In the present example, the ring bonds directly opposite the exocyclic C–O bonds are apparently shortened. Their lengths (C(3)–C(3)′, 1.355 Å, and C(6)–C(7), 1.369 Å) are, however, not nearly so short as the anomalous C(8)–C(9) bond[3] in the anion II, 1.288 Å.

C. The Pyridinium Ion. Bond distances in the pyridinium ion appear quite normal. The C–N distances, 1.337 and 1.345 Å, compare closely with 1.340 Å in pyridine,[28] as do our distances between β and γ carbons, 1.376 and 1.398 Å (pyridine, 1.394 Å). The distances between the α and β carbons, 1.361 and 1.362 Å, appear, however, to be slightly shorter than the 1.394-Å value in pyridine. Distortions from planarity, if any, are small: the maximum deviation from the least-squares plane through the ring atoms (Table IV) is 0.019 Å. The six hydrogen atoms were clearly resolved in chemically reasonable positions.

Acknowledgment. Our thanks go to C. L. Frye who recognized[16] the problems associated with the structure of these ions and who supplied us with the crystals.

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Four- and Five-Coordinate Nickel(II) Complexes with Monodentate Phosphines

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Abstract: Four- and five-coordinate nickel(II) complexes of phenyldimethylphosphine, $C_6H_5P(CH_3)_2$ (L), and pentafluorophenyldimethylphosphine, $C_6F_5P(CH_3)_2$ (L_F), have been synthesized and characterized. Whereas L gives both square-planar and five-coordinate complexes, L_F gives only square-planar $[Ni(L_F)_2X_2]$ complexes except for the five-coordinate $[Ni(L_F)_3(CN)_2]$. The intensely red-orange $[NiL_3(CN)_2]$ and $[Ni(L_F)_3(CN)_2]$ complexes are diamagnetic and nonelectrolytes in nitromethane. Both are assigned a *trans*-trigonal-bipyramidal structure on the basis of their electronic and vibrational spectra and a single-crystal X-ray study on $[NiL_3(CN)_2]$. Two other pentacoordinate complexes, $[NiL_3I_2]$ and $[NiL'_3(CN)_2]$ (where $L' = (C_6H_5)_2PCH_3$), were also isolated as solids. In contrast to the $[NiL_2X_2]$ complexes, none of the $[Ni(L_F)_2X_2]$ (X = Cl, Br, I, NCS) complexes showed any tendency to coordinate a third pentafluorophenyldimethylphosphine molecule in dichloromethane solution. Electronic spectra indicate that the ligand field strengths of $C_6H_5P(CH_3)_2$ and $C_6F_5P(CH_3)_2$ are very similar in analogous complexes. Dissociation constants of $[NiL_3X_2]$ complexes in dichloromethane solution showed that the stability of the pentacoordinate complexes is influenced by the anion and decreases in the order: $CN \gg I > Br > Cl > NO_2 > NCS$. The tendency to form pentacoordinate nickel(II) complexes is correlated with the electronegativity or polarizability of the anions rather than with their relative positions in the spectrochemical series. The reduced tendency of pentafluorophenyldimethylphosphine to stabilize five-coordinate complexes, as compared with phenyldimethylphosphine, is discussed from the viewpoint of electronic and steric factors.

Previous investigations in this laboratory have suggested that electronic considerations may be more important than steric factors in the formation of diamagnetic five-coordinate nickel(II) complexes.[1] Evaluation of these electronic factors should be attempted with monodentate ligands in order to eliminate any possibility that the geometry of the resulting complex is controlled by the symmetry or steric requirements of chelating ligands.

In contrast to the numerous stable five-coordinate complexes of nickel(II) with polydentate ligands,[1,2] most of those known with monodentate ligands are dissociated in solution as, for example, $Ni(CN)_5^{3-}$,[3] $[Ni(HP(C_6H_5)_2)_3X_2]$ (X = Cl, Br, I),[4] $[Ni(C_6H_5P(C_2H_5)_2)_3(C{\equiv}CC_6H_5)_2]$,[5] $[Ni(C_{14}H_{13}P)_3X_2]$ (X = Cl, Br, I; $C_{14}H_{13}P$ = 2-phenylisophosphindoline),[6] $[Ni(RPC_{12}H_8)_3X_2]$ (X = Cl, Br, I; $RPC_{12}H_8$ = 9-alkyl-9-phosphafluorenes),[7] $[Ni(C_6H_5P(C_2H_5)_2)_3(CN)_2]$,[8] $[NiL_3(CN)_2]$ (L = $P(OCH_3)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, $C_6H_5P(OC_2H_5)_2$, $P(OCH_2)_3CCH_3$).[9] However, dissociatively stable pentacoordinate $[NiL_3(CN)_2]$ complexes (where L = $C_6H_5P(OC_2H_5)_2$,[10,11] $C_6H_5P(OCH_3)_2$, $P(OC_2H_5)_3$,[11] and $P(OC_6H_5)_3$[9]) have been reported recently. Gray, *et al.*,[11] suggested that steric interactions of some bulky tertiary phosphines, such as $(C_6H_5)_3P$, may preclude formation of $[NiL_3(CN)_2]$ complexes. However, Verkade, *et al.*,[9] concluded from spectral studies with similar phosphite ligands that the importance of steric factors with $(C_6H_5)_3P$ had been overemphasized.

