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

$$^{n}f(\mathrm{L})^{\mathrm{Fe}}{}_{\mathrm{CO}} = 1.1472\,^{n}f(\mathrm{L})^{\mathrm{Ni}}{}_{\mathrm{CO}} - 2.732 \qquad \delta = \pm 0.03 \qquad (5)$$

where $^{n}f(\mathrm{L})^{\mathrm{M}}{}_{\mathrm{XO}}$ indicates the principal force constant for the XO oscillator, where $n$ CO groups have been replaced by ligand, L, and M is the metal under consideration.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 $\delta$ 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 $f_{\mathrm{NO}}$ is less sensitive to a change in ligand for the cobalt, iron, and manganese compounds relative to a change in the $f_{\mathrm{CO}}$ of nickel. In the cobalt and iron compounds, however, the $f_{\mathrm{CO}}$ is more sensitive to a change in ligand relative to the same standard. These equations allow predictions of either $^{n}f(\mathrm{L})^{\mathrm{M}}{}_{\mathrm{CO}}$, $^{n}f(\mathrm{L})^{\mathrm{M}}{}_{\mathrm{NO}}$, or $^{n}f(\mathrm{L})^{\mathrm{Ni}}{}_{\mathrm{CO}}$ to be made if one of the molecules is known. For example, the molecule $\mathrm{Co(NO)(PCl_3)_3}$ has not been reported; however, using $f_{\mathrm{CO}}$ for $\mathrm{Ni(CO)(PCl_3)_3}$ (Table V), $f_{\mathrm{NO}}$ for the cobalt derivative is predicted to be 14.29 and the NO stretching frequency at 1802 $\mathrm{cm^{-1}}$. 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 Equilibrium[1]

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 $\mathrm{(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2}$ ($n$ = 1, 2, or 3) are reported and studied by spectral and magnetic methods. In solution in organic solvents complexes of the type $\mathrm{Ni[(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2]X_2}$ 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 $\mathrm{Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]Br_3}$ 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 $\mathrm{Ni[(C_6H_{11})_2P(CH_2)_{\mathit{n}}P(C_6H_{11})_2]Br_2}$ ($n$ = 3, 4, 5) have been prepared by Issleib and Hohlfeld.[3] Chatt and Hart[4] described the complexes $\mathrm{Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]Cl_2}$ and $\mathrm{Ni(\mathit{o}\text{-}C_6H_4[P(C_2H_5)_2]_2)X_2}$, X = Cl, Br, I. Wymore and Bailar[5] reported $\mathrm{Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]X_2}$, $\mathrm{Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2](ClO_4)_2}$, and $\mathrm{Ni[(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2]Br_3}$. While the present investigation of complexes formed by nickel halides with the ditertiary phosphines $\mathrm{(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2}$ ($n$ = 1, 2, 3), abbreviated dpm, dpe, and dpp, respectively, was in progress, Booth and Chatt[6] 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 $\mathrm{Ni[(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2]_{\mathit{m}}X_2}$, where for $m$ = 1, $n$ = 2, 3, X = Cl, Br, I and for $m$ = 2, $n$ = 1, 2, X = Cl, Br, I, and $\mathrm{Ni[(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2]Br_3}$, for $n$ = 2, 3. The $\mathrm{Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]X_2}$ compounds exhibit a square-planar (diamagnetic) $\rightleftarrows$ 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, $\mathrm{Ni[(C_6H_5)_2P(CH_2)_{\mathit{n}}P(C_6H_5)_2]_2}$, 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

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(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. Hohlfeld, *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).**—$NiCl_2 \cdot 6H_2O$ (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 $Ni[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2Cl_2$: 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 $Ni[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2Br_2$: 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 $Ni[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2I_2$: C, 55.50; H, 4.07. Found: C, 55.73; H, 4.04.

**Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II).**[6]—$NiCl_2 \cdot 6H_2O$ (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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Cl_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Br_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]I_2$: 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 Chatt[6] as well as a new way. Ligand dpe (0.137 g, 0.344 mmole) and previously prepared $Ni(dpe)Br_2$ (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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Br_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2I_2$: 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 $NiCl_2 \cdot 6H_2O$ (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 $Ni[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]Cl_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]Br_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]I_2$: C, 44.68; H, 3.59. Found: C, 44.85; H, 3.74.

