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A Nuclear Magnetic Resonance Study on the Interconversion of the Complexes $[Ni(N_3P)X]B(C_6H_5)_4$ and the Crystal Structure of the Complex $[Ni(N_3P)Br]B(C_6H_5)_4$

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It is well known that $[Ni(N_3P)X]B(C_6H_5)_4$ complexes, where N_3P = bis(2-diethylaminoethyl)(2-diphenylphosphinoethyl)-amine, can be either high-spin five-coordinated or low-spin planar complexes when X = Cl or Br, and when X = I, only the low-spin form is formed.[1] The structure of the low-spin $[Ni(N_3P)Br]B(C_6H_5)_4$ compound was determined by X-ray analysis and refined to an R factor of 8.2%. The unit cell is monoclinic with $a = 12.077 \pm 0.004$ Å, $b = 25.230 \pm 0.012$ Å, $c = 16.254 \pm 0.018$ Å, and $\beta = 110° 39' \pm 2'$. This structure has shown that the chromophore is NiN_2PBr and therefore one N atom is not bonded. In $CDCl_3$ solution the chloro and bromo derivatives give rise to a temperature-dependent equilibrium between the trigonal-bipyramidal and planar forms. The thermodynamic functions $\Delta G°$, $\Delta H°$, and $\Delta S°$ of this equilibrium, calculated at 299°K from proton isotropic shift measurements, were found to be 1.0 and 1.1 kcal mole^{-1} ($\Delta G°$), 1.3 and 0.9 kcal mol^{-1} ($\Delta H°$), and 7.2 and 6.7 eu ($\Delta S°$) for the chloro and bromo derivatives, respectively. $\Delta G°$ for the iodo derivative has been estimated $\geqslant 2$ kcal mol^{-1}.

Introduction

In the course of a systematic study of the complexing properties of "hybrid" tripod ligands containing nitrogen and phosphorus as the donor atoms, the nickel(II) complexes of bis(2-diethylaminoethyl)(2-diphenylphosphinoethyl)amine (N_3P), having the general formula $[Ni(N_3P)X]B(C_6H_5)_4$(X = Cl, Br, I), were prepared and characterized.[1] All the complexes, except the iodo derivative which is only planar and diamagnetic, were isolated either as paramagnetic trigonal-bipyramidal[2] or planar diamagnetic isomers.[1] In the diamagnetic compounds the N_3P ligand is tridentate. The paramagnetic isomers can also be obtained by heating the latter complexes at about 160°.

The electronic spectra of the chloro and bromo derivatives, in deuteriochloroform solution, indicate the existence of a temperature-dependent equilibrium between the two forms, which has been investigated by a proton magnetic resonance study in order to determine the functions $\Delta G°$, $\Delta H°$, and $\Delta S°$ of the equilibrium.

An X-ray analysis of the diamagnetic bromo derivative has been performed in order to determine the chromophore of the planar form, *i.e.*, which atom of the N_3P set is not bound to the metal.

Experimental Section

The preparation and characterization of all the compounds have been reported elsewhere.[1] The absorption spectra were recorded with a Beckman DK-2 spectrophotometer using 1-cm silica cells. The solutions were $\simeq 10^{-2}$ M in $CDCl_3$. All the proton magnetic resonance spectra of the $CDCl_3$ solutions were recorded on a Varian DA-60 using the internal lock technique (on TMS).