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Table I. Properties and Analytical Data of the Nickel(II)–Phosphine Complexes[a]

Compound[b]	Color	Λ_M,[c] cm^2/(ohm mole)	% C		% H		% other	
			Calcd	Found	Calcd	Found	Calcd	Found
$NiL_3(CN)_2$[d]	Dark red	1.3	59.40	59.40	6.37	6.60	5.34	5.39 (N)
$Ni(L_F)_3(CN)_2$	Orange-red	0.2	37.76	38.10	2.28	2.42	3.52	3.47 (N)
NiL_3I_2	Black-green	21.5	39.60	39.90	4.58	4.30	34.65	32.76 (I)
$Ni(L_F)_2I_2$	Dark green	6.2	25.00	25.20	1.58	1.51	33.00	33.27 (I)
NiL_2Br_2[e]	Dark red	7.5	38.80	38.90	4.47	4.04		
$Ni(L_F)_2Br_2$	Maroon	2.9	28.50	28.80	1.79	1.65		
NiL_2Cl_2	Dark red	7.3	47.40	47.51	5.47	5.60	17.50	17.78 (Cl)
$Ni(L_F)_2Cl_2$	Dark red	4.2	32.80	32.70	2.07	2.13	12.10	11.97 (Cl)
$NiL_2(NCS)_2$	Orange	2.3	47.90	48.00	4.94	4.84	6.21	6.22 (N)
$Ni(L_F)_2(NCS)_2$[f]	Orange-red	0.8	34.20	34.07	1.92	1.97	4.44	4.29 (N)
$NiL_2(NO_2)_2$	Brown-yellow	2.7	45.00	45.21	5.19	5.27	6.56	6.36 (N)
$Ni(Ph_2PMe)_3(CN)_2$	Red	1.9	69.23	69.05	5.53	5.61	3.94	3.94 (N)
$Ni(Ph_2PEt)_2(CN)_2$	Yellow	1.9	66.80	67.06	5.61	5.52		

[a] All of these complexes are diamagnetic; μ_{eff} for NiL_3I_2 could not be determined due to sample decomposition on the Faraday balance. [b] L = $PhPMe_2$; L_F = $C_6F_5PMe_2$. [c] Molar conductance value of $\sim 10^{-3}$ *M* solution in nitromethane. Uni-univalent electrolytes exhibit Λ_M values in the range 75–95. [d] Calcd mol wt, 525; found, 520 in DMF. [e] Calcd mol wt, 495; found, 490 in benzene (0.016–0.037 *M*). [f] Calcd mol wt, 631; found, 622 in benzene.

Turco and coworkers have also considered the role of the anion in stabilizing five-coordinate nickel(II) complexes. They proposed that a "strong-field" anion was required for the formation of tris-phosphine complexes of nickel(II)[8,12] and cobalt(II).[13,14] However, the complex $[Ni(P(CH_3)_3)_3Br_2]$ is stable to air oxidation and to dissociation in dichloromethane solution.[15]

The present investigation was initiated to obtain some quantitative information on how the different anions and/or different electronic effects of phosphine ligands influenced the formation of pentacoordinate nickel(II) complexes. The results obtained in the reactions of nickel salts with phenyldimethylphosphine and pentafluorophenyldimethylphosphine are discussed and correlated with these factors.

Experimental Section

Reagents. Except for $NiI_2 \cdot 6H_2O$, all nickel salts were anhydrous. The phosphines were prepared by standard Grignard syntheses. Since the reaction of pentafluorophenylmagnesium bromide[16] with phosphorus trichloride is reported to yield $(C_6F_5)_2PCl$ as well as the desired $C_6F_5PCl_2$,[17,18] the material was fractionated before addition to excess methyl magnesium bromide. The resulting phosphine [collected at 58–61° (4.2 mm); 47–48° (0.4 mm) reported for $C_6F_5P(CH_3)_2$[19]] was identified as its methyl iodide derivative.[20] *Anal.* Calcd for $C_9H_9F_5PI$: C, 29.20; H, 2.46; I, 34.30. Found: C, 29.21; H, 2.59; I, 34.57. The corresponding unfluorinated phosphine, $C_6H_5P(CH_3)_2$, was distilled at 76° (7 mm) [lit.[21] 83–84° (13.5 mm)] and analyzed as the methyl iodide derivative. *Anal.* Calcd for $C_9H_{14}PI$: C, 38.60; H, 5.04; I, 45.35. Found: C, 38.83; H, 5.18; I, 45.22.

Preparation of the Complexes. All preparative work was carried out under an atmosphere of dry nitrogen. Since all of the syntheses followed the same general procedure of adding the phosphine to the appropriate nickel salt in absolute ethanol (usually in a 3:1 molar ratio), only the isolation of the $[Ni(C_6H_5P(CH_3)_2)_2Cl_2]$ complex is described in detail.

Phenyldimethylphosphine (1.0 g, 7.3 mmoles) was transferred *via* a syringe into a yellow-green solution of anhydrous $NiCl_2$ (0.33 g, 2.6 mmoles) in absolute ethanol (20 ml). After refluxing the solution to ensure that the reaction was complete, the deeply colored mixture was filtered, and the solution was concentrated and allowed to cool to room temperature. Dark red crystals (0.26 g) were collected on a sintered-glass frit and dried under nitrogen. Addition of petroleum ether (bp 30–60°) to the concentrated filtrate gave more red platelets (0.54 g), giving a total yield of 80%. With the exception of $[Ni(C_6H_5P(CH_3)_2)_3I_2]$ and $[Ni(C_6F_5P(CH_3)_2)_2Cl_2]$, all of the complexes appeared to be stable on exposure to the atmosphere.

Physical Measurements. Electronic and infrared spectra and conductance and magnetic measurements were obtained as previously described.[22] The dichloromethane solutions for the spectral measurements and the nitromethane solutions for the conductance measurements were freshly prepared. Elemental analyses were determined by P. Kovi, The Ohio State University, and by Galbraith Laboratories, Inc., Knoxville, Tenn. The latter also performed molecular weight determinations on a vapor pressure osmometer. Proton nmr measurements were made on $CDCl_3$ solutions with TMS as the internal standard.

Results and Discussion

The physical properties and analytical data of the four- and five-coordinate nickel(II) compounds are listed in Table I. The band maxima and extinction coefficients of the electronic absorption spectra are given in Table II.

