

On the ^{31}P NMR Spectrum of $[(n\text{-C}_4\text{H}_9)_3\text{P}]_2\text{NiCl}_2$

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nickel (II) complexes

An exceptional feature of nickel chemistry is the well documented diamagnetic-paramagnetic (*i.e.*, generally square planar-tetrahedral) equilibrium¹. Such equilibria have been observed for dihalobis(alkyldiarylphosphine)nickel(II) compounds, whereas dihalobis(triarylphosphine)nickel(II) compounds have generally pseudotetrahedral configurations and dihalobis(trialkylphosphine)nickel(II) and dihalobis(aryldialkylphosphine)nickel(II) compounds generally are diamagnetic and exhibit trans-square planar structures². Some exceptions include tricyclopropylphosphine, dicyclopropylphenylphos-

phine, and dicyclohexylphenylphosphine³. In many cases a convenient method of studying such equilibria is with proton magnetic resonance spectroscopy since paramagnetic species can result in large paramagnetic shifts for protons¹. However, ^{31}P NMR studies of paramagnetic species is quite limited³. We have further investigated the ^{31}P chemical shift of dichlorobis(tributylphosphine)nickel(II) in various solvents because some routine measurements in CH_2Cl_2 solution gave results which did not agree with the published chemical shift of the compound in tetrahydrofuran solution⁴. Measurements in other solvents are given in Table I, which lists the compounds in separate groups of non-coordinating and potentially coordinating solvents. It is seen that there is a large solvent dependence of the chemical shift. Further evidence is seen in Fig. 1, which shows a very large broadening of the ^{31}P signal as the chemical shift decreases. For previous ^{31}P NMR studies⁵, very slight (approx. 1 ppm at most) solvent shifts were observed, and so the nickel case is quite unusual. These data suggest that the non-coordinating solvents with large dipole moments shift the diamagnetic-paramagnetic equilibrium very slightly to the tetrahedral (paramagnetic) form, since the solvents with larger dipole moments could reasonably be expected to stabilize the isomer (tetrahedral) with the larger dipole moment. Fig. 2 shows the plot of dipole moment with ^{31}P chemical shift for $(\text{Bu}_3\text{P})_2\text{NiCl}_2$. With the exception of CH_3CCl_3 , it appears that a correlation between the chemical shift and dipole moment of the solvent does exist.

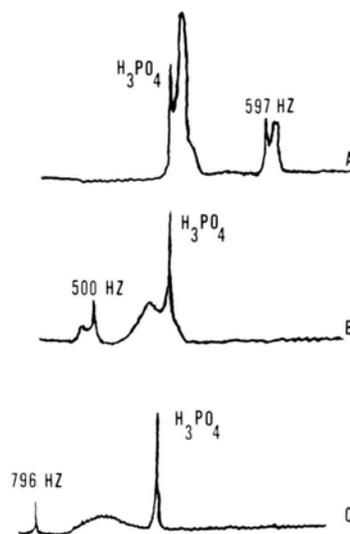
The poor fit of the correlation is probably caused by several factors. First, there is a relatively large error in the chemical shifts (several ppm) of the

Table I. Phosphorus-31 chemical shifts of $(\text{Bu}_3\text{P})_2\text{NiCl}_2$ in various solvents.

Non-coordinating solvent	Chemical shift ^a	Dipole moment ^b
CH_2Cl_2	-16.9	1.60
$\text{CH}_2\text{ClCHCl}_2$	-11.1	1.46
CH_2Br_2	-7.5	1.43
$\text{CH}_2\text{CHClCH}_2\text{Cl}$	-6.4	1.22
CHCl_3	-5.7	1.01
CH_3CCl_3	0	1.78
Toluene	+2.7	0.36
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \backslash \quad / \\ \quad \text{C}=\text{C} \\ \quad / \quad \backslash \\ \text{H} \quad \text{Cl} \end{array}$	+2.7	0
Benzene	+3.0	0
CS_2^c	+3.0	0
CCl_4	+3.6	0
Cyclohexane	+3.8	0
Potential coordinating solvent		
Dimethyl formamide	d	3.82
Acetone	d	2.88
Anisole	-1.0	1.38
Tetrahydrofuran	0	1.63
Ethyl acetate	+1.0	1.78
Diethyl ether	+3.2	1.15

^a ppm vs. 85% H_3PO_4 .^b Values taken from CRC Handbook of Chemistry and Physics, 50th ed., Chemical Rubber Co., Cleveland, Ohio 1970.^c Decomposition evident.^d No ^{31}P signal observed.

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Fig. 1. ^{31}P NMR spectrum of $(\text{Bu}_3\text{P})_2\text{NiCl}_2$ in (A) *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ (B) CHCl_3 , and (C) CH_2Cl_2 .