Collection of X-Ray Data.—The $[Ni(N_3P)Br]B(C_6H_5)_4$ red crystals are very stable to air and X-rays. The unit cell is monoclinic with $a = 12.077 \pm 0.004$ Å, $b = 25.230 \pm 0.012$ Å, $c = 16.254 \pm 0.018$ Å, $\beta = 110° 39' \pm 2'$, $V = 4634.4$ Å^3, $d_m = 1.27$ g cm^{-3}, $Z = 4$, $M = 885.46$, and $d_c = 1.267$ g cm^{-3}. The space group is $P2_1/c$ from systematic absences of reflections $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Cell parameters were determined by least-squares refinement of 19 selected 2ϑ values. The crystal used for the collection of the intensities was a parallelepiped of dimensions 0.30 × 0.20 × 0.08 mm. The radiation used was Mo Kα (λ 0.70926 Å), and the linear absorption coefficient was calculated to be 7.64 cm^{-1}. Data were collected on a four-circle Hilger automatic diffractometer, using a ϑ–ω scan technique. Scans of 120 sec, with steps of 0.02° and a count of 2 sec for each step, were taken across the peaks; background was counted for 10 sec on each side of the peak. Two standard reflections were counted periodically each 60 measurements of reflections. No differences larger than 5% were found in these measurements. Of the 4424 reflections measured, using the limitation $2\vartheta \leq 40°$, the 980 having intensity greater than 3.5 standard deviations on the intensity itself were considered observed reflections and were used in the structure analysis (see below). The intensities were calculated using the expression $I = P - 0.5(T_p/T_b)(B_1 + B_2)$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background. The standard deviations on the intensities were calculated with the expression $\sigma = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{1/2}$.[3]

Lorentz–polarization correction was applied to the observed reflections. Scattering factors for nonhydrogen and hydrogen atoms were taken from ref 4 and 5, respectively. No correction was made for absorption in view of the rather low linear absorption coefficient and the smallness of the crystal. Transmission factors were in the range 0.8–0.9.

Solution and Refinement of the Structure.—The positions of the bromine and nickel atoms were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of the nonhydrogen atoms except for some carbon atoms of the ethyl groups. In this structure one of the two arms with terminal nitrogen is free; *i.e.*, the terminal nitrogen is not bonded to the metal. A ΔF Fourier synthesis, calculated at this point, showed also the positions of the carbon atoms not found in the previous Fourier. This ΔF Fourier also evidenced that the ethyl groups linked to the nitrogen atom of the free arm (N_3) have two statistical positions, since this synthesis showed peaks corresponding to two different orientations of these groups.

Refinement was performed with the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[6] The minimized function was $\Sigma w(|F_o| - |F_c|)^2$ in which w is the weight assigned to the F_o values, in accordance with the following scheme: $w = 1$ for $F_o \leq 150$, and $\sqrt{w} = 150/F_o$ for $F_o > 150$. Individual isotropic temperature factors were used for boron and carbon atoms whereas heavier atoms were allowed to vibrate anisotropically. A ΔF Fourier synthesis calculated at an intermediate stage of the refinement showed 22 of the 62 hydrogen

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[1] L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2904 (1969).

[2] An X-ray analysis in progress in this laboratory on the $[Co(N_3P)Cl]ClO_4$ complex has shown that the structure of the coordination polyhedron is very close to a trigonal bipyramid. This compound is isospectral with the tetraphenylborate derivative which is isomorphous with the nickel analog.[1]

[3] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[4] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[5] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

[6] J. M. Stewart, Technical Report TR 64-6, University of Maryland, Computer Science Center, 1964.

TABLE I

POSITIONAL PARAMETERS ($\times 10^4$), ANISOTROPIC TEMPERATURE FACTORS[a] ($\times 10^4$), AND ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	8858 (4)	2573 (2)	1564 (2)	143 (6)	21 (1)	37 (2)	−2 (2)	29 (3)	−6 (1)
Ni	8936 (5)	2970 (2)	2856 (3)	72 (6)	16 (1)	25 (2)	−2 (3)	18 (3)	−6 (2)
P	8408 (10)	3705 (4)	2172 (6)	101 (15)	16 (2)	30 (6)	−5 (5)	36 (8)	−4 (3)
N(1)	8916 (24)	3346 (12)	3899 (15)	60 (34)	18 (7)	23 (16)	−17 (14)	−15 (18)	8 (9)
N(2)	9598 (26)	2330 (12)	3624 (16)	127 (38)	23 (8)	36 (15)	−22 (15)	23 (21)	6 (9)
N(3)	6172 (28)	3463 (13)	4551 (20)	130 (50)	31 (10)	74 (22)	20 (18)	17 (27)	−20 (12)

[a] Anisotropic thermal factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE II