Five-Coordinate Complexes. Solid compounds of the type $[Ni(PR_3)_3X_2]$ are formed by the reaction of nickel cyanide with phenyldimethylphosphine, pentafluorophenyldimethylphosphine, and methyldiphenylphosphine, and by the reaction of nickel iodide with phenyldimethylphosphine. The dark red crystalline cyanide complexes are diamagnetic and nonelectrolytes in nitromethane. Whereas $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ is a stable monomer in dimethylformamide (calcd mol wt, 525; found, 520), the other five-coordinate compounds are dissociated in solution as indicated by their electronic spectra (Table II). The visible spectrum of [Ni-

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Table II. Electronic Absorption Spectral Data[a]

Compound[b]	Solid state, cm^{-1} (Nujol mull)	Solution, cm^{-1} (ϵ)[c,d]	Solution and excess ligand, cm^{-1} [e]
$NiL_3(CN)_2$	23,500	23,800 (3800)[f] 34,500 37,700	23,800 (6300) (contains 80 molar ratio of L/Ni)
$Ni(L_F)_3(CN)_2$	23,500 30,800	23,800 (680) 28,600 (460) 36,400 (1330) 40,000 (4700)	23,800 (6000) (contains 380 molar ratio of L_F/Ni)
NiL_3I_2	16,300 22,000	16,300 (660) 22,600 (2260) 34,200 ($\geq$16,100)	15,400 (1085) 22,200 24,000 (sh) (contains 7.6 molar ratio of L/Ni)
$Ni(L_F)_2I_2$	17,900 22,800	17,100 (350) 22,500 (2330) 26,700 (5020)	No change
NiL_2Br_2	19,200 24,850	19,200 (500) 26,300 (8850)	15,150 (950) 20,700 (554) 27,800 34,500 (contains 49 molar ratio of L/Ni)
$Ni(L_F)_2Br_2$	18,500 20,800	19,600 (470) 26,100 (12,400)	No change
NiL_2Cl_2	20,800 26,300	20,600 (610)	15,050 (482) 22,750 (sh)
$Ni(L_F)_2Cl_2$	18,900 22,000 28,600	21,300 (390) 28,300 (13,100)	No change
$NiL_2(NCS)_2$	21,000 (sh) 26,800	20,800 (sh) 26,900 (11,600) 34,500 (38,700)	No change
$Ni(L_F)_2(NCS)_2$	20,800 (sh) 26,700 35,700	20,400 (sh) 26,300 (5700) 35,700 (28,000)	No change
$NiL_2(NO_2)_2$	30,000	29,700 33,900	18,700 (400) 22,700 (600) (contains 71 molar ratio of L/Ni)
$Ni((C_6H_5)_2PCH_3)_3(CN)_2$	20,000 25,000	20,000–25,000 (broad) 28,600 (1200)	

[a] Solution spectra are in dichloromethane unless specified otherwise; the energy values correspond to the peak maxima. [b] L = $C_6H_5P(CH_3)_2$ and L_F = $C_6F_5P(CH_3)_2$. [c] Band maxima reported are those observed by dissolving the compound in the solvent. [d] Molar extinction coefficients are in parentheses. [e] These maxima and ϵ values are obtained with ~10^{-4} *M* solutions of the complex which also contain the molar ratio of phosphine to Ni(II) that is specified. [f] Dimethylformamide solution.

$(C_6F_5P(CH_3)_2)_3(CN)_2]$ in CH_2Cl_2 in the presence of various amounts of excess $C_6F_5P(CH_3)_2$ is shown in Figure 1. The isosbestic point at 28,600 cm^{-1} verifies the presence of only two principal absorbing species; thus the equilibrium is represented by eq 1. Since the $[Ni(C_6H_5P(CH_3)_2)_3I_2]$ complex exhibits partial conductance (21.5 cm^2/(ohm mole)) in nitromethane, a second dissociation process is also indicated in this case (eq 2).

$$[Ni(C_6F_5P(CH_3)_2)_3(CN)_2] \rightleftharpoons [Ni(C_6F_5P(CH_3)_2)_2(CN)_2] + C_6F_5P(CH_3)_2 \quad (1)$$

$$[Ni(C_6H_5P(CH_3)_2)_3I_2] \rightleftharpoons [Ni(C_6H_5P(CH_3)_2)_3I]^+ + I^- \quad (2)$$

Both $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ and $[Ni(C_6F_5P(CH_3)_2)_3(CN)_2]$ exhibit an intense, symmetrical electronic band at 23,800 cm^{-1} in dichloromethane solution. (The band maximum occurs at ~23,500 cm^{-1} in the solid state.) This band may be assigned to the allowed ligand field transition $e' \rightarrow a_1'$, $(^1A_1 \rightarrow {}^1E')$ in D_{3h} symmetry.[1,11,23] The spectral data are quite similar to those of the known trigonal-bipyramidal complex [Ni(TAP)CN]ClO$_4$ (where TAP = $P[CH_2CH_2CH_2As(CH_3)_2]_3$).[24] The infrared spectra (Nujol mulls) of $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ and $[Ni(C_6F_5P(CH_3)_2)_3(CN)_2]$ show single, sharp absorptions at 2100 and 2110 cm^{-1}, respectively. Thus the cyanide groups are assigned to structurally equivalent positions, *i.e.*, the *trans* (or apical) positions of a trigonal bipyramid. The combination of electronic and infrared spectra, molecular weight, and conductance data strongly supports a *trans*-trigonal-bipyramidal geometry for the nickel cyanide complexes both in solution and in the solid state. In fact, the *trans*-trigonal-bipyramidal structure of $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ has been established by X-ray crystallography;[25] the geometry of the inner coordination sphere is represented in Figure 2.

The Ni–P (2.24 Å av) and Ni–C (1.85 Å av) bond distances in $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ are close to the values found previously for [Ni(TAP)CN]ClO$_4$.[24] The similarity of the two structures corroborates our earlier

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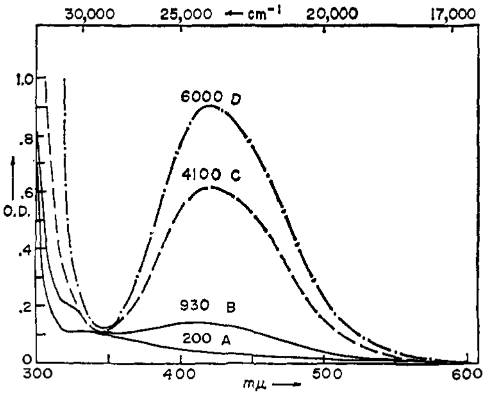

Figure 1. Electronic absorption curves for (A) 1.51×10^{-4} *M* $[Ni(C_6F_5P(CH_3)_2)_3(CN)_2]$ dissolved in dichloromethane; (B) solution A plus 3.8 mole ratio of excess $C_6F_5P(CH_3)_2$ ligand; (C) solution A plus 38 mole ratio of phosphine; (D) solution A plus 380 mole ratio of phosphine. The numbers 200, 930, 4100, and 6000 on curves A, B, C, and D, respectively, represent the molar extinction coefficients of the $[Ni(C_6F_5P(CH_3)_2)_3(CN)_2]$ complex at 23,800 cm^{-1}.

