

$${}^n f(L)^{Co}_{Co} = 1.1121 {}^n f(L)^{Ni}_{Co} - 2.123 \quad \delta = \pm 0.05 \quad (4)$$

$${}^n f(L)^{Fe}_{Co} = 1.1472 {}^n f(L)^{Ni}_{Co} - 2.732 \quad \delta = \pm 0.03 \quad (5)$$

where ${}^n f(L)^M_{XO}$ indicates the principal force constant for the XO oscillator, where n CO groups have been replaced by ligand, L, and M is the metal under consideration. The average deviation δ is the difference between the force constants calculated from these equations and those presented in the tables. Equation 5, for the paucity of points (three), is the least reliable. The slopes indicate that f_{NO} is less sensitive to a change in ligand for the cobalt, iron, and manganese compounds relative to a change in the f_{CO} of nickel. In the cobalt and iron compounds, however, the f_{CO} is more sensitive to a change in

ligand relative to the same standard. These equations allow predictions of either ${}^n f(L)^M_{Co}$, ${}^n f(L)^M_{NO}$, or ${}^n f(L)^{Ni}_{Co}$ to be made if one of the molecules is known. For example, the molecule $Co(NO)(PCl_3)_3$ has not been reported; however, using f_{Co} for $Ni(CO)(PCl_3)_3$ (Table V), f_{NO} for the cobalt derivative is predicted to be 14.29 and the NO stretching frequency at 1802 cm^{-1} . Force constants for other presently unknown molecules may be predicted in a similar manner.

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CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

Ditertiary Phosphine Complexes of Nickel. Spectral, Magnetic, and Proton Resonance Studies. A Planar-Tetrahedral Equilibrium¹

By GERALD R. VAN HECKE AND WILLIAM DEW. HORROCKS, JR.

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A number of complexes of nickel in oxidation states 0, II, and III with the ditertiary phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1, 2, \text{ or } 3$) are reported and studied by spectral and magnetic methods. In solution in organic solvents complexes of the type $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]X_2$ where $X = Br$ or I and $n = 2$ remain diamagnetic. The analogous complexes with $n = 3$ show a square-planar (diamagnetic)-tetrahedral (paramagnetic) equilibrium in solution. Isotropic proton magnetic resonance shifts were observed in these systems and thermodynamic parameters for the equilibrium were obtained from the temperature dependences of these shifts. The epr spectrum of polycrystalline $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Br_3$ shows an isotropic signal at $g = 2.218$.

Introduction

Although there have been a great many complexes prepared from the nickel halides and tertiary phosphines,² relatively few complexes prepared with ditertiary phosphines have been reported. Complexes of the type $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Br_2$ ($n = 3, 4, 5$) have been prepared by Issleib and Hohlfield.³ Chatt and Hart⁴ described the complexes $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]Cl_2$ and $Ni(o-C_6H_4[P(C_2H_5)_2])_2X_2$, $X = Cl, Br, I$. Wymore and Bailar⁵ reported $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]X_2$, $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2](ClO_4)_2$, and $Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]Br_3$. While the present investigation of complexes formed by nickel halides with the ditertiary phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1, 2, 3$), abbreviated dpm, dpe, and dpp, respectively, was in progress, Booth

and Chatt⁶ reported some nickel(II) complexes of these phosphines where $n = 1$ or 2 . We report here the preparation, optical spectra, magnetic susceptibilities, and in certain cases epr and pmr measurements for the nickel(II) and nickel(III) complexes $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_mX_2$, where for $m = 1, n = 2, 3$, $X = Cl, Br, I$ and for $m = 2, n = 1, 2$, $X = Cl, Br, I$, and $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Br_3$, for $n = 2, 3$. The $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]X_2$ compounds exhibit a square-planar (diamagnetic) \rightleftharpoons tetrahedral (paramagnetic) equilibrium in solution in contrast to the corresponding compounds where the phosphorus atoms are linked by a chain of only two carbons which remain diamagnetic in solution. Isotropic pmr shifts allow thermodynamic parameters to be obtained readily. Using a new method, two zerovalent nickel complexes, $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_2$, where $n = 2, 3$, were prepared.

Experimental Section

The ditertiary phosphines 1,1-bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane were prepared by the

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49(638)-1492, and by the National Science Foundation through Grant GP 3397.

(2) For a review see G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).

(3) K. Issleib and G. Hohlfield, *Z. Anorg. Allgem. Chem.*, **312**, 169 (1961).

(4) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

(5) C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

(6) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

method of Hewertson and Watson.⁷ 1,3-Bis(diphenylphosphino)propane was prepared as recently reported.⁸

Dichlorodi[1,1-bis(diphenylphosphino)methane]nickel(II).— $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.682 g, 2.87 mmoles) was dissolved in 15 ml of methanol and added to a benzene solution of the ligand dpm (1.780 g, 4.63 mmoles). An immediate dark red-brown solution was observed which yielded, upon reducing the volume by two-thirds and setting in a cold room, dark brown microcrystalline product that was dried *in vacuo*. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2$: C, 66.88; H, 4.91. Found: C, 67.20; H, 5.11.

Dibromodi[1,1-bis(diphenylphosphino)methane]nickel(II).⁶—To a filtered solution of NiBr_2 (0.878 g, 4.01 mmoles) dissolved in a minimum amount of methanol was added a solution of ligand dpm (1.038 g, 2.70 mmoles) in 10 ml of benzene. The resultant wine red solution was refluxed for 1 hr. The small dark red crystals obtained when the solvent volume was reduced and the solution cooled in a cold room were recrystallized from ethanol by cooling. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_2$: C, 60.91; H, 4.47. Found: C, 60.70; H, 4.60.