POSITIONAL PARAMETERS ($\times 10^4$), ISOTROPIC TEMPERATURE FACTORS, AND ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	B, Å^2
C(1)	9421 (38)	3889 (17)	3930 (26)	3.3 (1.1)
C(2)	8635 (46)	4165 (20)	3066 (32)	5.5 (1.4)
C(3)	9712 (38)	3056 (18)	4652 (26)	3.7 (1.1)
C(4)	9561 (41)	2448 (21)	4538 (30)	5.6 (1.2)
C(5)	7686 (39)	3270 (17)	3886 (27)	3.6 (1.1)
C(6)	7413 (47)	3559 (19)	4643 (30)	5.4 (1.3)
C(7)	929 (56)	2368 (26)	3683 (36)	8.8 (1.8)
C(8)	1627 (76)	2061 (34)	4091 (54)	16.8 (2.7)
C(9)	8917 (58)	1800 (24)	3348 (37)	8.5 (1.7)
C(10)	7569 (57)	1847 (23)	3025 (36)	8.7 (1.7)
C(11)	5565 (147)	2905 (65)	4622 (91)	12.4 (4.5)
C(11′)	5560 (128)	3756 (56)	4133 (89)	9.2 (3.8)
C(12)	4276 (80)	2955 (37)	4095 (53)	4.5 (2.0)
C(12′)	4879 (131)	3343 (66)	3700 (93)	12.9 (4.2)
C(13)	5785 (121)	3778 (58)	5233 (89)	8.7 (3.6)
C(13′)	6390 (130)	3557 (61)	5574 (97)	12.9 (5.0)
C(14)	5683 (105)	4240 (48)	4879 (79)	7.6 (3.1)
C(14′)	6269 (120)	4204 (54)	5591 (89)	8.3 (3.9)
C(15)	9384 (43)	3943 (18)	1622 (29)	4.1 (1.2)
C(16)	546 (46)	3914 (18)	2012 (29)	4.5 (1.2)
C(17)	1371 (44)	4024 (19)	1582 (31)	5.1 (1.2)
C(18)	873 (51)	4244 (20)	721 (34)	6.0 (1.4)
C(19)	9659 (57)	4233 (21)	270 (36)	7.1 (1.6)
C(20)	8907 (37)	4075 (17)	742 (27)	3.4 (1.1)
C(21)	6922 (47)	3858 (23)	1482 (32)	6.3 (1.3)
C(22)	6354 (60)	4330 (25)	1363 (38)	7.8 (1.6)
C(23)	5197 (69)	4407 (29)	847 (46)	10.7 (2.0)
C(24)	4508 (57)	3968 (29)	400 (38)	7.6 (1.6)
C(25)	5066 (68)	3508 (30)	476 (43)	6.6 (2.1)
C(26)	6277 (67)	3447 (28)	991 (45)	6.8 (1.9)
C(27)	1875 (46)	856 (19)	2278 (31)	5.0 (1.2)
C(28)	2235 (53)	603 (23)	3097 (37)	5.8 (1.6)
C(29)	1426 (51)	450 (18)	3438 (32)	3.8 (1.2)
C(30)	211 (52)	505 (21)	2987 (37)	5.6 (1.4)
C(31)	−154 (50)	752 (21)	2224 (36)	5.4 (1.4)
C(32)	605 (47)	909 (20)	1822 (29)	4.1 (1.2)
C(33)	3072 (49)	1688 (20)	1784 (28)	5.5 (1.2)
C(34)	2088 (41)	2036 (18)	1807 (27)	5.0 (1.1)
C(35)	2276 (40)	2578 (20)	1742 (25)	5.0 (1.1)
C(36)	3300 (48)	2773 (18)	1707 (28)	4.7 (1.2)
C(37)	4224 (44)	2399 (24)	1732 (29)	6.2 (1.3)
C(38)	4085 (51)	1881 (23)	1760 (32)	9.0 (1.4)
C(39)	2410 (38)	804 (18)	814 (26)	3.1 (1.0)
C(40)	1708 (44)	366 (19)	511 (30)	5.1 (1.2)
C(41)	1470 (45)	99 (20)	−334 (32)	4.9 (1.3)
C(42)	1964 (56)	371 (25)	−904 (39)	7.0 (1.7)
C(43)	2507 (43)	854 (21)	−703 (30)	2.7 (1.2)
C(44)	2759 (41)	1017 (18)	158 (29)	4.1 (1.1)
C(45)	4219 (52)	721 (23)	2384 (35)	6.1 (1.4)
C(46)	4872 (52)	1010 (23)	3208 (35)	6.0 (1.4)
C(47)	5974 (66)	772 (29)	3628 (42)	9.1 (1.9)
C(48)	6380 (64)	389 (31)	3341 (50)	7.6 (2.1)
C(49)	5742 (65)	109 (24)	2545 (43)	10.5 (1.7)
C(50)	4578 (57)	338 (24)	2002 (35)	7.1 (1.5)
B	2856 (53)	1050 (22)	1824 (33)	4.1 (1.4)

