and Venanzi, unpublished results, quoted in M. C. Browning, et al., ibid., 4816 (1961).

(12) This method can be used only with a tetrahedral, or at least an approximately tetrahedral, complex since only in this case has nickel half-filled dπ-orbitals. The authors believe, however, than when applicable the contact shift method is superior to that involving spin-spin coupling constants (ref. 9) or chemical shifts (ref. 13), in which cases it is much more difficult to determine the relative contribution of π- and σ-bonding effects.

(13) L. S. Meriwether and J. R. Leto, J. Am. Chem. Soc., **83**, 3192 (1961).

## Table I

N.M.R. Contact Shifts of Dihalobis(triphenylphosphine)nickel(II) Complexes[a,b]

| Compound | ortho | meta | para | para CH₃ |
|---|---|---|---|---|
| Ia | +383 (+0.00285) | −482 (−0.00321) | +670 (+0.00446) | ... |
| Ib | +471 (+0.00341) | −650 (−0.00433) | +776 (+0.00517) | ... |
| Ic | +495 (+0.00330) | −652 (−0.00434) | +772 (+0.00514) | ... |
| Id | +560 | −669 | ... | −885 (+25.7)[c] |

[a] In c.p.s. at 60 Mc./sec.  [b] Spin densities given in parentheses.  [c] $Q_{CH_3}$ in gauss.

co-workers' modification[14] of Venanzi's procedure[11a]; decomposition from 244°; reported[11a] decomposition at 247–250°.

Bis(triphenylphosphine)dibromonickel(II) (Ib), prepared according to Venanzi,[11a] had m.p. 217–220° dec.; reported[11a] 222–225° dec.

The related diiodo complex Ic was prepared via a modification of Venanzi's procedure[11a] involving the use of commercially available anhydrous nickel iodide (Amend Drug and Chemical Co., Inc.) in lieu of generating it in situ. The brown crystalline complex Ib thus obtained had m.p. 214–216° dec.; reported[11a] m.p. 218–220° dec.

Bis(tri-p-tolylphosphine)dibromonickel(II) (Id) prepared from tri-p-tolylphosphine[15] had m.p. 244–246° dec.; reported[16] m.p. 236–238° dec.

## Results

The n.m.r. spectra of the following compounds and of the corresponding ligands have been examined.
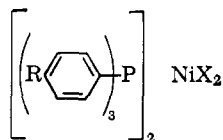


Ia, R = H; X = Cl
Ib, R = H; X = Br
Ic, R = H; X = I
Id, R = CH₃; X = Br

Contact shifts are defined as the differences in the resonance frequencies of corresponding protons of the paramagnetic chelate and the diamagnetic ligand. They are related to the hyperfine coupling constants by the equations

$$\left(\frac{\Delta f}{f}\right)_i = \left(\frac{\Delta H}{H}\right)_i = -a_i\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{6SkT}$$

where $\Delta f$ is the contact shift, $f$ is the frequency of the n.m.r. experiment, $\Delta H$ and $H$ are the corresponding magnetic fields, $a_i$ is the hyperfine coupling constant of the $i$th proton, and the other symbols have their usual significance. Spin densities $(\rho_{C_i})$ in the p$\pi$-orbitals of aromatic fragments may be obtained from the hyperfine coupling constants from the relationship

$$a_i = Q\rho_{C_i}$$

where $Q$ is a constant (−22.5 gauss).

(14) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, J. Am. Chem. Soc., **83**, 344 (1961).
(15) F. G. Mann and E. J. Chaplin, J. Chem. Soc., 527 (1937).
(16) M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton, and L. M. Venanzi, ibid., 4816 (1961).

The contact shifts are summarized in Table I. Figure 1 shows the n.m.r. spectra of compounds I. Although the lines are broad compared with those usually observed for diamagnetic compounds, resolution is complete. The widths diminish with increasing distance from the nickel atom. Assignment of the resonances is based on their relative intensities and on the results of methyl substitution. The contact shifts of compounds I are temperature dependent, and the relationship $1/T$ (Curie law) is approximately followed.