Diiododi[1,1-bis(diphenylphosphino)methane]nickel(II).—This compound was prepared in a manner similar to the bromide complex, yielding purple microcrystals. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{I}_2$: C, 55.50; H, 4.07. Found: C, 55.73; H, 4.04.

Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II).⁶— $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.319 g, 1.34 mmoles) dissolved in 30 ml of 2:1 2-propanol:methanol was added to a solution of ligand dpe (0.502 g, 1.26 mmoles) in 50 ml of warm 2-propanol. Orange feathery needle crystals precipitated out and were collected, washed with ether, and dried *in vacuo*, yielding 0.621 g, a 93.8% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2$: C, 59.20; H, 4.55. Found: C, 59.18; H, 4.74.

Dibromo[1,2-bis(diphenylphosphino)ethane]nickel(II).⁶— NiBr_2 (1.567 g, 7.15 mmoles) dissolved in a minimum amount of methanol was filtered hot and added to a warm solution of ligand dpe (1.912 g, 4.81 mmoles) in 20 ml of toluene. An immediate red gelatinous precipitate was formed, and after refluxing 2 hr, the cool solution yielded, when dried *in vacuo*, 2.4 g, an 80.4% yield of product. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_2$: C, 50.56; H, 3.89. Found: C, 50.16; H, 3.94.

Diiodo[1,2-bis(diphenylphosphino)ethane]nickel(II).—This was prepared in a manner similar to that used for the bromide complex; 1.78 g, or a 77.6% yield, of fine deep purple powder was collected. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{I}_2$: C, 43.88; H, 3.38. Found: C, 44.24; H, 3.82.

Dichlorodi[1,2-bis(diphenylphosphino)ethane]nickel(II).—Attempts to prepare this complex have so far been without success.

Dibromodi[1,2-bis(diphenylphosphino)ethane]nickel(II).—This complex was prepared by the method of Booth and Chatt⁹ as well as a new way. Ligand dpe (0.137 g, 0.344 mmole) and previously prepared $\text{Ni}(\text{dpe})\text{Br}_2$ (0.228 g, 0.369 mmole) were refluxed in 60 ml of 1:1 ethanol:water until a clear deep orange solution resulted. The solvent was reduced in volume by two-thirds and the resulting yellow powder collected and dried *in vacuo*, giving 0.295 g, or an 84.3% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_2$: C, 61.48; H, 4.73. Found: C, 61.63; H, 4.93.

Diiododi[1,2-bis(diphenylphosphino)ethane]nickel(II).—Prepared in a manner analogous to the one above, the orange solution yielded yellow-orange crystals that were collected and dried *in vacuo*. The 0.537 g of product represented a 64.7% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{I}_2$: C, 56.27; H, 4.33. Found: C, 56.41; H, 4.48.

Dichloro[1,3-bis(diphenylphosphino)propane]nickel(II).—A hot solution of ligand dpp (3.011 g, 7.31 mmoles) in 40 ml of 2-propanol was added to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.995 g, 8.37

mmoles) in 35 ml of 5:2 2-propanol:methanol. An immediate brown flaky precipitate was observed which on heating turned into a fine red microcrystalline powder. This red product was collected and dried *in vacuo*, giving 3.756 g of product, a 95% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2$: C, 59.88; H, 4.81. Found: C, 59.91; H, 5.00.

Dibromo[1,3-bis(diphenylphosphino)propane]nickel(II).— NiBr_2 (2.356 g, 10.75 mmoles) was dissolved in a minimum amount of 1-propanol, filtered, and added to a solution of ligand dpp (4.11 g, 9.99 mmoles) in 40 ml of 1-propanol. The resulting deep red solution was warmed briefly and on cooling gave red microcrystals that, dried *in vacuo* over concentrated H_2SO_4 , amounted to 3.57 g, or a 56.5% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_2$: C, 51.34; H, 4.12. Found: C, 51.32; H, 4.24.

Diiodo[1,3-bis(diphenylphosphino)propane]nickel(II).—This complex was prepared in the same manner as the bromide, yielding 3.53 g, a 48.8% yield of dark purple powder. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{I}_2$: C, 44.68; H, 3.59. Found: C, 44.85; H, 3.74.

Tribromo[1,2-bis(diphenylphosphino)ethane]nickel(III).—To $\text{Ni}(\text{dpe})\text{Br}_2$ powder (0.994 g) was added 2 ml of a 2 vol % bromine in benzene solution. The mix was stirred briefly, washed with a small amount of benzene, collected, and dried *in vacuo* at 70° overnight. The dark brown powder (0.989 g, 89% yield) obtained returns to the red color of the starting material after 2 months. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_3$: C, 44.76; H, 3.44. Found: C, 44.62; H, 3.62.

Tribromo[1,3-bis(diphenylphosphino)propane]nickel(III).—Prepared in the same manner starting with 0.972 g of $\text{Ni}(\text{dpp})\text{Br}_2$, the complex is a black powder that amounted to 1.055 g, or a 92.6% yield. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Br}_3$: C, 45.56; H, 3.66. Found: C, 45.54; H, 3.86.