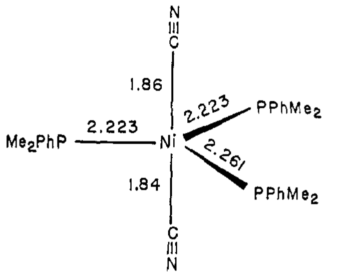

Figure 2. The inner coordination sphere of trigonal-bipyramidal $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ with the nickel–ligand bond lengths designated.[25]

suggestion[1] that the coordination number and structure of complexes with flexible aliphatic ligands such as $P[CH_2CH_2CH_2As(CH_3)_2]_3$ should reflect the preferred geometry that results from electronic interactions between the donor atoms and the metal cation. The only previous report of a low-spin, five-coordinate nickel(II) complex with regular trigonal-bipyramidal geometry is $[Ni(phosphite)_5](ClO_4)_2$, where phosphite = $P(OCH)_3(CH_2)_3$.[26] A recent X-ray analysis of $[Ni(TSP)Cl]ClO_4$ (where TSP is $P(o\text{-}C_6H_4SCH_3)_3$), which was synthesized in this laboratory,[27a] also shows that the $[Ni(TSP)Cl]^+$ cation has nearly a C_{3v} set of donor atoms around the Ni(II) ion.[27b]

The $[Ni((C_6H_5)_2PCH_3)_3(CN)_2]$ complex is assigned a distorted pentacoordinate structure since a broad absorption with two maxima (20,000 and 25,000 cm^{-1}) is observed in the electronic spectrum. The structure of the solid $[Ni(C_6H_5P(CH_3)_2)_3I_2]$ complex cannot be ascertained definitively from its electronic spectrum. However, the changes that occur in the electronic spectrum when excess phosphine is added demonstrate its dissociation to $[Ni(C_6H_5P(CH_3)_2)_2I_2]$ in solution. While σ-bonding considerations[11] suggest that the iodine atoms would be in axial positions of a trigonal bipyramid, it is noteworthy that phosphine atoms occupy the axial positions in the distorted structures of $[M(HP(C_6H_5)_2)_3X_2]$, where M = Co, Ni and X = Br, I.[28a] The optical electronegativity of R_3P ligands is comparable to iodide[28b] so there may be no strong preference for the axial position in the case of R_3P *vs.* iodide. From the electronic spectra one cannot definitively assign which trigonal-bipyramidal isomer of NiL_3I_2 exists in solution.

Addition of excess phosphine to solutions of the square-planar $[NiL_2X_2]$ complexes (L = $C_6H_5P(CH_3)_2$; X = Br, Cl, NO_2; and L = $(C_6H_5)_2PC_2H_5$ with X = CN) produces a new absorption band at lower energy than was observed for the corresponding four-coordinate complex. The new absorption gives the same spectrochemical series, *i.e.*, CN > NO_2 > Cl > Br, as was observed for the four-coordinate complexes (see later). The band positions (Table II) and color changes that occur when excess phosphine is added correspond with those reported for pentacoordinate nickel(II) complexes.[12,15,24] The first electronic band for $[Ni(P(CH_3)_3)_3Br_2]$[15] in CH_2Cl_2 solution occurs at 14,000 cm^{-1}, whereas the four-coordinate complex $[Ni(P(CH_3)_3)_2Br_2]$ absorbs at 18,500 cm^{-1}.[29] Therefore, the new band at 15,150 cm^{-1} in the blue solutions of $[Ni(C_6H_5P(CH_3)_2)_2Br_2]$ containing excess $C_6H_5P(CH_3)_2$ is attributed to the five-coordinate compound $[Ni(C_6H_5P(CH_3)_2)_3Br_2]$ and is assigned to the $^1A_1 \rightarrow {}^1E'$ transition for the assumed *trans*-trigonal-bipyramidal structure. The 19,760-cm^{-1} band for $[Ni(TAP)NO_2]ClO_4$ was resolved previously by Gaussian analysis into absorptions at 16,940, 20,030, and 24,450 cm^{-1}.[30] Thus the appearance of two new bands at 18,700 and 22,700 cm^{-1} in the maroon solution of $[Ni(C_6H_5P(CH_3)_2)_2(NO_2)_2]$ containing excess $C_6H_5P(CH_3)_2$ is consistent with formation of a five-coordinate complex. The asymmetric nature of the single band expected in this region is rationalized in terms of the steric and symmetry requirements of the nitro group. The isosbestic point at 23,800 cm^{-1} in the spectra of $[Ni(C_6H_5P(CH_3)_2)_2(NO_2)_2]$ solutions containing excess $C_6H_5P(CH_3)_2$ confirms the principal equilibrium between four- and five-coordinate complexes. The relative stability of the five-coordinate complexes formed in solution with excess phosphine is discussed later.

