Contribution from the Department of Chemistry, Temple University of the Commonwealth System of Higher Education, Philadelphia, Pa. 19122, U.S.A.

Some Nickel(II) Complexes Containing the Ligands Cyclohexyldiphenylphosphine, Dicyclohexylphenylphosphine and Tricyclohexylphosphine

Phillip J. Stone and Zvi Dori

Received October 21, 1970

The properties and structural characterization of some nickel(II) complexes of the general type $Ni[PPh_nCy_{3-n}]X_2$ *(where Cy = Cyclohexyl, Ph = phenyl and* $X = Cl^-, Br^-, I^-, NCS^-$*) are reported. The thiocyanate complexes are diamagnetic both in solution and in the solid state and have been assigned trans-planar configuration. Spectral and magnetic evidence that with the halo complexes, planar* $\rightleftarrows$ *tetrahedral equilibrium is established in solution. In general, the amount of the paramagnetic tetrahedral isomer follows the order* $PPh_3 > PPh_2Cy > PPhCy_2 > PCy_3$ *for a given halide, and* $I^- > Br^- > Cl^-$ *for a given phosphine. In addition, the tetrahedral form is favored in polar solvents. In the solid state, depending on the condition of crystallization, several of the halo complexes were isolated both as the paramagnetic tetrahedral isomer, and the diamagnetic square-planar isomer. These results are discussed in terms of the electronic and steric effects of the phosphine ligands.*

Introduction

The versatility of ligands containing phosphorus donor atoms in transition metal chemistry is well documented. These ligands are known to stabilize metal ions in unusual oxidation states and they apparently play an important role in the function of metal complexes as homogeneous catalysts.

The coordination number, stability and geometry that phosphine ligands impose on metal ions depend in general on both steric and electronic factors. Thus, Green and Saito[1] have suggested that the high stability of the complex $(PCy_3)_2Ni(H)Cl$ is largely due to the steric effects of the bulky cyclohexyl groups. Wilke *et al.*[2] have found that the stability of the complex $(R_3P)_2NiO_2$ follows the order $R = C_6H_5 < C_5H_{10}N < C_6H_{11}$. Moreover, a borohydride complex of nickel(II) has been obtained with tricyclohexylphosphine as the ligand, but the same complex can not be prepared with $(C_6H_5)_3P$.[3]

Thus, we have decided to investigate in some detail the electronic and steric properties of the ligands PPh_2Cy, $PPhCy_2$, and PCy_3. In this paper we report our results on nickel(II) complexes containing these ligands.

Experimental Section

All metal salts and triphenylphosphine were reagent grade and were used without further purification. Cyclohexyldiphenyl- and dicyclohexylphenylphosphines were prepared according to Issleib and Volker[4] and tricyclohexylphosphine was prepared by the method of Issleib and Brack.[5] Microanalyses were carried out by Galbraith Laboratories.

All preparative work was carried out under dry nitrogen. The complexes were synthesized by a general method as outlined below for the complex $Ni(PPh_2Cy)_2Cl_2$.

Preparation of $Ni(PPh_2Cy)_2Cl_2$. 1.0 g of $NiCl_2 \cdot 6H_2O$ (4.2 mmoles) in 100 ml of hot ethanol was added to a 100 ml ethanolic solution containing 2.95 g of PPh_2Cy (11 mmoles). The mixture was refluxed for 30 min and then cooled. The crystalline precipitate was filtered and washed with cold ethanol and then dry ether. An analytically pure sample was obtained by slow recrystallization from a chloroform-ethanol solution. Analytical data and physical properties are given in Table I.

Physical Measurements. All solution work was done under nitrogen with degassed solvents to prevent oxidation of the complexes. Spectral measurements were performed on a Cary 14 spectrophotometer using spectrograde solvents. Conductivity measurements were done on an Industrial Bridge Model RC16B2. Solid state magnetic susceptibility was measured by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Solution moments were determined by the method of Evans.[6]

Results and Discussion

The Thiocyanate Complexes. The physical properties of the thiocyanate complexes, which are depicted in Table I and II, clearly suggest that these complexes

---

(1) M.L.H. Green and T. Saito, *Chem. Commun.*, 208 (1969).
(2) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, *79*, 62 (1967).
(3) M.L.H. Green and H. Munakata, *Chem. Commun.*, *1969*, 1287.
(4) K. Issleib and H. Volker, *Chem. Ber.*, *94*, 393 (1961).
(5) K. Issleib and A. Brack, *Z. Anorg. Chem.*, *227*, 259 (1954).
(6) D.F. Evans, *J. Chem. Soc.*, *1959*, 2003.

