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Bonding in Ni(0) Complexes. II. The ^{31}P Nuclear Magnetic Resonance Spectra of Some Nickel–Carbonyl–Phosphine Complexes

BY L. S. MERIWETHER AND J. R. LETO

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High resolution ^{31}P nuclear magnetic resonance spectra of a large group of nickel–carbonyl–phosphine complexes have been obtained. The algebraic difference, $\delta^{P-M} - \delta^{P}$, between the chemical shift for free phosphine (δ^{P}) and the complexed phosphine (δ^{P-M}) has been used in analyzing the effect on the nickel–phosphine bonding caused (1) by changes in the substitution on the phosphine; (2) by the number of phosphine ligands; and (3) by chelation. Qualitative correlations between the position of the ^{31}P resonance and the Ni–P bond order are discussed.

Introduction

The utility of nuclear magnetic resonance (n.m.r.) spectra of the phosphorus isotope ^{31}P in chemical studies of both organic and inorganic compounds containing phosphorus has been well-established.[1] However, to date, no ^{31}P n.m.r studies on metal complexes of phosphorus-containing ligands have been reported. Having a large number of nickel–carbonyl–phosphine complexes available, we decided to examine the effect of complex formation on the ^{31}P chemical shift of the phosphines.

In the first paper of this series,[2] we reported work on the phosphine exchange and infrared spectra of nickel–carbonyl–phosphines of the type $Ni(CO)_x(PR_3)_y$, which led to the conclusion that nickel–phosphine bonds are primarily σ in character with strong contributions from π-bonding occurring only in complexes of phosphorus halides and phosphites. In an attempt to obtain an independent method of determining bond type in these complexes, the phosphorus n.m.r. spectra of about thirty-five complexes and the corresponding free phosphines have been determined and are reported in this paper. Although much new information has been obtained, it is possible to make only qualitative correlations between the phosphorus chemical shifts in these complexes and the metal–phosphorus bond order.

Experimental

All n.m.r. spectra were determined on a Varian Model 4300B high resolution n.m.r. spectrometer at a frequency of 16.2 Mc. and a field strength of about 9340 gauss. The ^{31}P chemical shifts are defined by the equation $\delta = 10^6 \times (H_C - H_R)/H_R$, where H_C and H_R are the magnetic fields required for resonance in the sample and the reference (85% orthophosphoric acid), respectively, and were obtained at 25 ± 2° to a precision of ± 1 p.p.m. The samples were analyzed in 5 ml. test-tubes filled with about 2 ml. of the pure liquid compounds or of concentrated solutions of the solid compounds in inert solvents. Changes in concentration and the presence of various inert solvents had no detectable effect on the position of the ^{31}P resonance, so corrections for changes in state[3] were unnecessary.

All of the free phosphines and complexes were available in this Laboratory. The phosphine complexes were prepared from $Ni(CO)_4$ and the free phosphine either by published methods or by similar methods which will be published elsewhere. It was impossible to separate the following mixtures: $Ni(CO)_3(PCl_3) + Ni(CO)_2(PCl_3)_2 + Ni(CO)(PCl_3)_3$; $Ni(CO)_3[P(C_2H_5)_3] + Ni(CO)_2[P(C_2H_5)_3]_2$; $[Ni(CO)_3]_2[P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2] + Ni(CO)_2[P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2]$ and $Ni(CO)_2[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2] + Ni_2(CO)_4[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2]_2$, although the pure monomeric dicarbonyl–diphosphine complexes of all but PCl_3 were obtained in other experiments. The assignment of n.m.r. peaks in these mixtures was made by comparing the relative peak areas with the relative concentrations of each component as determined by infrared analysis.[2]

Attempts to obtain n.m.r. data on the following group of phosphine complexes were unsuccessful because of the lack of a suitable solvent: $Ni(PBr_3)_4$, $Ni[P(C_6H_5)_3]_2Cl_2$, $Ni[P(CH_2CH_2CN)_3]_2Br_2$, $Ni[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2]Cl_2$, $Fe(CO)_4P(C_6H_5)_3$, $Co(CO)(NO)[P(C_6H_5)_3]_2$,[4] $Co(CO)(NO)[P(OC_6H_5)_3]_2$,[4] $Hg[P(CH_2CH_2CN)_3]_2Cl_2$, $Pt[P(C_6H_5)_3]_3$ and $Pt[P(C_6H_5)_3]_4$.