Four-Coordinate Complexes. When the nickel salts were mixed with excess $C_6H_5P(CH_3)_2$ and $C_6F_5P(CH_3)_2$, only four-coordinate $[Ni(PR_3)_2X_2]$ complexes were isolated when X = NCS, Cl, or Br. Whereas $C_6H_5P(CH_3)_2$ gave a black five-coordinate complex $[Ni(C_6H_5P(CH_3)_2)_3I_2]$, $C_6F_5P(CH_3)_2$ gave only the dark green $[Ni(C_6F_5P(CH_3)_2)_2I_2]$ complex. The yellow crystalline $[Ni((C_6H_5)_2PC_2H_5)_2(CN)_2]$ complex was obtained by refluxing $Ni(CN)_2$ with $(C_6H_5)_2PC_2H_5$ in ethanol in a 1:4 molar ratio. A metathesis reaction of $[Ni(C_6H_5P(CH_3)_2)_2Cl_2]$ with $NaNO_2$ gave the gold $[Ni(C_6H_5P(CH_3)_2)_2(NO_2)_2]$ compound.

These nine complexes are assigned a square-planar geometry on the basis of their diamagnetism, electronic spectral band positions and extinction coefficients, and their nonelectrolyte behavior in nitromethane. Both

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(28) (a) J. A. Bertrand and D. L. Plymale, *ibid.*, **5**, 879 (1966); (b) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, pp 5, 156.

(29) M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **39**, 595 (1961).

(30) G. S. Benner, Ph.D. Thesis, The Ohio State University, 1966.

$[Ni(C_6H_5P(CH_3)_2)_2Br_2]$ and $[Ni(C_6F_5P(CH_3)_2)_2(NCS)_2]$ are monomeric in benzene (Table I). The close agreement of electronic spectral maxima in solution and in the solid state for all of the four-coordinate complexes shows that association does not occur in the solid state. In addition, the electronic spectral patterns of these complexes (both in the solid state and in solution) are consistent with those of known square-planar $[Ni(PR_3)_2X_2]$ complexes.[29,31]

The infrared spectra of the two thiocyanate complexes in solution indicate that they have *trans*-square-planar geometry, since only one absorption band occurs in the region expected for the thiocyanate C≡N stretching vibration. The single absorptions at 2095 and 2085 cm^{-1} for $[Ni(C_6H_5P(CH_3)_2)_2(NCS)_2]$ and $[Ni(C_6F_5P(CH_3)_2)_2(NCS)_2]$, respectively, also suggest that the thiocyanate groups are N-bonded;[32a] furthermore, the position of the first visible absorption band (~21,000 cm^{-1} in both cases) would be closer to the values of the bromide complexes if the thiocyanate groups were S-bonded.[32b] The infrared bands at 855 and 862 cm^{-1}, which are not present in the spectra of the analogous halide complexes, are assigned to the C–S stretching vibration of N-bonded thiocyanate groups in the $C_6H_5P(CH_3)_2$ and $C_6F_5P(CH_3)_2$ complexes, respectively. In dichloromethane solutions, the integrated intensity[32c] of the C≡N infrared absorption (11.6×10^4 and 11.3×10^4 M^{-1} cm^{-2}, respectively) verifies that the thiocyanate groups are N-bonded in both $[NiL_2(NCS)_2]$ and $[Ni(L_F)_2(NCS)_2]$.

An extra band at 2130 cm^{-1} in the infrared spectrum of a Nujol mull of $[Ni(C_6F_5P(CH_3)_2)_2(NCS)_2]$ can be attributed to crystal-packing effects, being too far removed from the 2090-cm^{-1} band to be attributable to *cis*-bonded thiocyanate groups. Although the 2130-cm^{-1} band could conceivably be assigned to the cyanide stretching frequency of a bridging thiocyanate group,[33] a comparison of the visible spectra of both complexes makes a bridging thiocyanate appear unlikely. The lowest energy band for both complexes (which is observed near 21,000 cm^{-1} in both the solid state and solution spectra) does not increase in intensity or move to lower energy in the presence of excess of the appropriate phosphine. Therefore, both thiocyanate complexes are four-coordinate in the solid state and in solution (*cf.* the monomeric value of $[Ni(C_6F_5P(CH_3)_2)_2(NCS)_2]$ in benzene). Crystal lattice effects are also observed in the solid-state electronic spectra of $[Ni(C_6F_5P(CH_3)_2)_2Cl_2]$ and $[Ni(C_6F_5P(CH_3)_2)_2Br_2]$. In contrast to the analogous complexes of $C_6H_5P(CH_3)_2$, the lowest energy absorptions of these two complexes in the solid state appear as broad bands having two maxima, whereas single absorptions are observed in dichloromethane solutions.

Attempts to isolate four-coordinate nickel cyanide complexes of $C_6H_5P(CH_3)_2$, $C_6F_5P(CH_3)_2$, and $(C_6H_5)_2PCH_3$ were unsuccessful owing to the stability of the pentacoordinate $[Ni(ligand)_3(CN)_2]$ complex. Mixing the appropriate phosphine and nickel cyanide in a 2:1 molar ratio or a metathesis reaction between the corresponding four-coordinate nickel chloride complex and sodium cyanide always led to the isolation of dark red solids. In each synthesis the characteristic electronic absorption at ~23,000 cm^{-1} signified the presence of the pentacoordinate complex. We refluxed the five-coordinate complexes in petroleum ether and in the presence of excess nickel cyanide in attempts to displace the third phosphine ligand, but the red products that were isolated always showed the electronic absorption band near 23,000 cm^{-1}.

No difference in the ligand field strength of $C_6H_5P(CH_3)_2$ and $C_6F_5P(CH_3)_2$ was discerned in the five-coordinate nickel(II) cyanide complexes, but the visible spectra of solutions of the $[NiL_2X_2]$ (X = Cl, Br) complexes indicate that $C_6F_5P(CH_3)_2$ has a slightly higher ligand field strength than $C_6H_5P(CH_3)_2$ (Table II). For a given ligand the spectra of the four-coordinate $[NiL_2X_2]$ complexes produce the usual spectrochemical series,[34] $NO_2 > NCS > Cl > Br > I$. The molar extinction coefficient of the ligand field band was always lower for the $C_6F_5P(CH_3)_2$ complex than for the corresponding $C_6H_5P(CH_3)_2$ complex.