Di[1,2-bis(diphenylphosphino)ethane]nickel(0).⁹—The reaction was performed under N_2 in a glove box with deoxygenated solvents. To a mix of nickelocene (0.277 g, 1.46 mmoles) and the ligand dpe (1.165 g, 2.92 mmoles) was added 50 ml of toluene. The solution was refluxed 24 hr, the brown tar filtered off, and to the hot filtrate was added enough hot methanol to initiate crystallization. Golden yellow crystals were collected that seem stable as long as stored under N_2 . *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$: C, 72.98; H, 5.61. Found: C, 73.20; H, 5.74.

Di[1,3-bis(diphenylphosphino)propane]nickel(0).—This complex was prepared in the same manner as above, and small rectangular orange crystals representing a 66% yield were obtained. *Anal.* Calcd for $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$: C, 73.83; H, 5.89. Found: C, 73.30; H, 5.93.

Magnetic susceptibilities both for liquid and powder samples were measured using the standard Gouy method at room temperature. The susceptibilities were corrected for the diamagnetism of the ligands using values found in the tables given by Figgis and Lewis.¹⁰ Liquid susceptibilities were checked by the nmr method of Evans.¹¹ Optical spectra were recorded on a Cary Model 14 spectrophotometer. Mull spectra were obtained on Nujol mulls supported on filter paper. A Varian A60A spectrometer with a variable temperature probe was used to record the pmr spectra. The epr spectra were recorded with a Varian X-band instrument. The microanalyses were performed by either George I. Robertson, Jr., Florham Park, N. J., or Galbraith Laboratories, Knoxville, Tenn.

Complexes of Nickel(II)

dpm Complexes.—The ligand dpm reacts with nickel(II) halides to yield dark red diamagnetic compounds that analyze as $\text{Ni}(\text{dpm})_2\text{X}_2$, X = Cl, Br,

(9) Chatt and Hart⁴ first prepared this complex by successive replacements of CO by ligand.

(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 403.

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(7) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

(8) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

I. The optical spectra run in methylene chloride solution show only one band in the $\sim 20,000$ cm^{-1} region before strong charge-transfer absorption takes over. No bands are observed at energies less than $\sim 20,000$ cm^{-1} . The bands observed for $\text{Ni(dpm)}_2\text{X}_2$ in methylene chloride solution ($\sim 3 \times 10^{-4}$ M) are at 21,500 cm^{-1} (ϵ_{max} 2600 l. mole $^{-1}$ cm^{-1}), 20,000 cm^{-1} (ϵ_{max} 1900), and 18,700 cm^{-1} (ϵ_{max} 2300), for $X = \text{Cl, Br, I}$, respectively. Taking these complexes to be planar with C_{2v} symmetry, ligand field considerations predict four possible spin-allowed d-d transitions of which the $^1A_1 \rightarrow ^1B_2$ occurs at lowest energy ($^1A_1 \rightarrow ^1A_2$ in D_{4h}). It is to this transition that the bands at $\sim 20,000$ cm^{-1} are assigned. The three other predicted transitions $^1A_1 \rightarrow ^1A_2$, $^1A_1 \rightarrow ^1B_2$, $^1A_1 \rightarrow ^1B_1$ are undoubtedly swamped by the charge-transfer bands which dominate at higher energies. Support for such an assignment comes from recent calculations carried out on several square-planar nickel(II) complexes.¹² It should be noted that the band maximum moves to lower energy in the order $\text{Cl} > \text{Br} > \text{I}$, as expected from the spectrochemical series. Thus analyses, optical spectra, and the observed diamagnetism strongly suggest that these are square-planar compounds wherein the ligand dpm is acting as a monodentate donor. Booth and Chatt⁶ point out that while they were unable to prepare nickel(II) dpm complexes wherein the ligand is bidentate, palladium and platinum do form such chelate complexes. We have prepared the compound Ni(dpm)(CO)_2 ⁸ by the reaction of the ligand with Ni(CO)_4 . Direct reaction of elemental halogen with the carbonyl derivative offers a possible route to the nickel(II) dpm chelate, but this has not been attempted.

dpe Complexes.—The ligand dpe reacts with the nickel(II) halides to yield compounds that analyze as Ni(dpe)X_2 , $X = \text{Cl, Br, I}$, and $\text{Ni(dpe)}_2\text{X}_2$, $X = \text{Br, I}$. Most of these were first isolated by Booth and Chatt,⁶ though few physical measurements were reported. The Ni(dpe)X_2 complexes were found to be diamagnetic in the solid and in solution using the nmr method of Evans.¹¹ No isotropic nmr shifts indicative of paramagnetic entities were observed. The visible spectra of the Ni(dpe)X_2 complexes in methylene chloride show only one band at $\sim 20,000$ cm^{-1} before strong charge-transfer bands take over at higher energies (see Table I). This band may be assigned to $^1A_1 \rightarrow ^1B_2$ in C_{2v} symmetry, as in the dpm compounds. Square-planar geometry is ascribed then to these Ni(dpe)X_2 complexes.

The yellow $\text{Ni(dpe)}_2\text{X}_2$ complexes are more difficult to prepare. Attempts to prepare $\text{Ni(dpe)}_2\text{Cl}_2$ have met with failure, even refluxing Ni(dpe)Cl_2 with excess dpe in 1:1 ethanol-water did not yield a characterizable product. These seemingly hexacoordinate compounds appear to change coordination

TABLE I
OPTICAL SPECTRA OF Ni(dpe)X_2 AND $\text{Ni(dpe)}_2\text{X}_2$ COMPOUNDS
IN METHYLENE CHLORIDE SOLUTION

X	Ni(dpe)X_2		$\text{Ni(dpe)}_2\text{X}_2$ ^a	
	ν_{max}^b	ϵ_{max}^c	ν_{max}^b	ϵ_{max}^d
Cl	21,600	1.7×10^3
Br	20,800	1.7×10^3	21,000	1.9×10^4
I	19,200	2.0×10^3	19,600	1.4×10^4

^a Data reported for compounds prepared using present method. ^b cm^{-1} . ^c L. mole $^{-1}$ cm^{-1} . ^d Arbitrary since background not accounted for.