Table I. Physical Properties and Analytical Data for the Ni(II) Phosphine Complexes.

Compound	Color	M.P.,°C [a]	μ_{eff} (B.M.)	% C Calc.	Calc.	% H Calc.	Found	% Other Found	Found
$Ni(PPh_3)_2Cl_2$ [d]	dark blue	240°	3.24						
$Ni(PPh_3)_2Cl_2$	red [b]	240°	Diamag.	65.90	65.99	4.70	4.59		
$Ni(PPh_2Cy)_2Cl_2$	wine [c]		Diamag.						
$Ni(PPh_2Cy)_2Cl_2$	dark green	230°	3.30	64.80	64.39	6.30	6.06	10.60	10.98(Cl)
$Ni(PPhCy)_2Cl_2$	grape	226°-228°	Diamag.	63.70	63.54	7.97	7.99	10.45	11.45(Cl)
$Ni(PCy_3)_2Cl_2$	red	227°	Diamag.	62.60	60.94	9.57	9.28		
$Ni(PPh_2)_2Br_2$ [d]	dark green	205°	3.16	58.20	58.42	4.07	3.97		
$Ni(PPh_2Cy)_2Br_2$	dark green	200-203°	3.21	57.30	56.37	5.57	5.82	8.21	7.93(P)
$Ni(PPhCy)_2Br_2$	green-brown	200°	Diamag	56.40	55.97	7.05	6.69	20.85	20.20(Br)
$Ni(PCy_3)_2Br_2$	olive-green	204°	Diamag	55.50	55.79	8.47	8.50		
$Ni(PPh_3)_2I_2$ [d]	dark brown	202°	3.28	51.60	51.53	3.65	3.47		
$Ni(PPh_2Cy)_2I_2$	brown	168-170°	3.30	50.90	50.36	4.95	4.91	30.00	29.85(I)
$Ni(PPhCy)_2I_2$	wine-brown	202-203°	Diamag.	50.10	50.75	6.26	6.60	29.50	28.07(I)
$Ni(PCy_3)_2I_2$	brown	220°	3.10	49.50	49.87	7.56	7.84		
$Ni(PCy_3)_2I_2$	red-brown	220°	Diamag.						
$Ni(PPh_3)_2(NCS)_2$[10]	red	217°	Diamag.						
$Ni(PPh_2Cy)_2(NCS)_2$	red-orange	225°	Diamag.	64.10	63.78	5.90	6.02	8.71	8.21(P)
$Ni(PPhCy)_2(NCS)_2$	yellow	233°	Diamag.	63.00	61.46	7.45	7.34	8.57	7.92(P)
$Ni(PCy_3)_2(NCS)_2$	yellow-orange	230°	Diamag.	62.00	61.30	8.98	9.01		

[a] Uncorrected. [b] Isomerizes to green isomer at 60°C. [c] Isomerizes to green isomer at 160°C. [d] Similar values have been reported.[10,11,15]

have the *trans*-planar configuration both in solution and in the solid state. The electronic absorption spectra consist of two intense bands around 26,000 and 32,000 cm^{-1} with a shoulder on the low energy side of the band at 26,000 cm^{-1}. The band maxima shift to higher energy in the order $PPh_3 < PPh_2Cy < PPhCy_2 < PCy_3$. Turco *et al.*[7] have reported that the diamagnetic complex $Ni(PCy_3)_2(NCS)_2$ shows an additional intense absorption band around 11,500 cm^{-1} which might indicate the presence of a tetrahedral isomer (*Vide infra*), but we have failed to reproduce this result. We have found no indication of the existence of the paramagnetic isomer in a variety of different organic solvents.