Results and Discussion

The ^{31}P chemical shifts for the free phosphines and phosphine complexes are presented in Tables I–IV. Complex formation always causes a shift in the position of the phosphorus resonance, δ^{P}, to a new value, which we shall call δ^{P-M}. In most cases δ^{P-M} is more negative than δ^{P}, agreeing with the intuitive assumption that the formation of a donor bond from phosphorus to nickel results in a decrease of electron density on the phosphorus atom and thus a decrease in the shielding and in the δ-value. It has been found useful to consider the value of $\delta^{P-M} - \delta^{P}$ for each complex, *i.e.*, the magnitude and sign of the resonance shift on complex formation.

Before the data herein reported can be analyzed, a general consideration of the factors[3,5] influencing the absolute value of the ^{31}P resonance in phosphine complexes is advisable. The relative importance of these various factors then can be examined in the light of the data available. Finally, it may be possible to use these results to obtain a better understanding of the structural and bonding features of phosphines and their complexes. The following factors have been considered: (1) A temperature independent paramagnetic contribution in the diamagnetic complexes, (2) the formation of a donor σ-bond from phosphorus to nickel, (3) the contribution from $d\pi$-$d\pi$ back-donation from nickel to phosphorus, (4) aromatic ring current effects in the phenylphosphines, (5) inductive effects of the phosphine substituents, (6) bond rehybridization effects due to changes in phosphorus bond angles on complex formation, (7) electronegativities of the atoms joined to the

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[1] For a review of n.m.r. studies of phosphorus compounds see W. G. Schneider, J. A. Pople and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 346–356, and references quoted therein.

[2] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

[3] N. Muller, P. C. Lauterbur and J. Goldenson, *ibid.*, **78**, 3557 (1956).

[4] These compounds were kindly supplied by Prof. L. Malatesta.

[5] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

TABLE I

^{31}P CHEMICAL SHIFTS OF NICKEL–DICARBONYL–DIPHOSPHINE COMPLEXES (IN P.P.M. RELATIVE TO 85% ORTHOPHOSPHORIC ACID)

Phosphine	Free phosphine		$Ni(CO)_2(PR_3)_2$		
	State	δ^P	State	δ^{P-M}	$\delta^{P-M} - \delta^P$
PCl_3	Liquid	−215	Benzene soln.	−181	+34
$P(OC_2H_5)_3$	Liquid	−140	Liquid	−160	−20
$P(OC_6H_5)_3$	Liquid	−125	Benzene soln.	−146	−21
$P(C_6H_5)_3$	Benzene soln.	+ 6.6	Benzene soln.	−32.6	−39.2
$P(C_6H_5)_2(C_2H_5)$	Liquid	+12.0	Benzene soln.	−28.7	−40.7
$P(C_6H_5)(C_2H_5)_2$	Liquid	+16.2	Liquid	−23.2	−39.4
$P(C_2H_5)_3$	Liquid	+19.1	Liquid	−20.7	−39.8
$P(CH_2CH_2CN)_3$	Acetonitrile soln.	+23.4	Acetonitrile soln.	−20.4	−43.8
$P(CH_2CH_2CN)_2(n\text{-}C_8H_{17})$	Liquid	+25.3	Acetonitrile soln.	−18.9	−44.2
$P(n\text{-}C_8H_{17})_3$	Liquid	+31.8	Liquid	−13.3	−45.1
$P(n\text{-}C_4H_9)_3$	Liquid	+32.6	Liquid	−12.1	−44.7
$P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2$	Liquid	+19.3	Liquid	−21.9 −48.6	−41.2 −67.9
$P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2$	Acetonitrile soln.	+21.4	Acetonitrile soln.	−20.8 −44.9	−42.2 −66.3
$o\text{-}C_6H_4[P(C_2H_5)_2]_2$		(+16.2)[a]	Benzene soln.	−36.6	(−52.8)[a]