atoms. The hydrogen atoms found in this synthesis were introduced in the subsequent refinement with an overall temperature factor of 5.0 Å^2 and were not refined. Also the occupancy factors of the carbon atoms, showing two statistical positions, were refined: the results confirm that they are about 50%, and this value was assumed in the final refinement.

A terminal carbon atom of one ethyl group, C(8), belonging to the nitrogen linked to the nickel atom (N_2) showed a very high temperature factor and the distance from the other carbon atom of the ethyl group was unusually short (C(7)–C(8) = 1.16 (10) Å). However the R factor calculated without this carbon atom increased by about one unit and a ΔF Fourier synthesis showed a diffuse positive zone around the position of this atom. Therefore this atom was also included in the final refinement. Also in the free arm the temperature factors were found very high and this thermal motion seems to be transmitted to the whole structure. This feature can account for the small number of observed reflections.[7] At the end of refinement the R factor, defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 8.2%. The final values of the parameters and their standard deviations are shown in Tables I–III.

TABLE III

POSITIONAL PARAMETERS ($\times 10^3$) OF THE HYDROGEN ATOMS[a]

Atom	x/a	y/b	z/c
H(1′)	953	413	458
H(1″)	32	389	407
H(2′)	770	412	310
H(2″)	914	450	343
H(3′)	938	187	23
H(3″)	73	290	480
H(4′)	854	230	450
H(5′)	735	287	345
H(5″)	670	343	337
H(6′)	782	165	23
H(17)	222	407	200
H(20)	814	390	50
H(22)	670	467	206
H(25)	448	314	0
H(28)	305	65	340
H(29)	157	13	394
H(30)	947	33	332
H(35)	168	276	170
H(41)	908	38	60
H(43)	272	377	360
H(44)	330	150	22
H(50)	392	0	128

[a] The figure in parentheses refers to the carbon atom to which hydrogens are attached.

The standard deviations were calculated using the expression $\sigma_j = [\Sigma w\Delta F^2 a^{jj}/(m - n)]^{-1/2}$, where m is the number of reflections, n the number of parameters, and a^{jj} the jjth element of the inverse least-squares matrix. The rather high values of the standard deviations may be ascribed again to thermal motion and to the small number of observed reflections. A difference Fourier map calculated with the final parameters did not show any special feature. The maximum height of the peaks was one-fifth the height of a carbon atom which was not included in this calculation.

Results

The structure of the Br derivative consists of discrete

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[7] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