The Halo Complexes. The complexes $Ni(PPh_3)_2X_2$ ($X = Cl^-$, Br^-, I^-) are known to have a distorted tetrahedral geometry with a magnetic moment in the range of 3.20-3.40 B.M. both in solution and in the solid state.[8,9,10,11] The well known planar $(S=O) \leftrightarrows$ tetrahedral $(S=1)$ equilibrium is established in solution upon replacement of the phenyl rings of the phosphine ligands by cyclohexyl groups. The amount of the paramagnetic-tetrahedral isomer was found to depend on the phosphine ligand, the halide ion and the polarity of the solvent.

The electronic absorption spectra of the halo complexes are depicted in Table II. The $^3T_1(F) \mapsto {}^3A_2(\nu_2)$ and $^3T_1(F) \mapsto {}^3T_1(P)(\nu_3)$ transitions of the tetrahedral isomer are observed at approximately 11,000 and 15,000 cm^{-1}, respectively. Of particular interest is the observed trend in the position of the ν_2 transition as a function of the ligands, as depicted in Table II. For a constant phosphine, the band maximum associated with this transition follows that expected of halide ions in the spectrochemical series. For a given halide, on the other hand, the band maximum shifts to higher energy in going from PPh_3 to PPh_2Cy, but upon further substitution of cyclohexyl groups the band shifts to lower energy. The ν_3 transition behaves in a similar manner, but since in several of the complexes this transition appears as a shoulder, it is difficult to locate its exact maximum. Although this behavior is somewhat unexpected, it is by no means unique.[12]

The lowest energy spin-allowed transition of the planar isomer occurs at approximately 18,000 cm^{-1} and it overlaps with the ν_3 transition of the tetrahedral isomer. This band shifts to higher energy in the order $PCy_3 < PPhCy_2 < PPh_2Cy$ for a given halide (Table IIIF and $Cl^- > Br^- > I^-$ for a given phosphine.

The solution moments of the halo complexes are depicted in Table IV. As can be seen from Tables III and IV, the diamagnetic planar isomer is favored by non-polar solvents. In addition, the amount of the paramagnetic isomer decreases in the order $PPh_3 > PPh_2Cy > PPhCy_2 > PCy_3$ for constant halide, and $I^- > Br^- > Cl^-$ for constant phosphine. In polar solvents, such as choloroform the solution moments are, in general, higher but the same trends are observed.

By using the procedure described in the experimental section, all the halo complexes, with the exception of $Ni(PPh_2Cy)_2X_2$ ($X = Br^-$, I^-), can be isolated as the red-purple diamagnetic isomer. Under the same conditions, the latter two complexes crystallize as the green-brown paramagnetic tetrahedral isomer. If the crystallization is not slow, the diamagnetic complexes are usually contaminated with varying amounts of the tetrahedral form. This is evident from the Nujol spectra which are shown in Table II. Indeed,

---

(7) A. Turco, V. Scatturin, and G. Giacometti, *Nature*, *183*, 601 (1959).

(8) G. Garton, D.E. Henn, H.M. Powell, and L.M. Venanzi, *J. Chem. Soc.*, *1963*, 3625.

(9) J.A.J. Jarvis, R.H.B. Mais, and P.G. Owston, *J. Chem. Soc. A*, *1968*, 1473.

(10) L.M. Venanzi, *J. Inorg. Nucl. Chem.*, *8*, 137 (1958).

(11) F.A. Cotton, O.P. Faut, and D.M.L. Goodgame, *J. Amer. Chem. Soc.*, *83*, 344 (1961).

(12) L.H. Pignolet, W. De W. Horrocks, Jr., and R.H. Holm, *J. Amer. Chem. Soc.*, *92*, 1855 (1970).

Table II. Electronic Absorption Spectra of the Ni^{II} Phosphine Complexes.