[a] Calculated on assumption that δ^P for P,P,P′,P′-tetraethyl-*o*-phenylenediphosphine = δ^P for phenyldiethylphosphine.

phosphorus and (8) steric effects, including chelation.

Attempts have been made to estimate the effect of a "temperature independent paramagnetism" on δ^P and δ^{P-M} of the various species in solution. This term arises from the excitation of an electron from the ground-state orbital in a diamagnetic molecule (such as the phosphines and Ni(0) complexes under discussion) to an excited-state orbital, caused by a Zeeman-like interaction with the magnetic field.[1] The total diamagnetism is thus lowered and the resultant change (to more positive values) in χ_M for the species causes the resonance line to appear at lower fields than it would in the absence of such interaction. Since the excitation energy ΔE between the two orbitals appears in the denominator of the expression relating δ with χ_M, the effect is largest for very low-lying excited states.[6] For phosphorus, however, no such allowed transitions are predicted from the energy-level diagram or observed in the visible or ultraviolet absorption spectra of the free or complexed phosphines reported here. Thus we cannot fix the magnitude or even the existence of possible paramagnetic contributions to our chemical shifts.

The most extensive series of complexes available for examining the effects of σ- and π-bonding between nickel and phosphorus was the nickel–dicarbonyl–diphosphines (Table I). Eleven different complexes, $Ni(CO)_2(PL_3)_2$, were investigated. When L was an alkyl (including cyanoethyl) or aryl substituent, the values of $\delta^{P-M} - \delta^P$ were remarkably constant, falling in the range +39 to +45 p.p.m. In this series δ^P ranged from +7 to +33 p.p.m. and δ^{P-M} from −33 to −12 p.p.m. Rehybridization effects[6,7] should be relatively small here, since any changes in the C–P–C bond angles on complex formation probably are fairly constant through the series. Steric effects due to different phosphine substituents also appear to be unimportant, probably because of the large size of the nickel atom. The major effect on the chemical shift appears to be from the strong donor σ bond from P to Ni, resulting in a decrease in shielding of the phosphorus nucleus corresponding to a ^{31}P resonance shift of −42 ± 3 p.p.m. Any contribution from dπ − dπ back-donation from Ni to P must be either very small or constant through the series.

The effect of the diamagnetic anisotropy, resulting from the circulation of current in aromatic rings, on the ^{31}P chemical shifts of compounds with phosphorus directly attached to the aromatic ring has been examined briefly by Finegold.[7] However, the few compounds which he examined were anomalous, in that they did not show the expected resonance shifts to lower fields.[8] He assumed that for these compounds the inductive and bond rehybridizing effects were much larger than that due to the ring current.

Examination of δ^P and δ^{P-M} of some of the phenyl-, ethyl- and β-cyanoethylphosphines listed in Table I now allows reasonable assumptions to be made about the relative importance of the ring current and inductive effects in the phenylphosphines and their complexes. In the series of phenylethylphosphines (Table I), it appears that both the inductive and ring current effects of the phenyl group on the ^{31}P chemical shift are very small, since an average shift to lower field of only about 4 p.p.m. occurs on the substitution of an ethyl by a phenyl group. In phosphine compounds, the inductive effect of a β-cyanoethyl group has been found to be about the same as that of a phenyl group.[9] The replacement of an alkyl group by a β-cyanoethyl group in a phosphine results in a decrease in the ^{31}P chemical shift of 1.5–2.5 p.p.m. It follows that the ring current in the phenyl group causes a similar negative field shift of only about 1.5–2.5 p.p.m. The δ^{P-M} values of the complexes of the phenyl- and β-cyanoethylphosphines, where

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(6) R. Freeman, G. R. Murray and R. E. Richards, *Proc. Roy. Soc.* (*London*), **242A**, 455 (1957).