Ni(N$_3$P)Br$^+$ cations and B(C$_6$H$_5$)$_4^-$ anions. The coordination geometry around the nickel atom is square planar, the donor atoms being the phosphorus and two nitrogen atoms of the potentially tetradentate ligand and the bromine atom (Figure 1). The third nitrogen atom of the ligand is not bonded at all, the distance Ni–N(3) being 5.17 (3) Å. This is consistent with the identity of the electronic spectra of the Ni(N$_2$PDX)$^+$ complexes (X = Cl, Br, I; D = N, O, S) reported elsewhere.[8] Bond lengths and angles of the chromophore are reported in Table IV. The least-squares plane through the four donor atoms was found to have the equation 0.987x + 0.609y − 0.232z = 1 (monoclinic coordinates). The displacements of these atoms and of the metal from this plane are very small: Ni, −0.03; Br, −0.06; P, 0.06; N(1), −0.07; N(2), 0.06 Å. The metal donor atoms distances are in the range of values for analogous distances found in other square-planar nickel(II) complexes.[9] Also the distances and angles within the ligand and the anion are normal within two standard deviations, except for some distances and angles concerning ethyl groups bonded to the N(2) and N(3) atoms. This is probably due to high thermal motion and disorder effects, as mentioned in the previous section, which prevent an accurate location of these carbon atoms. Table V reports the average values of the distances. No intermolecular contacts shorter than 3.45 Å were found in this structure.

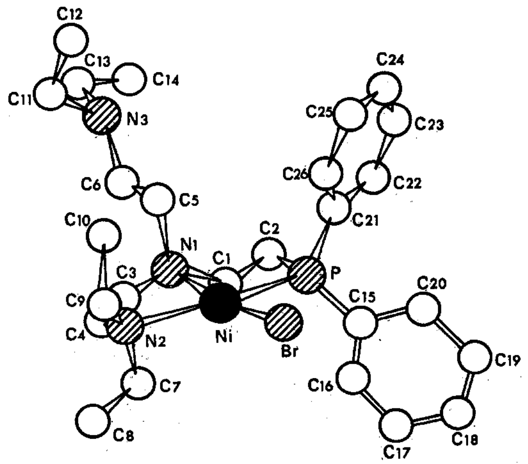


Figure 1.—A perspective view of the configuration of the complex cation Ni(N$_3$P)Br$^+$.

TABLE IV

DISTANCES AND ANGLES IN THE COORDINATION GROUP WITH THEIR ESTIMATED STANDARD DEVIATIONS

	Distance, Å	
Ni–Br	2.298	0.006
Ni–P	2.141	0.011
Ni–N(1)	1.951	0.025
Ni–N(2)	2.024	0.028
	Angle, Deg	
Br–Ni–P	89.7	0.3
Br–Ni–N(1)	175.6	0.9
Br–Ni–N(2)	95.5	0.8
P–Ni–N(1)	86.3	0.9
P–Ni–N(2)	172.5	0.9
N(1)–Ni–N(2)	88.6	1.1

TABLE V

AVERAGE VALUES OF THE DISTANCES (Å) IN THE LIGAND MOLECULE AND IN THE TETRAPHENYLBORATE WITH THEIR AVERAGE STANDARD DEVIATIONS

			Range^a
P–C	1.80	0.05	1.79–1.81
N–C	1.49	0.09	1.10–1.61
C–C (aliphatic)	1.46	0.13	1.16–1.64
C–C (phenyl groups)	1.39	0.08	1.25–1.49
B–C	1.69	0.08	1.64–1.78

[a] The unreasonable low values of some N–C and C–C (aliphatic) distances are due to the high thermal motion and disorder of the ethyl groups.

The electronic spectra of the chloro complex in deuteriochloroform solution between +25 and −20° are shown in Figure 2. By decreasing the temperature the peaks characteristic of the trigonal-bipyramidal NiN$_3$PCl chromophore (7–14 kK) gain in intensity whereas the peak at 16 kK due to the planar NiN$_2$PCl chromophore decreases in intensity. This behavior is reversible and the isosbestic point at *ca.* 16,000 cm^{-1} indicates the presence of a two-species equilibrium.

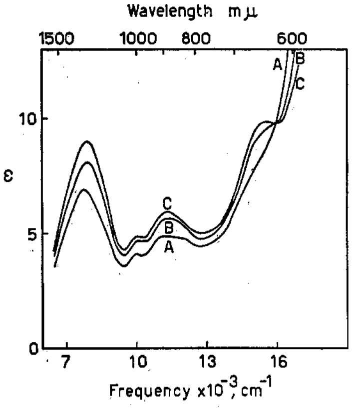
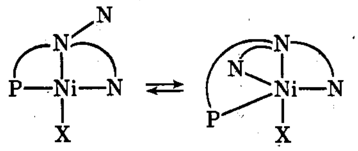


Figure 2.—Electronic spectra of the [Ni(N$_3$P)Cl]B(C$_6$H$_5$)$_4$ complex in deuteriochloroform solution: A, 25°; B, −13°; C, −25°.