Compound	Solvent	ν_{max} cm^{-1} (ε_{max})
$Ni(PPh_3)_2(NCS)_2$[15]	Reflection	18,200(sh)! 21,700.
$Ni(PPh_3)_2(NCS)_2$[15]	C_6H_6	23,500(2,600).
$Ni(PPh_2Cy)_2(NCS)_2$	Nujol	20,000(sh); 24,700. 30,800.
$Ni(PPh_2Cy)_2(NCS)_2$	C_6H_6	25,000(18,000) 31,600(31,000).
$Ni(PPh_2Cy)_2(NCS)_2$	$CHCl_3$	20,00(sh); 25,600(10,000); 32,000(16,000).
$Ni(PPhCy_2)_2(NCS)_2$	Nujol	21,300(sh); 25,800; 32,400.
$Ni(PPhCy_2)_2(NCS)_2$	C_6H_6	20,400(sh); 25,800(9,000); 32,500(30,000).
$Ni(PPhCy_2)_2(NCS)_2$	$CHCl_3$	20,800(sh); 26,400(12,000); 32,800(24,000).
$Ni(PCy_3)_2(NCS)_2$	Nujol	22,200(sh); 26,450; 32,600.
$Ni(PCy_3)_2(NCS)_2$	C_6H_6	26,500(15,500); 33,200(31,000).
$Ni(PCy_3)_2(NCS)_2$	$CHCl_3$	26,800(17,000); 33,700(30,000).
$Ni(PPh_3)_2Cl_2$ [d]	Nujol	8,850; 11,000; 16,700(sh); 18,000; 25,000.
$Ni(PPh_3)_2Cl_2$[15] [e]	C_6H_6	11,400(76); 17,4000-19,000(sh); 25,000(3,000).
$Ni(PPh_2Cy)_2Cl_2$	Nujol [a]	8,780; 18,500(sh); 21,000; 24,800; 31,200.
$Ni(PPh_2Cy)_2Cl_2$	Nujol [b]	9,100; 11,500; 17,000; 18,500; 23,800; 26,000; 29,400.
$Ni(PPh_2Cy)_2Cl_2$	C_6H_6	9,100(4); 11,220(30); 19,150(650); 25,600(10,000).
$Ni(PPh_2Cy)_2Cl_2$	$CHCl_3$	9,250(15); 11,420(50); 19,250(sh); 25,600. [c]
$Ni(PPhCy_2)_2Cl_2$	Nujol	20,400; 26,000; 33,300(sh).
$Ni(PPhCy_2)_2Cl_2$	C_6H_6	9,100(<1); 11,100(2); 20,200(520); 26,100(13,000).
$Ni(PPhCy_2)_2Cl_2$	$CHCl_3$	9,000(2); 11,100(7); 20,400(sh); 25,800(5,500); 29,600(1,700).
$Ni(PCy_3)_2Cl_2$	Nujol	20,400; 25,400; 34,000.
$Ni(PCy_3)_2Cl_2$	C_6H_6	10,300(<1); 19,200(420); 25,100(15,000); 31,000(1,400).
$Ni(PCy_3)_2Cl_2$	$CHCl_3$	9,520(3); 10,380(5); 15,400(sh); 18,000(250); 25,300(2,500); 29,200(1,500); 34,500(sh).
$Ni(PPh_3)_2Br_2$ [d]	Nujol	8,600; 10,800; 14,900(sh); 17,100; 22,600.
$Ni(PPh_3)_2Br_2$[15]	C_6H_6	10,900(160); 17,500(300); 23,500(5,200).
$Ni(PPh_3)_2Br_2$	$CHCl_3$	8,600(4); 10,900(130); 17,000; [c] 23,000. [c]
$Ni(PPh_2Cy)_2Br_2$	Nujol	8,850; 11,360; 15,900; 18,100; 21,750(sh); 24,000.
$Ni(PPh_2Cy)_2Br_2$	C_6H_6	11,200(40); 17,600(550); 23,850(6,000); 29,800(sh).
$Ni(PPh_2Cy)_2Br_2$	$CHCl_3$	8,850(20); 11,400(140); 18,200(sh); 23,900(1,500).
$Ni(PPhCy_2)_2Br_2$	Nujol	17,550(sh); 20,000(sh); 23,600; 32,300(sh).
$Ni(PPhCy_2)_2Br_2$	C_6H_6	10,800(6); 18,600(470); 23,800(11,000); 34,450(sh).
$Ni(PPhCy_2)_2Br_2$	$CHCl_3$	11,030(22); 18,100(300); 23,800(2,000).
$Ni(PCy_3)_2Br_2$	Nujol	17,000(sh); 20,000(sh); 23,650.
$Ni(PCy_3)_2Br_2$	C_6H_6	8,930(<1); 10,300(4); 17,400(540); 23,900(7,250).
$Ni(PCy_3)_2Br_2$	$CHCl_3$	8,930(3); 10,260(10); 16.400(200); 19,200(sh); 25,600(1,300); 27,400(1,300); 33,300(sh).
$Ni(PPh_3)_2I_2$ [d]	Nujol	9,700; 14,300(sh); 16,100(sh); 17,800(sh); 21,300; 23,800(sh).
$Ni(PPh_3)_2I_2$ [d]	C_6H_6	10,000(600); 13,500(sh); 15,000(600); 18,500(sh); 21,500(7,000); 23,500(8,000).
$Ni(PPh_3)_2I_2$	$CHCl_3$	10,100(600); 13,300(sh); 14,300(sh).
$Ni(PPh_2Cy)_2I_2$	Nujol	10,750; 13,700; 14,900; 15,400(sh); 18,700(sh); 23,200(sh); 25,800; 33,300(sh).
$Ni(PPh_2Cy)_2I_2$	C_6H_6	10,480(82); 13,900(sh); 15,700(550); 24,400(sh); 27,400(4,000); 33,300(7,000).
$Ni(PPh_2Cy)_2I_2$	$CHCl_3$	10,600(170); 15,300(310); 17,850(sh); 25,000(sh); 27,500(5,000); 32,900(13,000).
$Ni(PPhCy_2)_2I_2$	Nujol	8,700; 9,700; 13,150(sh); 14,100(sh); 15,750; 20,000; 25,000(sh); 30,300(sh); 32,200(sh).
$Ni(PPhCy_2)_2I_2$	C_6H_6	8,920(sh); 9,930(113); 13,500(sh); 15,100(300); 17,550(sh); 23,500(2,500); 28,800(2,000).
$Ni(PPhCy_2)_2I_2$	$CHCl_3$	10,370(119); 13,300(200); 15,650(250); 17,850(sh); 20,600(sh); 24,700(2,500); 30.800(4,000).
$Ni(PCy_3)_2I_2$	Nujol [a]	8,700; 9,300(sh); 13,700(sh); 14,800; 18,200(sh); 20,000; 25,000(sh); 27,000.
$Ni(PCy_3)_2I_2$	Nujol [b]	8,700; 9350; 13,000(sh); 13,700(sh); 14,800; 24,200; 29,600.
$Ni(PCy_3)_2I_2$	C_6H_6	8,700(sh); 9,550(140); 13,300(400); 13,900(sh); 18,200(sh); 24,400(3,600); 29,600(3,400).
$Ni(PCy_3)_2I_2$	$CHCl_3$	9,560(130); 13,300(190); 13,900(sh); 18,500(sh); 20,000(640); 22,700(sh); 24,800(1,400); 27,800(sh); 30,500(1,300).