**Tribromo[1,2-bis(diphenylphosphino)ethane]nickel(III).**—To $Ni(dpe)Br_2$ 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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Br_3$: 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 $Ni(dpp)Br_2$, the complex is a black powder that amounted to 1.055 g, or a 92.6% yield. *Anal.* Calcd for $Ni[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]Br_3$: 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 $Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$: 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 $Ni[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]_2$: C, 73.38; 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 $Ni(dpm)_2X_2$, X = Cl, Br,

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[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).

[9] Chatt and Hart[4] 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).

I. The optical spectra run in methylene chloride solution show only one band in the ~20,000 $cm^{-1}$ region before strong charge-transfer absorption takes over. No bands are observed at energies less than ~20,000 $cm^{-1}$. The bands observed for $Ni(dpm)_2X_2$ in methylene chloride solution (~3 × $10^{-4}$ *M*) are at 21,500 $cm^{-1}$ ($\epsilon_{max}$ 2600 l. $mole^{-1}$ $cm^{-1}$), 20,000 $cm^{-1}$ ($\epsilon_{max}$ 1900), and 18,700 $cm^{-1}$ ($\epsilon_{max}$ 2300), for X = 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 ~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 Cl > Br > 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 Chatt[6] 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 = Cl, Br, I, and $Ni(dpe)_2X_2$, X = 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 ~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.

Table I

Optical Spectra of $Ni(dpe)X_2$ and $Ni(dpe)_2X_2$ Compounds in Methylene Chloride Solution

| X | $Ni(dpe)X_2$ |  | $Ni(dpe)_2X_2$[a] |  |
|---|---|---|---|---|
|  | $\nu_{max}$[b] | $\epsilon_{max}$[c] | $\nu_{max}$[b] | $\epsilon_{max}$[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.

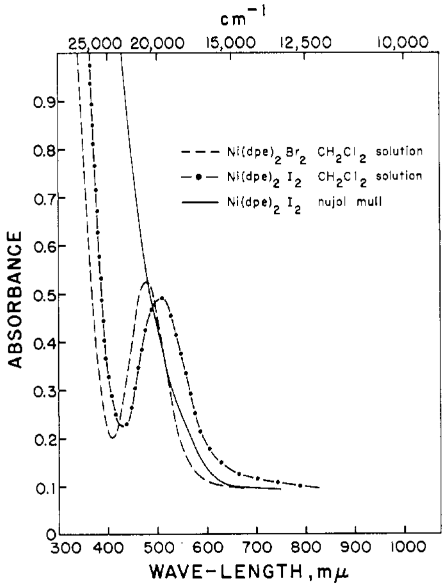

Figure 1.—Optical spectra in methylene chloride solution of $Ni(dpe)_2X_2$ for X = Br (4.04 × $10^{-4}$ *M*), X = I (3.54 × $10^{-4}$ *M*) in 1-cm cells and of the Nujol mull of $Ni(dpe)_2I_2$.

The yellow $Ni(dpe)_2X_2$ complexes are more difficult to prepare. Attempts to prepare $Ni(dpe)_2Cl_2$ 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 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 $Ni(dpe)_2I_2$ mull spectrum is shown, the bromide spectrum is quite similar. Because of the low conductivity of these dpe complexes in nitrobenzene, Booth and Chatt[6] suggest an octahedral coordination in the solid with dissociation upon solution. To assure the identity of $Ni(dpe)_2Br_2$ synthesized as previously reported[6] 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 conductivity[6] 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

$$Ni(dpe)_2X_2 \rightleftharpoons Ni(dpe)X_2 + dpe$$

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

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(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 $Ni(dpe)_2X_2$ 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 $Ni(dpe)_2X_2$ 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($\alpha$-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 $Ni(dpp)X_2$, X = Cl, Br, I, are obtained. As solids these are diamagnetic and mull spectra show only one band at ~20,000 $cm^{-1}$, which is ascribed to the ${}^1A_1 \rightarrow {}^1B_2$ transition, characteristic, as in the dpm and dpe complexes, of $C_{2v}$ square-planar geometry. The solution spectra in methylene chloride show the ~20,000 $cm^{-1}$ band as well as one at about 12,000 $cm^{-1}$. Table II presents a summary of the optical data, while Figure 2 shows the spectra recorded on methylene chloride solutions for X = Cl, Br, I and the mull spectrum of the iodide. The appearance of a band in the region 12,500–10,000 $cm^{-1}$ is indicative[16,17] of the presence of a tetrahedral isomer. If the apparent intensity of the band at ~12,200 $cm^{-1}$ is proportional to the fraction of tetrahedral isomer present, then this fraction decreases in the order $Ni(dpp)I_2 > Ni(dpp)Br_2 > Ni(dpp)Cl_2$. 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 $\nu_{max}$ | Methylene chloride solution[a] $\nu_{max}$[b] | $\nu_{max}$[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] ~5 × $10^{-4}$ *M*. [b] $\epsilon$ in l. $mole^{-1}$ $cm^{-1}$ in parentheses, $\nu$ in $cm^{-1}$.