Proton magnetic resonance spectra of the chloro and bromo derivatives in CDCl$_3$ show small upfield and downfield isotropic shifts (Figure 3) which increase by decreasing the temperature. The temperature dependences of the chemical shifts are shown in Figure 4. No apparent isotropic shifts are shown by the NiN$_3$PI$^+$ complex in the range of temperature +26 to −50° (see Figure 3).

Discussion

Pmr spectra as well as electronic spectra are consistent with an equilibrium of the type (X = Cl, Br)



diamagnetic paramagnetic

The equilibrium is shifted toward the right by decreasing the temperature. The pmr peaks, which are averaged over the two forms in rapid (on nmr time

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[8] R. Morassi and L. Sacconi, *J. Chem. Soc.* 1487 (1971).

[9] R. L. Braun and E. C. Lingafelter, *Acta Crystallogr.*, **21**, 546 (1966); F. D. Ayres, P. Pauling, and G. B. Robertson, *Inorg. Chem.*, **3**, 1303 (1964); B. T. Kilbourn and H. M. Powell, *J. Chem. Soc.*, 1688 (1970).

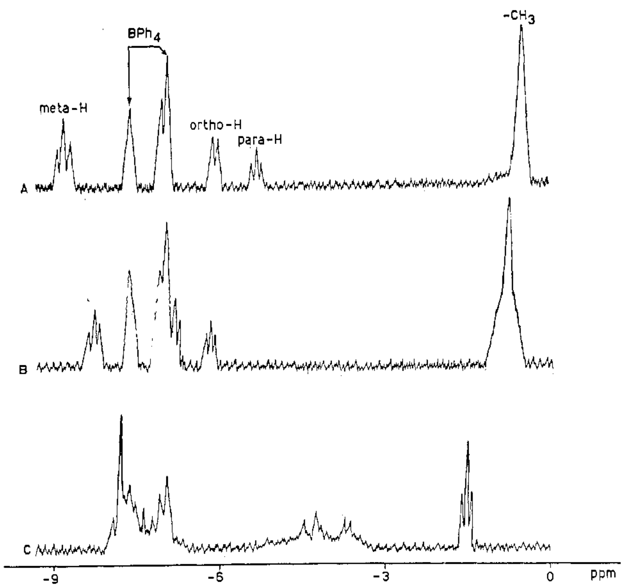

Figure 3.—Pmr traces: A, [Ni(N$_3$P)Cl]B(C$_6$H$_5$)$_4$; B, [Ni(N$_3$P)Br]B(C$_6$H$_5$)$_4$; C, [Ni(N$_3$P)I]B(C$_6$H$_5$)$_4$ (ppm from internal TMS, in CDCl$_3$ at 26°).

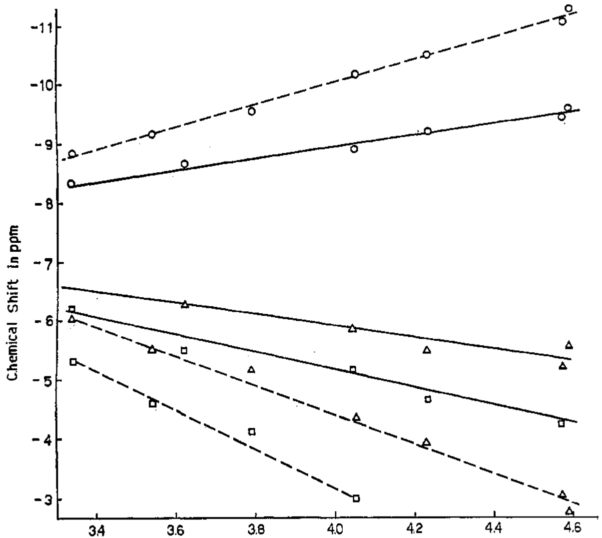

Figure 4.—Chemical shift dependence on $1/T$ for the [Ni(N$_3$P)Cl]B(C$_6$H$_5$)$_4$ (dotted line) and [Ni(N$_3$P)Br]B(C$_6$H$_5$)$_4$ (solid line) complexes: ○, meta protons; △, ortho protons; □, para protons.