## Discussion

All of these compounds are paramagnetic in solution. In a paramagnetic complex the d-orbitals of the Ni contain unpaired electrons, and $\pi$-bonding with the ligand, when possible, can give rise to spin densities in the carbon p$\pi$-orbitals of the aromatic groups. In an odd-alternant system, spin correlation with the lower filled $\pi$-orbitals results in alternating positive and negative spin densities, and both high- and low-field shifts of the aromatic protons are observed. Thus, spin in a phosphorus d-orbital may be further delocalized by structures B and C, leading to high-field shifts for the ortho and para protons and to a low-field shift for the meta protons. These shifts do not
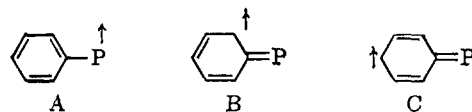


attenuate rapidly with distance from the metal and are, in fact, often largest at the para or $\gamma$-position.[10] If, on the other hand, nickel–ligand spin transfer does not occur in the $\pi$-system, spin can only be delocalized through the $\sigma$-system. This is the case, for example, in a regular octahedral nickel chelate, e.g., Ni-(phenanthroline)₃⁺²,[17] since the unpaired electrons are in the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals which do not have the correct symmetry for $\pi$-bonding with the ligand. In such cases it has been found[17] that the proton shifts are uniformly to low field and fall off rapidly with increasing distance from the metal atom.

From Table I it is apparent that the results are compatible with spin delocalization in the aromatic $\pi$-system through metal–ligand $\pi$-bonding. It will be noted that the CH₃ group of compound Id is shifted in the opposite direction from that of the replaced proton in compound Ib, as required by the hyperconjugative mechanism. A value of $Q_{CH_3} = +25.7$ gauss is obtained from the relative shifts (assuming $Q_{CH} = -22.5$) and the agreement between this value
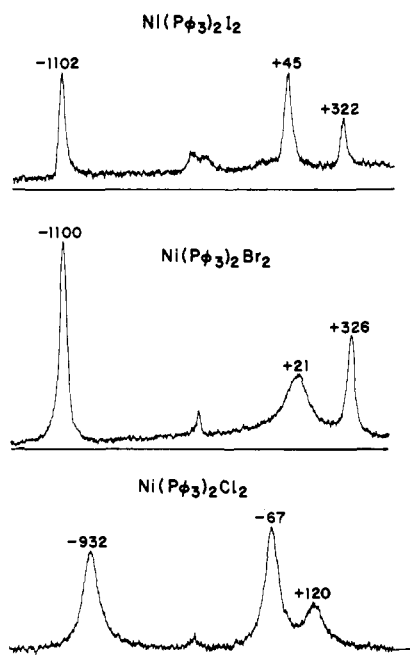
(17) J. C. Rowell, private communication.

Ni(Pϕ₃)₂I₂

−1102    +45    +322

Ni(Pϕ₃)₂Br₂

−1100    +21    +326

Ni(Pϕ₃)₂Cl₂

−932    −67    +120

Fig. 1.—N.m.r. spectra of bis(triphenylphosphine)nickel(II) halides.

Ni(Pϕ₃)₂I₂ + Pϕ₃

−1102    +45    +322

Ni(Pϕ₃)₂Br₂ + Pϕ₃

Ni(Pϕ₃)₂Cl₂ + Pϕ₃

Fig. 2.—N.m.r. spectra of bis(triphenylphosphine)nickel(II) halides in the presence of excess triphenylphosphine.

and the e.p.r. value[18] of $+27$ gauss substantiates the conclusion that the spin is predominantly in the $\pi$-system. The spin distribution in the phenyl ring[19] is also very similar to that previously observed for cases where the spin is known to be in the $\pi$-system (see Table II). These compounds differ from the aminotroponeimineates[10] and salicylaldimines[20] previ-

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Table II

Relative $\pi$-Spin Densities on Phenyl Ring[a]

| | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| ortho | +0.572 | +0.607 | +0.641 | +0.701 | +0.608 | +0.824 |
| meta | −0.719 | −0.838 | −0.845 | −0.744 | −0.752 | −0.382 |
| para | +1.000 | +1.000 | +1.000 | +1.000 | +1.000 | +1.000 |