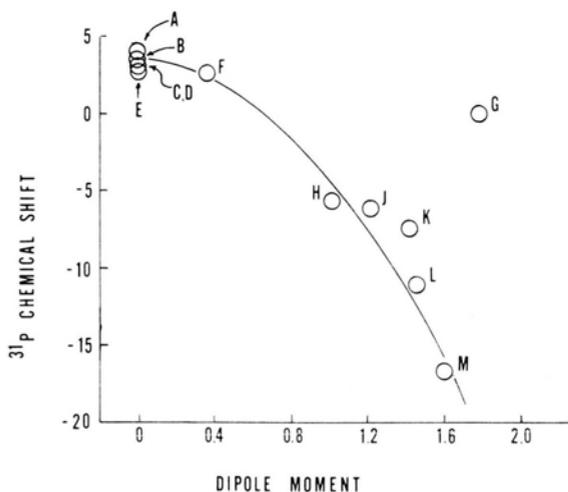


Fig. 2. Variation of ^{31}P chemical shift of $(\text{Bu}_3\text{P})_2\text{NiCl}_2$ and the dipole moment. Solvent: A, Cyclohexane; B, CCl_4 ; C, CS_2 ; D, C_6H_6 ; E, *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$; F, $\text{CH}_3\text{C}_6\text{H}_5$; G, CH_3CCl_3 ; H, CHCl_3 ; J, $\text{CH}_3\text{CHClCH}_2\text{Cl}$; K, CH_2Br_2 ; L, $\text{CH}_2\text{ClCHCl}_2$; and M, CH_2Cl_2 .

broad peaks. Second, dipole moments are not always well known and significant differences in dipole moments have been determined for the same compound⁶. And third, there appears to be a dependence of the dipole moment with the solvent system used to determine the dipole moment⁶. Such changes probably do occur at the necessarily large concentration of the complexes needed to observe phosphorus-31 NMR signals (see Experimental). It is of interest to note that CH_3CCl_3 deviates significantly from the curve. The reason for this is not clear.

The chemical shifts of the potentially coordinating solvents also show a large variance in the observed phosphorus-31 chemical shifts (Table I). However any correlation of the observed chemical shifts would necessitate consideration of five coordinate species (low and high spin cases), six coordinate species and ligand exchange, all of which could occur rapidly on an NMR time scale. That rapid ligand exchange does occur was demonstrated by addition of excess Bu_3P to a benzene solution of $(\text{Bu}_3\text{P})_2\text{NiCl}_2$, resulting in the slow disappearance of the complex's signal and the appearance of a new peak at +31 ppm ($\delta\text{Bu}_3\text{P} = +33$ ppm). It was also noted the $(\text{Bu}_3\text{P})_2\text{NiCl}_2$ reacted slowly with CCl_4 and CS_2 .

Similar large deviations of chemical shifts were observed with $(\text{Et}_3\text{P})_2\text{NiCl}_2$ (-15.7 ppm in THF, unobserved in CH_2Cl_2 , -19.3 ppm reported⁴ in THF) and $(i\text{-Pr}_3\text{P})_2\text{NiCl}_2$ (-72.8 ppm in CH_2Cl_2 , -44.0 ppm reported⁴ in THF).

It should be pointed out that our modest resolution would not allow for meaningful concentration studies, although it is likely that the observed

chemical shifts do exhibit such dependence. Likewise a wider range of dipole moments was not studied because the peaks broadened so much that they were undetectable when solvents with large dipole moments were employed.

Only slight changes are observed in the PMR spectrum of $(\text{Bu}_3\text{P})_2\text{NiCl}_2$ in C_6D_6 , CDCl_3 and d_6 -acetone. Considering that chemical shifts of up to 130 ppm have been observed in some PMR studies¹, it is likely that the equilibrium lies almost completely toward the diamagnetic isomer, even in very polar solvents. This greater sensitivity of phosphorus-31 NMR toward observing the diamagnetic-paramagnetic equilibrium is presumably due to the close proximity of the phosphorus atom to the source of paramagnetism, and possibly to the π bonding overlap of the nickel 3d orbitals containing the unpaired electrons with the empty 3d orbitals of phosphorus.

Experimental

Phosphorus-31 NMR spectra were recorded on a Varian Associates DP-60 spectrometer, operating at 24.3 MHz as previously described⁷. In general, spectra were recorded by sweeping five times with increasing field and five times with decreasing field. The ten values were averaged. The extreme broadness of the peaks observed in some spectra required extrapolation of the slopes to determine the center of the signals. Spectra were recorded in CH_2Cl_2 , CHCl_3 , C_6H_6 , CCl_4 , CS_2 , and acetone with reagent grade solvents. Toluene, cyclohexane, THF, and ether were dried over sodium-benzophenone and distilled prior to use. The other solvents were purified by taking a middle 5 ml fraction from the distillation of a 50 ml sample. Solutions were prepared with 1.0 g of complex in 2.0 ml of solvent. Complexes were prepared by the method of FLUCK and LORENZ⁴.

PMR spectra were recorded on a Varian Associates A-60-A spectrometer, with TMS as an internal standard.

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¹ For reviews see R. H. HOLM, *Acc. Chem. Research* **2**, 307 [1969]; D. R. EATON and W. D. PHILLIPS, *Adv. Mag. Resonance* **1**, 103 [1965].

² L. QUE, JR. and L. H. PIGNOLET, *Inorg. Chem.* **12**, 156 [1973], and references cited therein.

³ G. A. WEBB, *Ann. Rev. NMR Spect.* **3**, 211 [1970].

⁴ E. FLUCK and J. LORENZ, *Z. Naturforsch.* **22b**, 1095 [1967].

⁵ J. F. NIXON and A. PIDCOCK, *Ann. Rev. NMR Spect.* **2**, 345 [1969].

⁶ A. L. MCCLELLON, *Table of Experimental Dipole Moments*, W. H. Freeman and Co., San Francisco 1963.

⁷ S. O. GRIM, R. L. KEITER, and W. McFARLANE, *Inorg. Chem.* **6**, 1133 [1967].