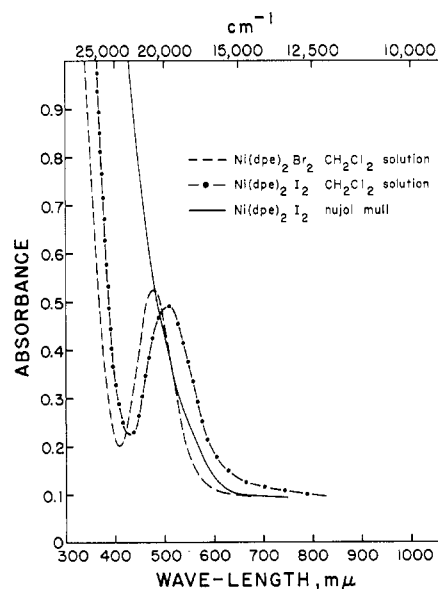
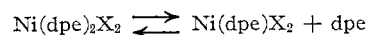


Figure 1.—Optical spectra in methylene chloride solution of $\text{Ni(dpe)}_2\text{X}_2$ for $X = \text{Br}$ (4.04×10^{-4} M), $X = \text{I}$ (3.54×10^{-4} M) in 1-cm cells and of the Nujol mull of $\text{Ni(dpe)}_2\text{I}_2$.

on going from solid to solution as is qualitatively indicated by a color change from a yellow solid to a red solution upon dissolution. In Figure 1 the optical spectra for solution and mull are compared. While only the $\text{Ni(dpe)}_2\text{I}_2$ mull spectrum is shown, the bromide spectrum is quite similar. Because of the low conductivity of these dpe complexes in nitrobenzene, Booth and Chatt⁶ suggest an octahedral coordination in the solid with dissociation upon solution. To assure the identity of $\text{Ni(dpe)}_2\text{Br}_2$ synthesized as previously reported⁶ and the compound prepared here *via* the reflux procedure, mull and solution spectra in nitrobenzene and methylene chloride were recorded. The mull spectra and the solution spectra in the two solvents are identical; the solution spectra show one band at 20,800 cm^{-1} characteristic of a square-planar species. The reported conductivity⁶ was measured on a red nitrobenzene solution. This low conductivity combined with the difference in the mull and optical spectra (Figure 1) suggests a dissociation in solution of the type



where Ni(dpe)X_2 is the species responsible for the spectrum. The observation of only the one band at $\sim 20,000$ cm^{-1} in the solution spectrum discounts the possibility of the dissociation of a halogen to give a

(12) For a very recent review see H. B. Gray in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekkar, New York, N. Y., 1965, p 239.

pentacoordinate species since three additional bands would then be expected.¹³ The observed mull spectrum of the $\text{Ni(dpe)}_2\text{X}_2$ compounds may be explained by assuming a diamagnetic hexacoordinate structure where the chelating phosphines define a plane and the halogens occupy the axial positions. Conditions for diamagnetism in d^8 compounds having a tetragonal component in an octahedral ligand field have been discussed by Maki.¹⁴ The assumption of diamagnetism in these hexacoordinate $\text{Ni(dpe)}_2\text{X}_2$ complexes requires the presence of a weak axial ligand field due here to the halogens. The hexacoordinate species then should show a band approximately characteristic of the NiP_4 chromophore at energies higher than those for the NiP_2X_2 chromophore. The bands due to NiP_4 apparently fall in the region obscured by strong charge-transfer absorption. Analogous behavior was observed for the diiodobis(α -lutidine)nickel(II) compounds.¹⁵ The postulated dissociation is thus quite reasonable in light of the experimental evidence.

dpp Complexes.—Upon mixing alcoholic solutions of dpp and nickel halides dark red or purple microcrystalline powders of composition Ni(dpp)X_2 , $\text{X} = \text{Cl, Br, I}$, are obtained. As solids these are diamagnetic and mull spectra show only one band at $\sim 20,000 \text{ cm}^{-1}$, which is ascribed to the $^1\text{A}_1 \rightarrow ^1\text{B}_2$ transition, characteristic, as in the dpm and dpe complexes, of C_{2v} square-planar geometry. The solution spectra in methylene chloride show the $\sim 20,000 \text{ cm}^{-1}$ band as well as one at about $12,000 \text{ cm}^{-1}$. Table II presents a summary of the optical data, while Figure 2 shows the spectra recorded on methylene chloride solutions for $\text{X} = \text{Cl, Br, I}$ and the mull spectrum of the iodide. The appearance of a band in the region $12,500\text{--}10,000 \text{ cm}^{-1}$ is indicative^{16,17} of the presence of a tetrahedral isomer. If the apparent intensity of the band at $\sim 12,200 \text{ cm}^{-1}$ is proportional to the fraction of tetrahedral isomer present, then this fraction decreases in the order $\text{Ni(dpp)I}_2 > \text{Ni(dpp)Br}_2 > \text{Ni(dpp)Cl}_2$. Unfortunately, attempts to isolate the tetrahedral isomers have been without success to date.