Equilibrium Constants. An evaluation of the tendency of nickel(II) to achieve pentacoordination is made possible by the fact that some of these nickel(II) complexes exist as both four- and five-coordinate compounds in solution. The equilibrium constants in dichloromethane solution have been determined by a spectrophotometric method for equilibria of the type

$$Ni(PR_3)_2X_2 + PR_3 \underset{K^{-1}}{\overset{K}{\rightleftarrows}} Ni(PR_3)_3X_2 \qquad (3)$$

By assuming only that the new absorption observed when excess phosphine was added to solutions of the four-coordinate complex obeys Beer's law, the graphical method of Rose and Drago[35] allows an estimation of K^{-1}, the instability constant, and ϵ_5, the molar extinction coefficient, of the five-coordinate compound. The values obtained, along with the resultant equilibrium constants and changes in free energy, are listed in Table III. A plot of K^{-1} against ϵ_5 for $[Ni(C_6H_5P(CH_3)_2)_3Br_2]$ is illustrated in Figure 3; the intersection represents the unique values of these parameters that satisfy all of the initial concentrations of $[Ni(C_6H_5P(CH_3)_2)_2Br_2]$ and $C_6H_5P(CH_3)_2$. The numbers on the lines represent the molar ratios of phosphine to four-coordinate complex. The increasing absorption at ~14,800 cm^{-1} is due to $[Ni(C_6H_5P(CH_3)_2)_3Cl_2]$ as

Table III. Equilibrium Parameters for the Five-Coordinate Ni(II) Complexes

Compound	K^{-1}, mole/l.	ϵ_5[a]	K, $(mole/l.)^{-1}$	$-\Delta F^{25°}$, kcal/mole
$Ni((C_6H_5)_2PC_2H_5)_3(CN)_2$	195×10^{-3}	925	5.1	0.97
$Ni(C_6H_5P(CH_3)_2)_3Br_2$	1.93×10^{-3}	1000	520	3.7
$Ni(C_6H_5P(CH_3)_2)_3Cl_2$	42.0×10^{-3}	665	24	1.9

[a] The value of the extinction coefficient is obtained from the graphical method.[35]

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(32) (a) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965), and references cited therein; (b) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966); (c) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

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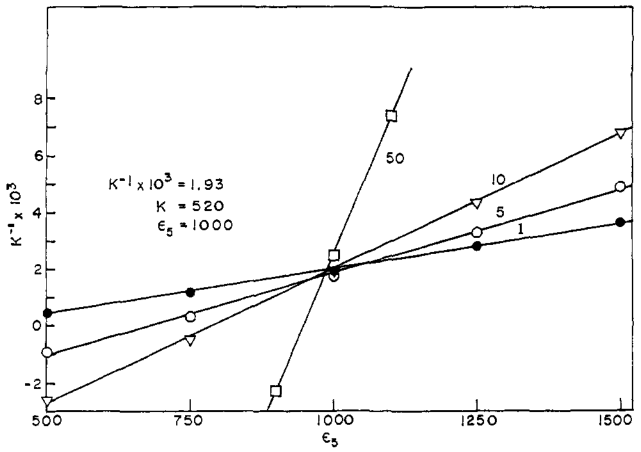


Figure 3. A plot of K^{-1} against arbitrary ϵ_5 values for $[Ni(C_6H_5P(CH_3)_2)_3Br_2]$ in dichloromethane solution. The numbers 1, 5, 10, and 50 on the lines represent the molar ratios of phosphine to the four-coordinate $[Ni(C_6H_5P(CH_3)_2)_2Br_2]$ that give the unique solution of K^{-1} and ϵ_5.

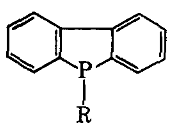
$C_6H_5P(CH_3)_2$ is added to the red CH_2Cl_2 solutions of $[Ni(C_6H_5P(CH_3)_2)_2Cl_2]$; an isosbestic point occurs at 18,500 cm^{-1} for the 0.83×10^{-3} *M* nickel solutions.

The inability to isolate four-coordinate nickel cyanide complexes with $C_6H_5P(CH_3)_2$, $(C_6H_5)_2PCH_3$, and $C_6F_5P(CH_3)_2$ in this work, although the $[NiL_3(CN)_2]$ complexes are formed readily, suggests a markedly enhanced stability of the five-coordinate complexes when cyanide is the anion.

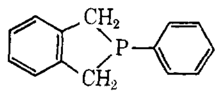
Excess $C_6H_5P(CH_3)_2$ was added to solutions of $[Ni(C_6F_5P(CH_3)_2)_2X_2]$ (X = Br, I), and, similarly, excess (~50:1 molar ratio) $C_6F_5P(CH_3)_2$ was added to solutions of $[Ni(C_6H_5P(CH_3)_2)_2X_2]$ (X = Cl, Br) to determine if five-coordinate nickel complexes containing both phosphines were formed. The visible spectra (band positions and extinction coefficients) showed that, in the latter case, the principal species in solution is $[Ni(C_6F_5P(CH_3)_2)_2X_2]$; *i.e.*, for X = Cl, ϵ is 390 at 21,300 cm^{-1}, and for X = Br, ϵ is 430 at 19,600 cm^{-1}. No new absorption appeared near 15,000 cm^{-1}; therefore exchange of phosphine ligands occurred rather than addition of a third ligand. $[Ni(C_6F_5P(CH_3)_2)_2X_2]$ (X = Br, I) also exchanged phosphine ligands in an analogous manner when excess (~65:1 molar ratio) $C_6H_5P(CH_3)_2$ was added to their solutions; *i.e.*, the resultant solutions give electronic spectral bands as expected for $[Ni(C_6H_5P(CH_3)_2)_3X_2]$ (X = Br, I). Additional evidence for the rapid exchange of phosphine groups was obtained from the proton nmr spectra of $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ and $[Ni(C_6F_5P(CH_3)_2)_2(NCS)_2]$ in deuteriochloroform. The peaks at τ 8.45 and 8.01, respectively, remain sharp and shift upfield toward the free ligand values (τ 8.61 for $C_6H_5P(CH_3)_2$ and 8.42 for $C_6F_5P(CH_3)_2$) upon addition of ligand.