(7) H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958).

(8) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(9) W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960); W. A. Henderson, Jr., and S. A. Buckler, *ibid.*, **82**, 5794 (1960).

TABLE II

CHELATED NICKEL-CARBONYL-PHOSPHINE COMPLEXES

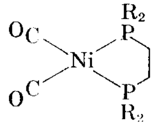
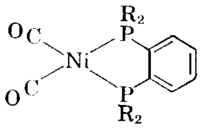
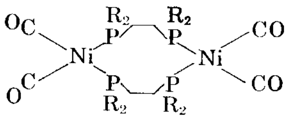
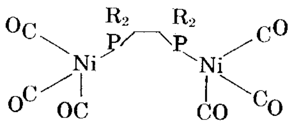
	 IA	 IB	 II	 III
IR, ν_{CO}(cm.$^{-1}$)				
R = C_2H_5	1930, 1992	1925, 1986[11]	1915, 1978[11]	2000, 2060
CH_2CH_2CN	1950, 2000	....	....	....
N.m.r., δ^{P-M} (p.p.m.)				
R = C_2H_5	−48.6	36.6	(*ca.* −21.9)	−21.9
CH_2CH_2CN	−44.9	....	−20.8	....
N.m.r., $\delta^{P-M} - \delta^{8}$ (p.p.m.)				
R = C_2H_5	−67.9	(−52.6)	(*ca.* −41.2)	−41.2
CH_2CH_2CN	−66.3	....	−42.2	....

TABLE III

^{31}P CHEMICAL SHIFTS OF VARIOUS NICKEL(0)-PHOSPHINE COMPLEXES

	Free phosphine		$Ni(CO)_3(PL_3)$		$\delta^{P-M} -$	$Ni(CO)_2(PL_3)_2$		$\delta^{P-M} -$	$Ni(CO)(PL_3)_3$		$\delta^{P-M} -$	$Ni(PL_3)_4$		$\delta^{P-M} -$
Phosphine	State	δ^P	State	δ^{P-M}	δ^P	State	δ^{P-M}	δ^P	State	δ^{P-M}	δ^P	State	δ^{P-M}	δ^P
PCl_3	Liquid	−215	Benzene soln.	−185	+30	Benzene soln.	−181	+34	Benzene soln.	−177	+38	Benzene soln.	−170	+45
$PCl_2(C_6H_5)$	Liquid	−164										Benzene soln.	−152	+12
PF_3	Liquid (−70°)	− 97[a]										Liquid	−127[b]	−30
$P(OC_2H_5)_3$	Liquid	−140	Liquid	−157	−17	Liquid	−160	−20	Liquid	−163	−23	Cyclohexane soln.	−160	−20
$P(C_6H_5)_3$	Benzene soln.	+ 6.6	Benzene soln.	− 42.9	−49.5	Benzene soln.	− 32.6	−39.2						
$P(C_2H_5)_3$	Liquid	+ 19.1	Liquid	− 47.0	−66.1	Liquid	− 20.7	−39.8						

[a] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **21**, 279 (1953). [b] Center of quartet with P–F coupling of 84 p.p.m.