TABLE II
OPTICAL SPECTRA OF Ni(dpp)X_2 COMPLEXES IN THE SOLID STATE AND METHYLENE CHLORIDE SOLUTION

X	Nujol mull	Methylene chloride solution ^a	
	ν_{max}	ν_{max}^b	ν_{max}^b
Cl	...	21,300 (940)	12,200 (26)
Br	20,000	20,400 (640)	12,050 (120)
I	17,900	20,000 (1550)	11,500 (320)

^a $\sim 5 \times 10^{-4} \text{ M}$. ^b ϵ in $\text{l. mole}^{-1} \text{ cm}^{-1}$ in parentheses, ν in cm^{-1} .

Square-planar \rightleftharpoons tetrahedral equilibria in nickel(II) chelates have been studied recently^{18,19} employing

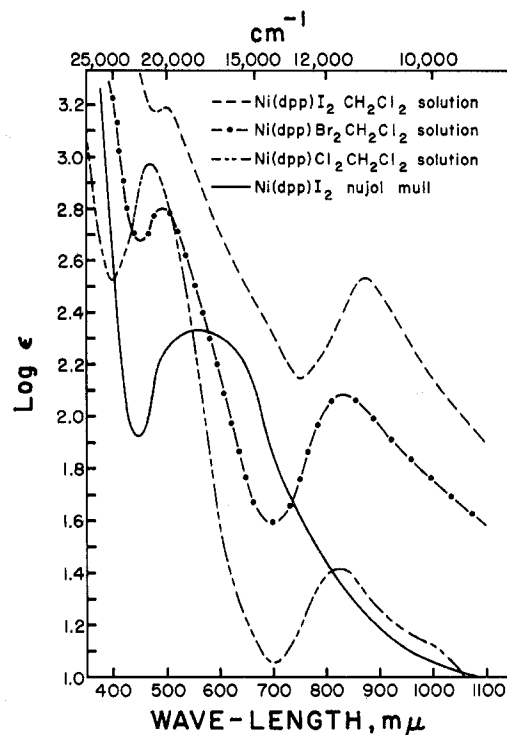


Figure 2.—Optical spectra of Ni(dpp)X_2 in methylene chloride solution for $\text{X} = \text{Cl}$ ($4.47 \times 10^{-4} \text{ M}$), $\text{X} = \text{Br}$ ($7.84 \times 10^{-4} \text{ M}$), $\text{X} = \text{I}$ ($1.02 \times 10^{-3} \text{ M}$) recorded in 1-cm cells and of the Nujol mull of Ni(dpp)I_2 (absorbance of mull arbitrary units).

the temperature dependencies of isotropic pmr shifts to determine the pertinent thermodynamic parameters. In a solution with conformational equilibrium between a square-planar ($S = 0$) and tetrahedral ($S = 1$) species eq 1 and 2 apply,²⁰ where $\Delta\nu_i$ is the isotropic

$$\frac{\Delta\nu_i}{\nu} = -\frac{A_i \gamma_e g\beta S(S+1)}{2S \gamma_H} \frac{1}{3kT} [\exp \Delta G^\circ/RT + 1]^{-1} \quad (1)$$

$$\Delta G^\circ = RT \ln [(\mu_\infty/\mu_{\text{eff}})^2 - 1] \quad (2)$$

resonance shift for the i th proton defined by $\Delta\nu_i = \nu_{i,\text{paramag}} - \nu_{i,\text{diamag}}$, γ_e and γ_H are the magnetogyric ratios of the electron and proton, respectively, A_i is the isotropic hyperfine interaction constant, μ_∞ is the magnetic moment of the pure tetrahedral species, μ_{eff} is the effective magnetic moment of a solution containing both diamagnetic and paramagnetic species, ΔG° is the standard free energy change of the equilibrium (planar species on reactant side), and all other symbols have their usual significance.

Due to the limited solubility of the chloro complex only the bromo and iodo complexes were studied, the latter being the more soluble. The effective magnetic moment of Ni(dpp)Br_2 in nitrobenzene solution at 22° was found by the Gouy method to be 2.12 BM, while for Ni(dpp)I_2 , μ_{eff} values of 2.62 BM at 23° in nitrobenzene and 2.73 BM at 24° in chloroform were measured. The temperature dependence of

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(18) R. H. Holm, A. Chakravorty, and L. J. Theriot, *ibid.*, **5**, 625 (1966), and references therein.

(19) For a recent review see D. R. Eaton and W. D. Phillips in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, p 103.

(20) W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 3779 (1965).

the magnetic susceptibility of a solution of Ni(dpp)Br_2 in nitrobenzene was measured by the nmr method of Evans.¹¹ Equation 2 was used to obtain ΔG° for the planar-tetrahedral equilibrium as a function of temperature. The results are shown in Figure 6 without error flags (the estimated uncertainty is ± 200 cal/mole) and agree to within experimental error with those determined from pmr isotropic shift measurements (*vide infra*).