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[a] A, compound Ia; B, compound Ib; C, compound Ic; D, N,N′-diphenylaminotroponeimineatenickel(II); E, phenylazo group of γ-(phenylazo)-N,N′-diphenylaminotroponeimineatenickel(II); F, phenylazo group of bis[N-(m-tolyl)-5-phenylazosalicylaldimine]nickel(II).

ously discussed in that the s- and p-electrons of the coordinating nitrogen or phosphorus are already completely utilized in $\sigma$-bonding, and there is no lone pair to donate electrons to the Ni by $p\pi$–$d\pi$ bonding. The observed spin in the $\pi$-system of the phenylphosphines must, therefore, arise from donation from the Ni to the phosphorus by $d\pi$–$d\pi$ overlap. If this is the case, it might be anticipated that there would be some compensating $\pi$-donation from the halogen to the Ni.

(18) A. D. McLachlan, Mol. Phys., 1, 233 (1958).

(19) The possibility of conjugation between phosphorus and a phenyl group has been demonstrated by the recent observation of hyperfine splittings for both P and the phenyl protons in the [(C₆H₅)₃P]⁻ radical. However, our results in which the phenyl rings are equivalent are to be contrasted with the results of the e.s.r. study of the triphenylphosphine anior where the odd electron is localized on only one phenyl ring: M. W. Hanna, J. Chem. Phys., 37, 685 (1962).

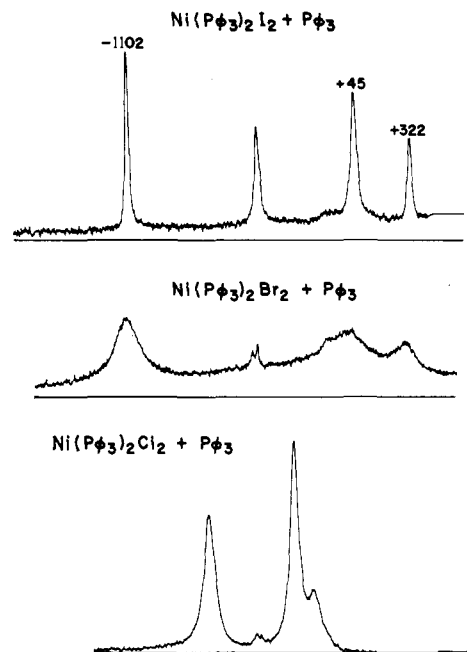(20) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, J. Am. Chem. Soc., 84, 3968 (1962).

Numerically the observed shifts correspond to the delocalization of approximately 1/100th of an unpaired electron to the phenyl ring. Transfer of spin density from the phosphorus atom to the phenyl depends on $p\pi$–$d\pi$ overlap which is probably rather poor so that there may be considerably more spin on the phosphorus atom. The figure of 1/100th, therefore, represents a lower limit for the spin transfer by $d\pi$–$d\pi$ interaction, and the true value could well be greater by as much as an order of magnitude which would make it comparable to the $p\pi$–$d\pi$ transfer in nickel(II) aminotroponeimineates.

## Ligand Exchange

Finally we wish to report some observations on the relative lability of these phosphine complexes. Figure 2 illustrates the effect of adding excess triphenylphosphine to solutions of $Ni[(C_6H_5)_3P]_2X_2$ [where $X$ = Cl, Br, or I] in deuteriochloroform. Comparison with Fig. 1 shows that the rate of ligand exchange is different in the three cases. In the case of the iodide, the exchange is slow by the n.m.r. criterion so that the effect is to introduce a new peak for uncomplexed triphenylphosphine at a "diamagnetic" frequency. In the case of the chloride, the exchange is fast so that no new peaks appear but the resonances assume positions intermediate between those of the diamagnetic ligands and the fully paramagnetic complexes. The case of the bromide is intermediate with considerable broadening and some shift of the lines. Since the shifts between the diamagnetic and paramagnetic line positions are of the order of 500 c.p.s., in this latter case the lifetime of the complex is of the order $10^{-3}$ sec. The intermediate exchange situation for the iodide can be reached by heating to $+60°$ and that for the chloride by cooling to $-20°$.