TABLE IV

^{31}P CHEMICAL SHIFTS FOR MISCELLANEOUS METAL-PHOSPHINE COMPLEXES

Complex	State	δ^{P-M}	$\delta^{P-M} - \delta^P$
$Ni[P(n\text{-}C_4H_9)_3]_2(C{\equiv}C{-}C_6H_5)_2$	Benzene soln.	−15.1	−47.7
$Ni[P(n\text{-}C_4H_9)_3]_2(CO)_2$	Liquid	−12.1	−44.7
$Ni[P(n\text{-}C_4H_9)_3]_2Cl_2$	Benzene soln.	+ 1.5	−31.1
$\{Cu[P(n\text{-}C_4H_9)_3]I\}_4$	Benzene soln.	+26	− 6.6
$Ni[P(C_6H_5)_3]_2(CNS)_2$	Tetrahydrofuran soln.	0	− 6.6
$Ni[P(C_6H_5)_3]_2(CO)_2$	Benzene soln.	−32.6	−39.2
$Fe[P(C_6H_5)_3]_2(CO)_3$	Benzene soln.	+ 9.5	+ 2.9
$Fe[P(C_6H_5)_3](NO)_2$[a]	Benzene soln.	−50.8	−57.4
trans-$Mo[P(C_2H_5)_3]_2(CO)_4$	Chloroform soln.	−29.0	−48.1
cis-$Mo[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2](CO)_4$	Acetone soln.	−53.0	−74.4

[a] This complex was kindly supplied by Prof. L. Malatesta.

the phosphorus is essentially tetrahedral, are similarly influenced by the inductive and ring current effects, showing that these effects operate independently of the hybridization of the phosphorus, as expected. Thus the anomalous effects noted by Finegold must be due primarily to bond rehybridization, which we have also found to be very important in phosphorus compounds (see below).

When L was aryloxy, alkoxy or chloro, both δ^{P} and δ^{P-M} had large negative values and $\delta^{P-M}-\delta^{P}$ for the nickel–dicarbonyl–diphosphine complexes was -21, -20 and $+34$ p.p.m., respectively (Table I). The more negative δ-values of these phosphorus compounds are consistent with the greater electronegativity of oxygen and chlorine compared to carbon and with the low basicity of these phosphines. The more positive values of $\delta^{P-M}-\delta^{P}$ suggest a lessened net electron drift from P to Ni and, in the case of the PCl_3 complex, even a complete reversal of this "normal" drift resulting in an increase in the phosphorus shielding. These results can be accounted for in several ways—a weaker σ-bond from P to Ni, an increase in the back-donation from Ni to P, a strong drift of electrons from P to L and variable changes in the L–P–L bond angles in forming the complex, resulting in large rehybridization effects.

The structures of only a few simple trivalent phosphorus compounds (PL_3) have been determined. In most of these the L–P–L bond angle is about 100°.[10] Hence these P–L bonds appear to have much less s-character than those in the metal–phosphine complexes, where the quadrivalent phosphorus atom is assumed to form approximately tetrahedral sp^3 bonds ($\angle$L–P–L $\sim$ 109°). The unshared pair of electrons in the spherically symmetrical 3s orbital of the free phosphine strongly shields the phosphorus nucleus. If we assume that in the trialkyl- and triaryl-phosphine complexes the phosphorus bond angles are perfectly tetrahedral, then the decrease in shielding resulting from the complete hybridization of the 3s with the three 3p orbitals can be related to a ^{31}P shift to lower fields of about 40 p.p.m. In the case of the phosphite and phosphorus halide complexes the L–P–L angles may not quite reach 109°, resulting in a limited and unequal sharing of the 3s orbital among the four phosphorus substituents and consequently a smaller down-field shift in the ^{31}P resonance. In the final analysis, however, it would seem that, for the simple monodentate phosphine complexes, the values of $\delta^{P-M} - \delta^{P}$ are most critically determined by the electronegativities of the particular atoms joined to the phosphorus and that any bond hybridization differences are a direct result of these electronegativity effects.