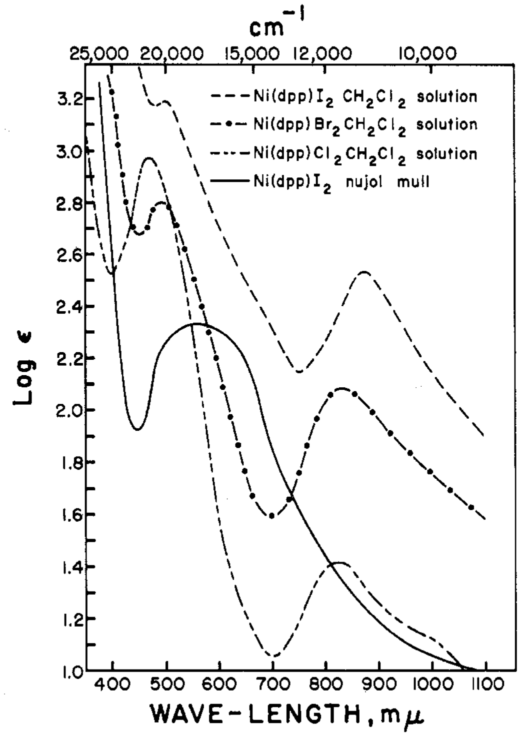

Figure 2.—Optical spectra of $Ni(dpp)X_2$ in methylene chloride solution for X = Cl (4.47 × $10^{-4}$ *M*), X = Br (7.84 × $10^{-4}$ *M*), X = I (1.02 × $10^{-3}$ *M*) recorded in 1-cm cells and of the Nujol mull of $Ni(dpp)I_2$ (absorbance of mull arbitrary units).

Square-planar ⇄ tetrahedral equilibria in nickel(II) chelates have been studied recently[18,19] employing 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

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

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

resonance shift for the $i$th proton defined by $\Delta\nu_i = \nu_{i,paramag} - \nu_{i,diamag}$, $\gamma_e$ and $\gamma_H$ are the magnetogyric ratios of the electron and proton, respectively, $A_i$ is the isotropic hyperfine interaction constant, $\mu_\infty$ is the magnetic moment of the pure tetrahedral species, $\mu_{eff}$ is the effective magnetic moment of a solution containing both diamagnetic and paramagnetic species, $\Delta G°$ 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 $Ni(dpp)I_2$, $\mu_{eff}$ 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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(13) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(14) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(15) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

(16) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958), and other papers in this series, especially IV, *ibid.*, 693 (1962).

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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 $\Delta G°$ 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 $\alpha$ and $\beta$ 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 (pseudocontact) 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 $\alpha$ and $\beta$ 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.

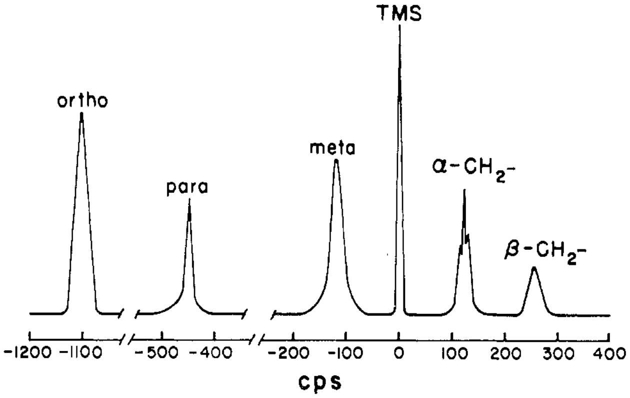

Figure 3.—Pmr spectrum of Ni(dpp)$I_2$ in $CDCl_3$ at 38°.