Except when X = CN, none of the square-planar $[Ni(C_6F_5P(CH_3)_2)_2X_2]$ complexes showed any tendency to add a third $C_6F_5P(CH_3)_2$ ligand in solution. The isolation of $[Ni(C_6H_5P(CH_3)_2)_3I_2]$ under the same conditions that gave only $[Ni(C_6H_5P(CH_3)_2)_2X_2]$ (where X = Br, Cl) suggests a greater stability of the five-coordinate compound when the anion is iodide. Hayter arrived at the same conclusion in a study of the $[Ni(HP(C_6H_5)_2)_3X_2]$ complexes (X = Cl, Br, I).[4] With a given phenylphosphine ligand, the formation of pentacoordinate nickel(II) complexes is influenced by the anion, and the stability of the $[NiL_3X_2]$ complexes follows the order: $CN \gg I > Br > Cl > NO_2 > NCS$. The tendency of the phosphines to form five-coordinate complexes is $C_6H_5P(CH_3)_2 > C_6F_5P(CH_3)_2$ and $C_6H_5P(CH_3)_2 > (C_6H_5)_2PCH_3 > (C_6H_5)_2PC_2H_5$. These results are discussed in the following sections from the viewpoint of steric and electronic factors.

Steric Factors. Monodentate (as opposed to polydentate) ligands should exert a minimum symmetry or steric influence on the stereochemistry adopted in a coordination compound. However, evidence may be cited from the literature where a cursory evaluation might indicate that the steric requirements of some monodentate phosphines preclude attainment of pentacoordination for nickel(II). For example, nickel halides do not give five-coordinate complexes with excess $(C_6H_5)_2PCH_3$[4] or $(C_6H_5)_2PC_2H_5$,[6] but pentacoordinate $[Ni(ligand)_3X_2]$ complexes have been prepared with phosphines that contain the same type of substituents, *i.e.*, 9-alkyl-9-phosphafluorenes (I) (alkyl = CH_3 and C_2H_5)[17] and 2-phenylisophosphindoline (II).[6] With



I



II

ligands I and II the formation of pentacoordinate complexes was attributed to the decreased steric interaction of the cyclic phosphines. The $[Ni(C_6H_5P(CH_3)_2)_3X_2]$ complexes (X = Cl, Br, I) appear to have stabilities comparable to those of phosphine II. Thus the apparent lower stability of the five-coordinate nickel halide complexes of $(C_6H_5)_2PCH_3$ and $(C_6H_5)_2PC_2H_5$ relative to those formed with I may not be due solely to the steric factor. The difference in behavior conceivably could be attributed to a change in hybridization of the phosphorus atom when the phenyl rings are joined. Hence the σ-donor properties of the phosphorus atom would differ from a noncyclic ligand with essentially the same inductive groups. Gray, *et al.*,[11] suggested that $(C_6H_5)_3P$ did not form a five-coordinate nickel cyanide complex because of its bulkiness since σ-bonding considerations (no evidence was found for π bonding) should make it a better ligand than the more electronegative phosphite ligands which form five-coordinate complexes. However, $(C_6H_5O)_3P$, which is as bulky as $(C_6H_5)_3P$ (due to the approximately 120° P–O–C angles), forms the dissociatively stable $[Ni((C_6H_5O)_3P)_3(CN)_2]$ complex[9] and appears to contradict the argument that steric hindrance prevents entry of a third $(C_6H_5)_3P$ ligand into the coordination sphere. Furthermore, the existence of $[Ni(QP)X]ClO_4$[36] (where QP is $P(C_6H_4PPh_2)_3$) demonstrates that even four bulky $P(C_6H_5)_3$ groups around nickel(II) are possible, although the stability in this case could be attributed to the chelate effect.

Some of our results suggest that interligand interaction may influence the stability or formation of five-

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(36) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

coordinate complexes. For example, $(C_6H_5)_2PC_2H_5$ formed $[Ni((C_6H_5)_2PC_2H_5)_2(CN)_2]$ even when mixed in a 4:1 molar ratio whereas $(C_6H_5)_2PCH_3$ gave only $[Ni((C_6H_5)_2PCH_3)_3(CN)_2]$ even when mixed in a 2:1 ratio. Since the inductive effects of the CH_3 and C_2H_5 groups are very similar, the lower stability of $[Ni((C_6H_5)_2PC_2H_5)_3(CN)_2]$ is ascribed to the different steric requirements of the methyl and ethyl groups. Perturbed infrared and electronic absorptions are observed in some of the solid square-planar complexes of $C_6F_5P(CH_3)_2$ and are attributed to crystalline lattice effects. This may suggest that the larger C_6F_5 groups may prevent close approach of a third phosphine ligand in the $Ni(C_6F_5P(CH_3)_2)_2X_2$ series, but a more probable reason is the reduced σ-donor properties of $C_6F_5P(CH_3)_2$ as compared to $C_6H_5P(CH_3)_2$. The steric requirements of $C_6F_5P(CH_3)_2$ do not preclude fromation of pentacoordinate nickel(II) cyanide complexes. We attempted to isolate Ni(II) complexes of $(C_6F_5)_2PCH_3$, but no reaction occurred when either nickel cyanide or nickel bromide was refluxed with $(C_6F_5)_2PCH_3$ in absolute ethanol. It was reported earlier that $(CF_3)_2PCH_3$ does not form Ni(II) complexes although square-planar $[Ni(\text{ligand})_2X_2]$ complexes were isolated with $CF_3P(CH_3)_2$.[29] Whether the reduced coordinating ability of phosphines containing two perfluoro substituents, as compared to those containing only one C_6F_5 or CF_3 group, might be attributed to the larger steric requirement or to the lower σ-character of the phosphine or a combination of these factors is not yet clear.

In contrast to the behavior of $(C_6F_5)_2PCH_3$, $(C_6H_5)_2PCH_3$ (L′) gives $[NiL'_3(CN)_2]$ complexes rather easily. The size of the anion also is not an important factor in formation of $[NiL_3X_2]$ complexes since a pentacoordinate solid was isolated with the largest halide (iodide), and in solution the dissociation stability increases in the order Cl < Br < I (Table III). Thus, the order of stability of pentacoordinate complexes as observed in this study may be correlated with the differing (1) electronic properties of the anions and (2) σ-donor properties of phosphines.