scale) equilibrium, shift further from the diamagnetic positions by decreasing the temperature and at the same time become wider because of the increase in the paramagnetic form.[10] The assignment of the peaks due to the aromatic protons (as shown in Figure 3) is based on first-order spin–spin coupling ($J \simeq$ 8cps) and on intensity considerations. The isotropic shift pattern is very similar to those previously found for bis(triphenylphosphino)nickel halide complexes.[11] This indicates the lack of any appreciable anisotropic contribution to the total isotropic shifts. Moreover the chemical shifts of the B(C$_6$H$_5$)$_4$$^-$ ion, being constant with temperature, rule out the possibility of magnetic anisotropy operating through ion pairing.[12] A small upfield shift of the methyl signal has been frequently found in cases where the existence of dipolar shift contributions has been excluded.[13]

In absence of dipolar shifts, if the temperature dependence of Fermi contact shifts is known, the thermodynamic functions of the equilibrium may be easily calculated.[10,14] When the paramagnetic species has an orbitally nondegenerate ground state without any populated magnetically active excited state, the relation between the contact shift and $\Delta G°$ is given by the equation[15,16]

$$\frac{\Delta\nu_i}{\nu} = \frac{-a_i\gamma_e g\beta S(S+1)}{6S\gamma_H kT}\,[\exp(\Delta G°/RT) + 1]^{-1}$$

The five-coordinate NiN$_3$PX$^+$ complexes will probably fit this condition because of a lack of symmetry in the chromophore.[17] In any case a linear dependence of contact shifts on $1/T$ for a small range of temperatures is observed even when a more complicated equation is expected to be valid.[18] This is the case of pseudotetrahedral nickel complexes[14,19] and of some octahedral cobalt complexes.[20] Initial $\Delta G°$ values, which allow us to calculate the constant of the relation between contact shift and $1/T$, have been determined, for chloro and bromo derivatives, by magnetic measurements using Evans' method at −55°[21] (equilibrium constants K = 0.38 and 0.26 for the chloro and bromo complexes, respectively).[22]

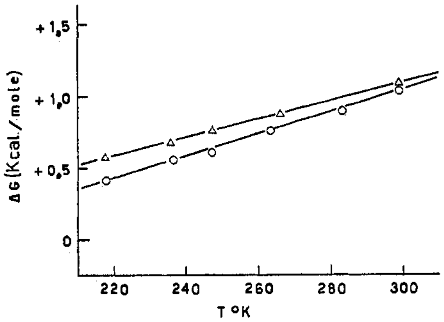

Figure 5.—ΔG *vs.* T: △, [Ni(N$_3$P)Br]B(C$_6$H$_5$)$_4$; ○, [Ni(N$_3$P)Cl]B(C$_6$H$_5$)$_4$.

A plot of $\Delta G°$ (calculated on the shifts of the meta protons) against T is reported in Figure 5. At 299°K

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$\Delta G°$ values are 1.0 and 1.1 kcal mol^{-1} for the chloro and bromo derivatives. The $\Delta H°$ and $\Delta S°$ values of 1.3 and 0.9 kcal mol^{-1} and 7.2 and 6.7 eu, respectively, for chloro and bromo complexes have been calculated by the least-squares method. Since no sizable isotropic shifts have been observed for the iodo derivative, $\Delta G°$ will presumably be >2 kcal mol^{-1}.