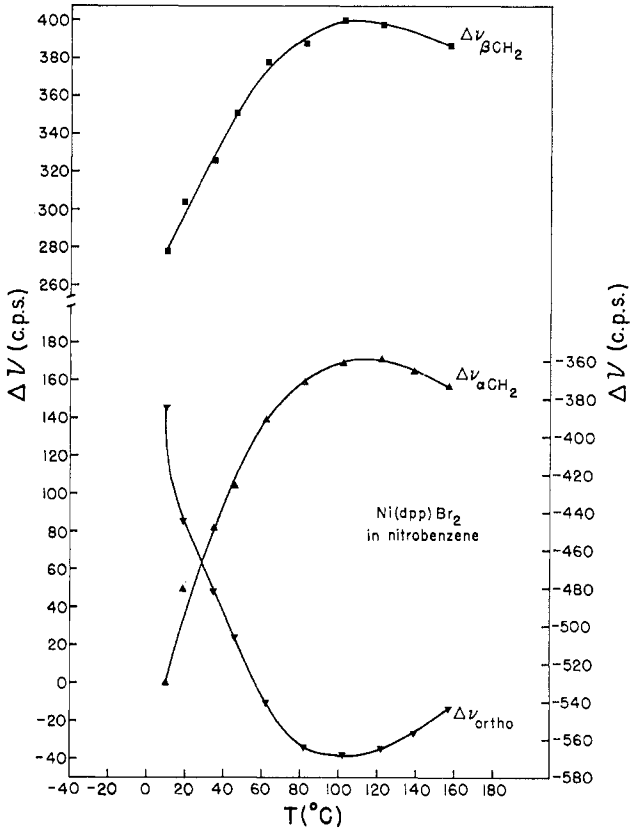

Figure 4.—Isotropic shifts of the phenyl *ortho* and $\alpha$ and $\beta$ methylene protons of Ni(dpp)$Br_2$ in nitrobenzene *vs.* temperature. The phenyl protons are referenced to −438 cps from TMS as diamagnetic position, while the $\alpha$ and $\beta$ methylene protons are referenced to the diamagnetic 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.

In order to calculate thermodynamic parameters for the conformational equilibria in solution from the temperature variation of the isotropic shifts using eq 1, $A_i$ values, which contain both contact and dipolar contributions, must be obtained. This was done by calculating $\Delta G°$ at one temperature with eq 2 from the $\mu_{eff}$ of the solutions obtained by the Gouy method. To do this, however, $\mu_\infty$ 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 $Ni[PR(C_6H_5)_2]_2X_2$, R = alkyl.[17] Using $\Delta G°$ obtained from eq 2 and the

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[21] W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

[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).

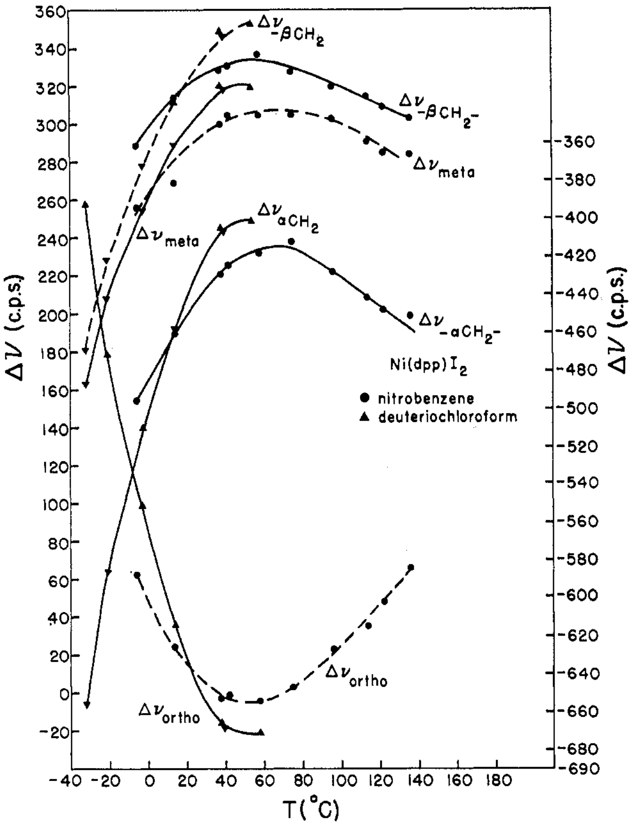

Figure 5.—Isotropic shifts of the phenyl *ortho*, *meta*, and $\alpha$ and $\beta$ methylene protons of $Ni(dpp)I_2$ in nitrobenzene and deuteriochloroform *vs.* temperature. The phenyl protons are referenced to −438 cps from TMS as diamagnetic position, while the $\alpha$ and $\beta$ methylene protons 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.