The effect of chelation on the chemical shifts of complexed phosphines was also investigated (Tables I and II). The diphosphine ligands $R_2PCH_2CH_2PR_2$ had δ^{P}-values practically identical with the corresponding $R_2PC_2H_5$ compounds, further supporting the observation[7] that substitution two or more carbon atoms away from the phosphorus has little or no effect on the chemical shift. Since a sample of free P,P,P′,P′-tetraethyl-*o*-phenylenediphosphine was not available, δ^{P} for this compound was assumed to be the same as that for $P(C_6H_5)(C_2H_5)_2$. Three phosphine complexes were available as pure, monomeric compounds, $Ni(CO)_2[P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2]$, $Ni(CO)_2[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2]$ and $Ni(CO)_2\{o\text{-}C_6H_4[P(C_2H_5)_2]_2\}$,[11] which are assumed to have 5-membered ring chelate[12] structures (IA and IB, Table IV). In some of the attempts to prepare the nickel carbonyl complex of $P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2$, an inseparable mixture was obtained, whose infrared spectrum indicated the presence of the above dicarbonyl (IA, R = C_2H_5) along with a tricarbonyl complex. Slight variations in reaction conditions in the synthesis of the $P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2$ complex also resulted in a mixture of the above dicarbonyl (IA, R = CH_2CH_2CN) with a second dicarbonyl complex.

The tentative identification of all of these complexes has been made by a combination of n.m.r. and infrared analysis, as follows. From the similarity of their infrared carbonyl frequencies and δ^{P-M} values (Table II) the three pure monomeric complexes are assigned structures IA (R = C_2H_5 and CH_2CH_2CN) and IB (R = C_2H_5). The values of $\delta^{P-M} - \delta^{P}$ for these complexes (-67.9, -66.3 and -52.6 p.p.m., respectively) are much more negative than those obtained for the unchelated complexes of the trialkyl- and triarylphosphines (-42 ± 3 p.p.m.). This is attributed to the presence of the phosphorus atoms in a planar 5-membered ring, in which the C–P–C and Ni–P–C bond angles are distorted from the approximately tetrahedral angles which obtain in the unchelated complexes. The resulting change in hybridization might be expected to have a marked effect on the position of the phosphorus resonance. This effect of ring size on the position of the phosphorus resonance also has been observed with cyclic phosphonium salts.[13] Certain phosphonium salts containing phosphorus in a 5-membered ring have ^{31}P chemical shifts about 20 p.p.m. more negative than the corresponding 6-membered ring and non-cyclic compounds. Hence, it may be possible to use this unusually large resonance shift as a diagnostic test for the presence of phosphorus in a 4- or 5-membered chelate or heterocyclic ring.

It is now possible to make logical structural assignments for the two diphosphine complexes that were not isolated in a pure state. The tricarbonyl complex of $P(C_2H_5)_2CH_2CH_2P(C_2H_5)_2$ probably has structure III (R = C_2H_5) since (1) the infrared carbonyl bands are in the region of a nickel–tricarbonyl–monophosphine,[2] (2) δ^{P-M} is in the normal range for unchelated complexes and (3) no other ^{31}P resonance peaks are observed, proving the absence of any uncomplexed phosphine groups. The second dicarbonyl complex obtained from $P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2$ must have structure II (R = CH_2CH_2CN) since (1) it has the infrared spectrum of a dicarbonyl complex, (2) δ^{P-M} is again in the normal range, prov-

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[10] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell Univ. Press, Ithaca, N. Y., 1960, p. 112.

[11] We are indebted to Dr. J. Chatt for a sample of this complex.

[12] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[13] M. Epstein and S. A. Buckler, unpublished results.

ing the absence of a small chelate ring and (3) it contains no uncomplexed phosphine groups. During the preparation of IA ($R = C_2H_5$), Chatt and Hart[12] obtained a small yield of the analogous complex (II, $R = C_2H_5$) whose δ^{P-M} can be assumed to be about -21.9 p.p.m.