The pmr spectrum of Ni(dpp)I_2 in deuteriochloroform is illustrated in Figure 3; assignments were made on the basis of relative peak areas, spin-spin splittings, and line widths. Two signals of relative areas 2:1 appear upfield from tetramethylsilane. The one of area 2 has a triplet structure and the other the shape expected for an unresolved quintet. These are assigned to the methylene protons α and β to the phosphorus atom, respectively. In addition to weak signals attributable to free ligand from some slight dissociation or solvolysis, three peaks appear downfield from TMS with relative areas (reading downfield) 4:2:4. The peak of area 2 occurs quite near the free ligand phenyl proton resonance position and its position is slightly affected by addition of excess ligand. The other peaks assigned to coordinated ligand protons are unaffected by addition of free ligand. The two remaining resonances have approximately equal areas and are therefore assigned to the phenyl ring *ortho* and *meta* protons. The one shifted downfield shows the greatest broadening at low temperatures and is therefore tentatively assigned to the *ortho* proton, which would be most effectively relaxed due to the proximity of the paramagnetic center. The pattern of the phenyl proton isotropic shifts is entirely different from that found for the dihalobis-(triphenylphosphine)nickel(II) and -cobalt(II) compounds and the corresponding acetylacetonate adducts.^{21,22} This fact plus the observation of an upfield shift for the methylene proton resonances is perhaps indicative of a significant dipolar (pseudo-contact) contribution to the shifts owing to *g*-tensor anisotropy. Such dipolar shifts have been definitely established in the pmr spectra of some tetrahedrally coordinated nickel(II) complexes.²³ For the present purposes the detailed origin of the observed isotropic shifts is unimportant and further discussion of this point will be postponed. Figure 4 shows the temperature dependences of the isotropic resonance shifts of the phenyl *ortho* protons and the α and β methylene protons of the chelate ring of Ni(dpp)Br_2 in nitrobenzene solution, while Figure 5 shows the corresponding data for Ni(dpp)I_2 in nitrobenzene and deuteriochloroform solutions.

In order to calculate thermodynamic parameters for the conformational equilibria in solution from the temperature variation of the isotropic shifts using eq

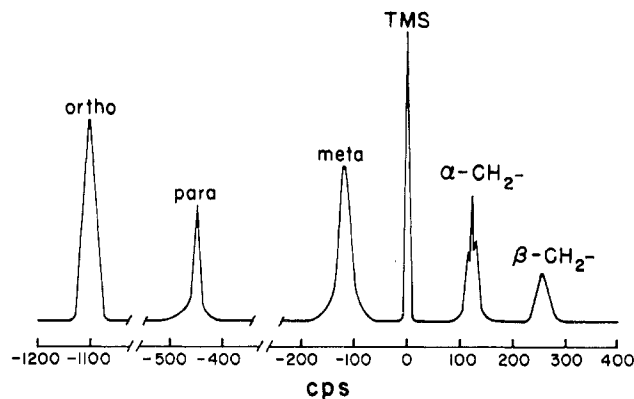


Figure 3.—Pmr spectrum of Ni(dpp)I_2 in CDCl_3 at 38° .

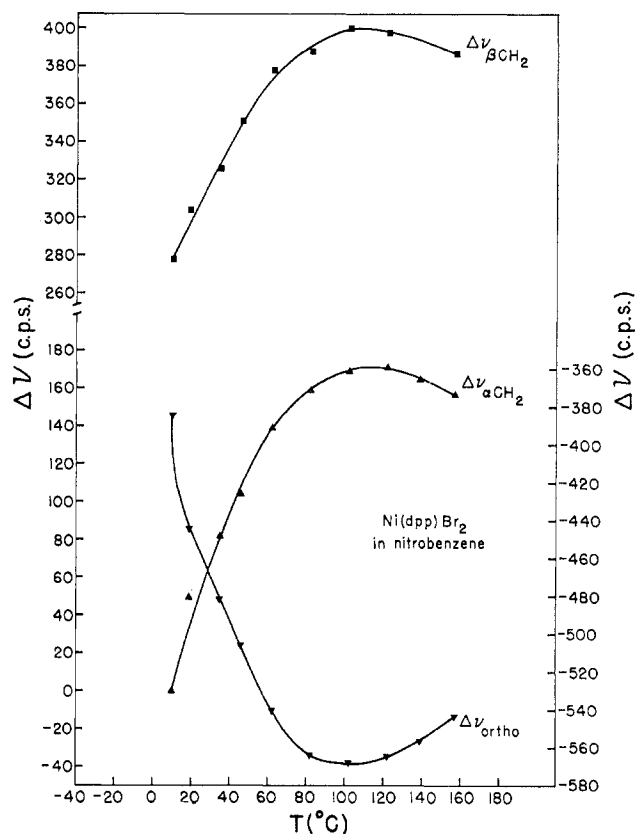


Figure 4.—Isotropic shifts of the phenyl *ortho* and α and β methylene protons of Ni(dpp)Br_2 in nitrobenzene vs. temperature. The phenyl protons are referenced to -438 cps from TMS as diamagnetic position, while the α and β methylene protons are referenced to the diamagnetic positions -122 and -90 cps from TMS, respectively. Note the break in scale along the left-side ordinate and the negative scale on the right-side ordinate.

1, A_i values, which contain both contact and dipolar contributions, must be obtained. This was done by calculating ΔG° at one temperature with eq 2 from the μ_{eff} of the solutions obtained by the Gouy method. To do this, however, μ_∞ must be known or estimated. As the tetrahedral isomers of these complexes have not been isolated, reasonable estimates of $\mu_\infty = 3.05$ and 3.10 BM for Ni(dpp)Br_2 and Ni(dpp)I_2 , respectively, were obtained from the observed moments of the tetrahedral isomers of the complexes $\text{Ni}[\text{PR}(\text{C}_6\text{H}_5)_2]_2\text{X}_2$, $\text{R} = \text{alkyl}$.¹⁷ Using ΔG° obtained from eq 2 and the

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(22) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

(23) G. N. LaMar, *ibid.*, **41**, 2992 (1964).