Electronic Factors. The different behavior of the anions and phosphines may be examined in relation to their polarizability and relative σ- and π-bonding ability. Turco, *et al.*,[8] have shown that complexes of the type $[Ni(PR_3)_2X_2]$ do not attain pentacoordination by addition of purely σ-donor ligands such as amines. However, $[Ni(S_2PR_2)_2]$ forms 1:1 adducts with secondary amines, but this behavior is attributed to the strong nephelauxetic effect of the $R_2PS_2^-$ ligands.[37] The $R_2PS_2^-$ ligands remove negative charge from the metal *via* π bonding, thereby increasing the tendency of the complex to add a fifth ligand that is a σ donor. Similar reasoning has been utilized to explain the higher stability of nickel and cobalt halide complexes with diphenylphosphine ($pK_a = 4.55$) than with the more basic tertiary phosphines.[8] However, the recent isolation of stable pentacoordinate $[Ni(P(CH_3)_3)_3X_2]$[15,38] complexes shows that the ligand basicity ($P(CH_3)_3$ $pK_a = 6.50$) cannot be the only factor in the formation of $[Ni(PR_3)_3X_2]$ complexes.

The particular influence of the cyanide anion in stabilizing pentacoordination is not related solely to its high position in the spectrochemical series since the halide ions gave more stable complexes with $C_6H_5P(CH_3)_2$ than did either NO_2 or NCS ions. The observed stability order of the anions resembles the nephelauxetic series or a polarizability or electronegativity scale. The stability of the five-coordinate complexes increases with polarizability of the ligand.[39] A lower electronegativity (and concomitant higher polarizability) of an anion would favor more covalent bonding; evidence for such an effect is given in the relative molar extinction coefficients of the visible absorption bands of the complexes. The particularly high value of ϵ for $[Ni(C_6H_5P(CH_3)_2)_3(CN)_2]$ reflects the extensive mixing of ligand and nickel orbitals as does the relatively short Ni–C (1.85 Å)[25] bond distance. It is somewhat surprising that the NO_2^- and NCS^- ligands are not as effective as the halides at stabilizing five-coordinate nickel(II) complexes with these phosphine ligands in view of their expected greater π-bonding ability.[40] Indeed, cobalt(II) complexes of the type $[Co(PR_3)_2X_2]$ add a third phosphine ligand when X = NCS but not when X = Cl, Br, I.[13,14] Rigo, *et al.*,[8] also observed that thiocyanate functions differently toward Co(II) as compared to Ni(II). The recent report that $(CH_3)_3P$ forms five-coordinate complexes with nickel cyanide and nickel halides but not with nickel thiocyanate[38] is also consistent with the present observations. In trigonal-bipyramidal complexes of Ni(II) with phosphine ligands, apparently the σ donation and polarizability of the anion are more important than any possible π-bonding ability. It may be significant than that neither $(C_6H_5)_2PF$ nor $C_6H_5PCl_2$, both of which would be better π acceptors than either $C_6H_5P(CH_3)_2$ or $(C_6H_5)_2PCH_3$, gave any perceptible reaction when refluxed with nickel cyanide. The σ-donor character of the latter two phosphines is smaller than for other good π acceptors such as phosphites that are known to form pentacoordinate nickel(II) complexes.[9,11]

The π-bonding ability of $C_6F_5P(CH_3)_2$ must be less than that of $C_6H_5P(CH_3)_2$. According to infrared and nmr data,[41,42] there is a net π transfer of charge from the C_6F_5 ring to phosphorus owing to $p\pi$–$d\pi$ back-bonding. For example, the phosphorus atom in $C_6F_5P(CH_3)_2$ [$\delta(^{31}P)$ +47.8 ppm] is shielded better than in $C_6H_5P(CH_3)_2$ [$\delta(^{31}P)$ +46.0 ppm].[43] In the nickel complexes, the π donation from the C_6F_5 ring to phosphorus should decrease the importance of $Ni \rightarrow P$ ($d\pi$–$d\pi$) interaction owing to the competition of the $Ni \rightarrow P$ and $C_6F_5 \rightarrow P$ π processes for the same d orbitals. Whether the different behavior between $C_6F_5P(CH_3)_2$ and $C_6H_5P(CH_3)_2$ that was observed in this work is influenced by lower π-bonding ability of the fluorinated ligand cannot be ascertained definitively at present.

The generally lower molar extinction coefficients for a $C_6F_5P(CH_3)_2$ complex, as compared with the corre-

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(43) M. Fild, I. Hollenberg, and O. Glemser, *Z. Naturforsch.*, **22b**, 253 (1967).

sponding $C_6H_5P(CH_3)_2$ complex, indicate that pentafluorophenyldimethylphosphine exhibits a lower polarizability and is less effective in covalent bonding with nickel. The difference in ligand field strength between these two phosphines is most marked with the least polarizable anion, chloride. The lower tendency of $C_6F_5P(CH_3)_2$ to form pentacoordinate nickel(II) complexes can be related to the difference in electronegativity of the C_6F_5 and C_6H_5 groups. Several independent methods[41] indicate that the electronegativity of the C_6F_5 group is somewhat lower than that of Br but greater than that of the C_6H_5 group. $C_6F_5P(CH_3)_2$ would have a contracted σ-donor orbital; consequently, it would not overlap as effectively as $C_6H_5P(CH_3)_2$ in the equatorial positions of a trigonal bipyramid.

It is concluded that *both* the σ and π properties of $C_6F_5P(CH_3)_2$ should make it a poorer ligand than $C_6H_5P(CH_3)_2$ for stabilizing trigonal-bipyramidal nickel(II) complexes, as observed in this study. However, this argument does not explain the comparable spectrochemical influence of the two phosphines. Further discussion on this dilemma awaits the X-ray crystallography data on $[Ni(C_6F_5P(CH_3)_2)_3(CN)_2]$ and the results of other studies that are being initiated.

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