It is possible that the order of lability of these complexes, i.e., Cl > Br > I, is also determined by the $d\pi$–$p\pi$ bonding. As was pointed out above, the

donation of electrons from the nickel to the phosphine will probably be partly compensated by π-donation from the halogen to the nickel. Such donation may be expected to decrease in the order I > Br > Cl leading to the prediction of the strongest phosphine π-bond in the iodide. This is in accord with the order of the labilities. It may be noted that consideration of the σ-bonding would lead to the opposite order since the phosphine donates to the nickel and the electronegativity decreases in the order Cl > Br > I. If these reasonings are correct, it would appear that the π-

bonding is more important than the σ-bonding in determining the relative stability of these complexes. A very similar conclusion was reached by Allen and Cook,[21] who found that the relative stability of the complexes $(Ar_3P)_2Pt(ac)$ (where ac = acetylene) was increased by electron-withdrawing substituents on the acetylene and also by electron-donating substituents on the phosphine. This is in accord with predictions based on considerations of the π-bonding but contrary to those based on the σ-bonding.

(21) A. D. Allen and C. D. Cook, Can. J. Chem., 41, 1235 (1963).

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# Molecular Asymmetry in the Coordination of Olefins with Transition Metals. trans-Dichloro(olefin)(amine)platinum(II) Complexes[1]

BY GASTONE PAIARO AND ACHILLE PANUNZI

By crystallization of solutions of trans-dichloro(olefin)[(R or S)-α-phenethylamine]platinum(II), in which the olefin was propylene, styrene, or trans-2-butene, only one diastereoisomer was obtained. In the case of trans-2-butene, it was found that the type of diastereoisomer obtained depended upon the nature of the solvent. By removal of the amine ligand from the complex with trans-2-butene it was possible to obtain the corresponding enantiomeric anion as the $Pt(NH_3)_4^{+2}$ salt.

## Introduction

An olefinic compound without substituent asymmetric groups, and which does not have symmetry planes perpendicular to the plane of the double bond, possesses two enantiomorphic (nonsuperimposable) faces.[2]

When, by any reaction, the double bond of an olefin is bound in a π-complex to whatever center, each of the unsaturated carbon atoms, if linked to two different substituent groups, $\begin{smallmatrix}R\\R'\end{smallmatrix}>C=$, becomes asymmetric. Accordingly, if an olefinic compound with nonsuperimposable faces is π-bonded to a coordinative center (M), a pair of enantiomorphs is obtained.

If the center is asymmetric or is connected to an asymmetric environment, a diastereoisomeric pair is obtained.
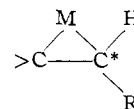
We can define the carbon atoms of the olefin bound to the coordination center as (R) or (S) according to the nomenclature proposed by Cahn, Ingold, and Prelog,[3] applied to the three-membered cyclic core
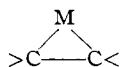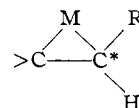


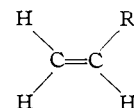The "sequence rule" states the order
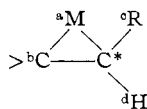


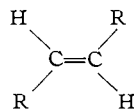and therefore in



the asymmetric atom C* is (R), while in



the atom C* is (S).[4]

Clearly, in the case of an olefinic compound of the type



(for example, styrene, propylene) (Fig. 1a and a′), only one asymmetric carbon is formed by coordination; in the case of an olefin of the type



(for example, trans-2-butene) (Fig. 1b and b′), two asymmetric carbon atoms having the same configura-

(1) For a preceding brief communication on this subject see G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, Makromol. Chem., 71, 184 (1964).

(2) (a) G. Natta, M. Peraldo, M. Farina, and G. Bressan, ibid., 55, 139 (1962); (b) M. Farina and G. Bressan, ibid., 61, 79 (1963); (c) C. L. Arcus, J. Chem. Soc., 2801 (1955).

(3) R. S. Cahn, C. K. Ingold, and V. Prelog, Experientia, 12, 93 (1956).

(4) In a preceding work, ref. 1, the atoms C* were designated as r and s.