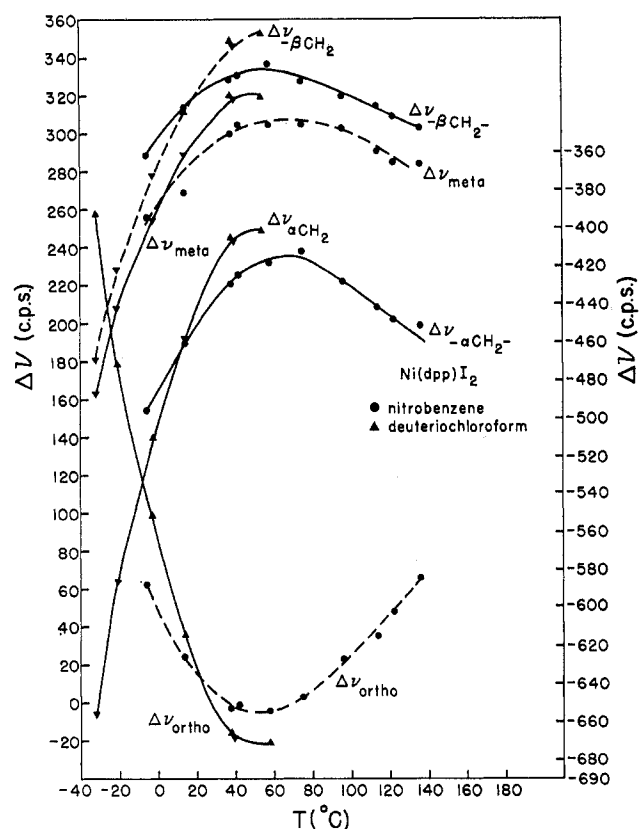


Figure 5.—Isotropic shifts of the phenyl *ortho*, *meta*, and α and β methylene protons of Ni(dpp)I_2 in nitrobenzene and deuteriochloroform vs. temperature. The phenyl protons are referenced to -438 cps from TMS as diamagnetic position, while the α and β methylene protons are referenced to the diamagnetic positions -122 and -90 cps from TMS, respectively. Note the break in scale along the left-side ordinate and the negative scale on the right-side ordinate.

observed isotropic shift at the same temperature for the proton in question, the unknown A_i values were calculated by eq 1; they are assumed to be independent of temperature. The ΔG° values were computed as a function of temperature from the observed isotropic shifts using eq 1. Figure 6 shows the results which may be fit quite well by eq 3. The *ortho* proton

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

shifts were used to obtain the free energies. The thermodynamic parameters ΔS° and ΔH° are indicated in Table III. The estimated uncertainty in ΔG° is ± 120 cal/mole. The major sources of error are the measurement of ΔG° from the solution magnetic susceptibility used to calculate A_i and the uncertainty in μ_∞ . Less satisfactory plots of ΔG° vs. T are obtained for values of μ_∞ other than those chosen.

A moderate amount of thermodynamic data is available for the square-planar-tetrahedral equilibrium in complexes of the type Ni(chelate)_2 where chelate is an anionic bidentate ligand.^{18,19} The present is the first study of this sort for monochelate complexes. The values of ΔH° and ΔS° (Table III) for Ni(dpp)Br_2 and Ni(dpp)I_2 in nitrobenzene are quite similar, with both the enthalpy and entropy contributions favoring

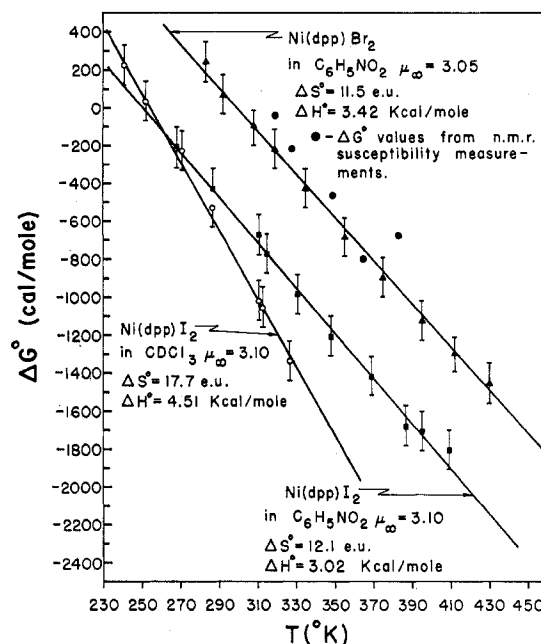


Figure 6.— ΔG° vs. T for observed square-planar-tetrahedral equilibria in Ni(dpp)X_2 ($X = \text{Br, I}$) systems.