These $\Delta G°$ values indicate that the planar form is favored in the order $\mathrm{Cl} < \mathrm{Br} \ll \mathrm{I}$. This is consistent with the softness and π-bonding capacity of the halogens.[23] The $\Delta S°$ values, which again favor the planar form, are consistent with the entropy loss due to the attachment of a donor group which is already partially hindered.[24] Finally, the values of $\Delta H°$ are so small also on account of the large increase in bond distances in passing from the planar to trigonal-bipyramidal or tetragonal-pyramidal structures.[25] These values account for the relatively narrow range for the existence of five-coordinate nickel complexes. In fact, by going from planar complexes to hexacoordinated adducts, five-coordinate intermediates generally are just barely detectable or not formed at all.[24,26,27]

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Preparation and Proton Magnetic Resonance Spectra of Some Tetrakis(arylmethylphosphine)platinum(0) and -palladium(0) Compounds

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Several new tertiary phosphine complexes of platinum(0), including tetrakis(methyldiphenylphosphine)platinum(0) (I), tetrakis(dimethylphenylphosphine)platinum(0) (II), and tetrakis(dimethylpentafluorophenylphosphine)platinum(0) (III), have been prepared. Low-temperature nmr spectroscopic studies of I show the loss of one phosphine molecule below −30° consistent with tris(methyldiphenylphosphine)platinum(0) being the most stable species at this temperature; above −30° rapid exchange of phosphine occurs. The spectra of II and III suggest no loss of phosphine; apparently the tetracoordinate species is the most stable. Tetrakis(methyldiphenylphosphine)palladium(0) did not show any evidence of dissociation. Reactions of I and III with perfluorobut-2-yne and of I with trimethyltin chloride are described.

Introduction

The chemistry of phosphine complexes of zerovalent platinum and palladium has attracted much attention since Malatesta's first report.[1] Most of the studies[2] have used triphenylphosphine as a ligand, although this is not appropriate for proton magnetic resonance spectroscopic studies. Molecular weight measurements[2] of tetrakis(triphenylphosphine)platinum(0) have shown that the tetracoordinate species dissociates to tris- or bis-coordinate complexes by liberation of one or two molecules of triphenylphosphine, respectively

$$[(C_6H_5)_3P]_4Pt \underset{K_1}{\overset{-(C_6H_5)_3P}{\rightleftharpoons}} [(C_6H_5)_3P]_3Pt \underset{K_2}{\overset{-(C_6H_5)_3P}{\rightleftharpoons}} [(C_6H_5)_3P]_2Pt$$

In particular, bis(triphenylphosphine)platinum(0) has been described as the reaction intermediate in a number of oxidative addition reactions. From a kinetic study of the reaction of tris(triphenylphosphine)platinum(0) with diphenylacetylene or triphenyltin chloride,[3,4] the dissociation constant, K_2, of tris(triphenylphosphine)platinum(0) into the corresponding bis-coordinate complex and triphenylphosphine was calculated as (1.4–1.8) $\times 10^{-4}$ *M*. This stability of the tris-coordinate complex which has a planar structure[5] is thought to be due to strong platinum–phosphine bonding.

We have prepared tetrakis(methyldiphenylphosphine)platinum(0), tetrakis(dimethylphenylphosphine)platinum(0), tetrakis(dimethylpentafluorophenylphosphine)platinum(0), and tetrakis(methyldiphenylphosphine)palladium(0) and have studied their behavior with respect to phosphine exchange and dissociation by means of proton magnetic resonance spectroscopy at low temperatures. Some aspects of their chemical behavior are also described.

Experimental Section

Nmr measurements were made on a Varian HA-100 spectrometer with variable-temperature accessories. Samples were sealed under vacuum and measured in 8 wt % solutions in toluene-d_8 (Merck Sharp and Dohme Co. Ltd.). Analyses were carried out by Gygli Microanalysis Laboratory, Toronto. Tetrakis(methyldiphenylphosphine)palladium(0) was prepared by the method of Mukhedkar, *et al.*,[6] from methyldiphenylphosphine and π-allyl-π-cyclopentadienylpalladium.

Preparation of Tetrakis(methyldiphenylphosphine)platinum(0) (I).—To *cis*-bis(methyldiphenylphosphine)dichloroplatinum (1.27 g), suspended in 30 ml of a 2:1 ethanol–water mixture, was added methyldiphenylphosphine (0.76 g) with stirring under nitrogen. The suspension turned to a clear bright yellow solu-

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