The effect on δ^{P-M} of the variation of the number of phosphine ligands on nickel is outlined in Table III. A complete series of complexes, from the tricarbonyl-monophosphine to the tetrakis-phosphine, was available only with PCl_3 and $P(OC_2H_5)_3$. In the PCl_3 series, δ^{P-M} increases in rather regular fashion from -185 to -170 p.p.m., giving $\delta^{P-M} - \delta^{P}$ values of $+30$, $+34$, $+38$ and $+45$ p.p.m. Each additional phosphine ligand produces a small and fairly constant increase in shielding. The $P(OC_2H_5)_3$ series follows a similar pattern except that each added phosphine causes a small decrease in shielding; in this case, however, this trend is reversed slightly in the tetrakis-compound. The $\delta^{P-M} - \delta^{P}$ values for the four available tetrakis-phosphine complexes were scattered. The substitution of C_6H_5 for Cl in PCl_3 reduces considerably the increase in phosphorus shielding on complex formation, as expected. The value of $Ni(PF_3)_4$ ($\delta^{P-M} - \delta^{P} = -30$) is rather surprising, but it may be the result of the large electronegativity difference between F and Cl and special bond rehybridization effects in the phosphorus fluorides.

Examination of the di- and tricarbonyl complexes of $P(C_6H_5)_3$ and $P(C_2H_5)_3$ reveals more negative values of δ^{P-M} and larger negative values of $\delta^{P-M} - \delta^{P}$ for the tricarbonyl complexes. This would seem to indicate a much stronger Ni–P σ-bond in the tricarbonyls than in the dicarbonyls of the trialkyl- and triarylphosphines, but it may simply be a demonstration that the phosphorus chemical shifts in these complexes are far more sensitive to σ-bonding effects than to changes in π-bonding. Since the phosphites and phosphorus halides are good π-bonding ligands, substitution of a strongly π-bonding CO by these ligands would be expected to have little over-all effect on the bonding of the other three ligands; but substitution of CO by a weak π-bonder, such as a trialkyl- or triaryl-phosphine, might cause much reshuffling in the other three ligand bonds.

The phosphorus resonance data for a few miscellaneous phosphine complexes are given in Table IV. Too few data are available to permit conclusions regarding the effect of metals other than nickel and of ligands other than CO on the phosphorus chemical shift in phosphine complexes. Nevertheless, it is surprising to find that changes in complex stereochemistry and oxidation state of the metal may have little effect on $\delta^{P-M} - \delta^{P}$. The presumably planar diacetylide and dichloride complexes of nickel with two molecules of $P(n\text{-}C_4H_9)_3$ have values of $\delta^{P-M} - \delta^{P}$ (-47.7 and -31.1 p.p.m., respectively) not greatly different from the tetrahedral dicarbonylbis-(tri-*n*-butylphosphine)-nickel (-44.7 p.p.m.). Nevertheless, examination of the $\delta^{P-M} - \delta^{P}$ of a large number of diphosphine complexes of Ni(II) salts might provide some help in the assignment of planar or tetrahedral structures to these complexes. There may be some correlation between Ni–P σ-bond strength and $\delta^{P-M} - \delta^{P}$ in the $P(n\text{-}C_4H_9)_3$ complexes, since these latter values become more positive with decreasing chemical stability of the complex, an indication of the decreasing tendency for phosphorus to donate its unshared electron pair to the metal. But the results obtained with the $P(C_6H_5)_3$ complexes remain unexplained. Of the two molybdenum complexes reported, it may be noted that the diphosphine complex, *cis*-$Mo[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2](CO)_4$, which is monomeric and thus contains a 5-membered chelate ring, has the expected large negative value for $\delta^{P-M} - \delta^{P}$.

In conclusion, the analysis of the ^{31}P n.m.r. spectra of a large number of metal–phosphine complexes has provided qualitative information on metal-phosphorus bonding but, unfortunately, has not produced a quantitative measure of metal–phosphorus bond order. On the other hand, it has demonstrated the great usefulness of n.m.r. in identification of phosphine complexes and for studying reactions of metal–phosphine systems. We are currently applying this technique to the study of phosphine exchange reactions of certain metal complexes, *e.g.*, tetrakis-phosphine–nickel(0) and diphosphine–nickel(II) dihalide complexes, for which infrared techniques are unsuitable.

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