TABLE III
THERMODYNAMIC PARAMETERS FOR THE
PLANAR-TETRAHEDRAL EQUILIBRIUM^a

Solvent	Ni(dpp)Br_2	Ni(dpp)I_2	
	Nitrobenzene	Nitrobenzene	Chloroform
ΔH° ^b	3.42	3.02	4.51
ΔS° ^c	11.5	12.1	17.7
K_{eq} (300°K)	1.00	2.68	3.85

^a Planar species on left-hand side of chemical equation. ^b ± 0.4 kcal/mole. ^c ± 1.0 eu.

the tetrahedral form of the iodide slightly more than that of the bromide. This is qualitatively consistent with our visible and near-infrared results and with magnetic susceptibility measurements¹⁶ on benzene solutions of the complexes $\text{Ni[R(C}_6\text{H}_5)_2\text{P]}_2\text{X}_2$, $R = \text{butyl, benzyl, allyl}$, where the percentage of tetrahedral form in solution was found to increase in the order $\text{Cl} < \text{Br} < \text{I}$. Browning, *et al.*,¹⁶ attributed the varying fraction of tetrahedral isomer in solution as R is varied to changing electronic factors rather than steric ones. Our results show the dpe complexes (two-carbon chain linking the phosphorus atoms) to be entirely diamagnetic in solution while the dpp complexes (three-carbon chain) exist as equilibrium mixtures of the two forms, suggesting that steric factors are paramount in determining the position of the equilibrium. An infrared study⁸ of the dpp and dpe derivatives of Ni(CO)_4 and $\text{Co(CO)}_3(\text{NO})$ shows these ligands to have only extremely small differences in their π -acceptor abilities. The increased chain length of dpp allows the $-\text{P(C}_6\text{H}_5)_2$ moieties to "spread out" and interact more strongly with the halogens in the planar form, thus favoring the tetrahedral isomer. Further, Molecular Framework Models show that while both dpp and dpe are capable of coordinating in a square-planar fashion without undue ring-angle

strain, there is considerably more angle strain involved in the tetrahedral form of the dpe chelate than for the corresponding dpp complex, again favoring the tetrahedral form of the latter.

Owing to the limited solubility of these complexes, no general study of the effect of solvent on the conformational equilibrium was possible. The iodide was sufficiently soluble in deuteriochloroform to obtain shifts, and our results indicate a considerably larger positive entropy effect for this solvent than for nitrobenzene, suggesting a particularly effective solvation of the planar form of Ni(dpp)I₂ by chloroform. It should be recalled²⁰ that there is a contribution of 2.2 eu to the observed ΔS° from the degeneracy of the triplet state. The remaining contribution arises principally from the preferential solvation of the planar form. This latter effect appears to be somewhat higher than that generally found for the Ni(chelate)₂ complexes, perhaps due to the necessarily polar character of the *cis* planar arrangement in Ni(dpp)X₂.

Complexes of Nickel(0)

Two zerovalent nickel ditertiary phosphine compounds Ni[(C₆H₅)₂P(CH₂)_nP(C₆H₅)₂]₂ where *n* = 2, 3 have been prepared, following a suggestion of Olechowski, *et al.*,²⁴ through the direct reaction of nickelocene and a ditertiary phosphine. Ni(dpe)₂ has been previously reported while Ni(dpp)₂ is new. Refluxing the reactants in toluene with precipitation of the complex by addition of methanol produced the compounds in good yield without having to use the highly toxic nickel tetracarbonyl.

Complexes of Nickel(III)

Two complexes of nickel(III) have been isolated: Ni[(C₆H₅)₂P(CH₂)_nP(C₆H₅)₂]₂Br₃, *n* = 2, 3. These were prepared by direct action of a benzene solution of bromine on the corresponding solid nickel(II) compounds. Once prepared, decomposition is observed on dissolution in other solvents. The room-temperature powder magnetic moments are $\mu_{\text{eff}} =$

2.02 and 1.93 BM for Ni(dpe)Br₃ and Ni(dpp)Br₃, respectively. Powder epr signals have been observed at room and liquid nitrogen temperature. In particular for Ni(dpp)Br₃ one broad symmetrical resonance with $\Delta H_{1/2} = 122$ gauss (derivative peak to peak) centered at *g* = 2.218 was observed. Calculating μ_{eff} from eq 4 with *g* = 2.218 and assuming a low-

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \quad (4)$$

spin d⁷ system, *i.e.*, *S* = 1/2, $\mu_{\text{eff}} = 1.92$ BM, in excellent agreement with the moment measured by the Gouy method. This moment is characteristic of low-spin d⁷ and agrees with the values of 1.7–1.9 BM reported for Ni[(C₂H₅)₃P]₂Br₃²⁵ and 2.00 BM reported for Ni(TEP)Br₃.⁵ The optical mull and solution spectra appear qualitatively similar, even though some decomposition on dissolution was observed. The Ni(dpe)Br₃ mull spectrum shows two steplike shoulders occurring at 7950 and 14,100 cm⁻¹ on an intense absorption peaked at 20,800 cm⁻¹. Only a very intense absorption beginning at 25,000 cm⁻¹ was observed in the higher energy region. The Ni(dpp)Br₃ mull spectrum agrees qualitatively with the band envelopes observed for the low-energy transitions in Ni(dpe)Br₃; the corresponding transitions are at 7580, 13,500, and 20,600 cm⁻¹. In contrast to the dpe complex, however, a shoulder at 25,000 cm⁻¹ and peak at 29,400 cm⁻¹ are observed in the higher energy region. These spectra are not readily interpretable. For either trigonal bipyramidal (C_{2v} symmetry) or square pyramidal geometry (C_s symmetry), the d orbital degeneracy is completely removed and four spin-allowed transitions are predicted. No unambiguous assignment can be made. Further, the expected *g*-tensor anisotropy is not apparent in the powder epr data even at liquid nitrogen temperature. Clearly additional work is needed to understand the electronic and magnetic properties of these complexes.

Acknowledgment.—We wish to thank Professor J. Turkevich and Mr. G. Kemmerer for enabling us to obtain the epr spectra.

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