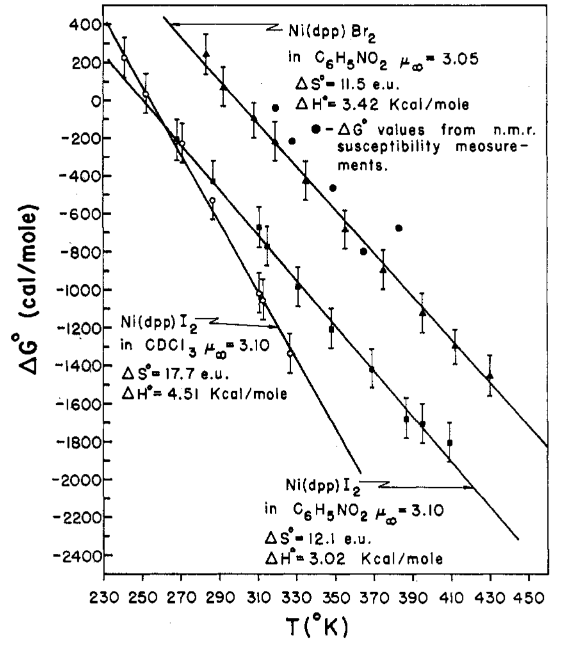

Figure 6.—$\Delta G°$ *vs.* $T$ for observed square-planar–tetrahedral equilibria in $Ni(dpp)X_2$ (X = Br, I) systems.

TABLE III

THERMODYNAMIC PARAMETERS FOR THE PLANAR–TETRAHEDRAL EQUILIBRIUM[a]

| Solvent | $Ni(dpp)Br_2$ Nitrobenzene | $Ni(dpp)I_2$ Nitrobenzene | Chloroform |
|---|---|---|---|
| $\Delta H°$[b] | 3.42 | 3.02 | 4.51 |
| $\Delta S°$[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.

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 $\Delta G°$ 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

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

shifts were used to obtain the free energies. The thermodynamic parameters $\Delta S°$ and $\Delta H°$ are indicated in Table III. The estimated uncertainty in $\Delta G°$ is ±120 cal/mole. The major sources of error are the measurement of $\Delta G°$ from the solution magnetic susceptibility used to calculate $A_i$ and the uncertainty in $\mu_\infty$. Less satisfactory plots of $\Delta G°$ *vs.* $T$ are obtained for values of $\mu_\infty$ 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 $\Delta H°$ and $\Delta S°$ (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 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 measurements[16] on benzene solutions of the complexes $Ni[R(C_6H_5)_2P]_2X_2$, R = butyl, benzyl, allyl, where the percentage of tetrahedral form in solution was found to increase in the order Cl < Br < 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 study[8] of the dpp and dpe derivatives of $Ni(CO)_4$ and $Co(CO)_3(NO)$ shows these ligands to have only extremely small differences in their $\pi$-acceptor abilities. The increased chain length of dpp allows the $-P(C_6H_5)_2$ 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 $Ni(dpp)I_2$ by chloroform. It should be recalled[20] that there is a contribution of 2.2 eu to the observed $\Delta S°$ 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)$X_2$.

### Complexes of Nickel(0)

Two zerovalent nickel ditertiary phosphine compounds $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_2$ 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: $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Br_3$, $n$ = 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 $\mu_{eff}$ = 2.02 and 1.93 BM for $Ni(dpe)Br_3$ and $Ni(dpp)Br_3$, respectively. Powder epr signals have been observed at room and liquid nitrogen temperature. In particular for $Ni(dpp)Br_3$ one broad symmetrical resonance with $\Delta H_{1/2}$ = 122 gauss (derivative peak to peak) centered at $g$ = 2.218 was observed. Calculating $\mu_{eff}$ from eq 4 with $g$ = 2.218 and assuming a low-

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

spin d$^7$ system, *i.e.*, $S = {}^1/_2$, $\mu_{eff}$ = 1.92 BM, in excellent agreement with the moment measured by the Gouy method. This moment is characteristic of low-spin d$^7$ and agrees with the values of 1.7–1.9 BM reported for $Ni[(C_2H_5)_3P]_2Br_3$[25] and 2.00 BM reported for $Ni(TEP)Br_3$.[5] The optical mull and solution spectra appear qualitatively similar, even though some decomposition on dissolution was observed. The $Ni(dpe)Br_3$ 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 $Ni(dpp)Br_3$ mull spectrum agrees qualitatively with the band envelopes observed for the low-energy transitions in $Ni(dpe)Br_3$; 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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[25] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).