[a] Square-planar isomer. [b] Tetrahedral isomer. [c] Decomposition interferes with the determination of ε_{max}. [d] Similar values have been reported.[11,15]. [e] We observe extensive decomposition.

those samples which were used for these measurements generally exhibit magnetic moments of between 0.3-0.9 B.M.

By varying the conditions of crystallization, several of the (diamagnetic) complexes were obtained as the pure tetrahedral isomer. Thus, fast precipitation from a concentrated ethanol solution yields the dark green paramagnetic $Ni(PPh_2Cy)_2Cl_2$, $Ni(PPhCy_2)_2Br_2$ (momentarily) and $Ni(PCy_3)_2I_2$.

It has been shown previously, that both in solution and in the solid state the complex $Ni(PPh_3)_2Cl_2$ exists exclusively as the tetrahedral isomer.[9,10,11] We have found fast precipitation of this complex from a concentrated methylene chloride solution affords a red diamagnetic compound which isomerizes very readily to the known tetrahedral form. The isomerization is enhanced when the complex is slightly moist with solvent or Nujol, or when under the light beam of the

Table III. ν^2 and the lowest spin-allowed transition of the squ are-planar isomer of NiL_2X_2 in cm^{-1}.

Solvent	$L=PPh_3$,	PPh_2Cy,	$PPhCy_2$	PCy_3
		$X=Cl^-$ (ν_2)		
Nujol	11,000	E1,500	—	—
C_6H_6	*a*	11,220(30)	11,100(2)	10,300(<1)
$CHCl_3$	*a*	11,420(50)	11,100(7)	10,380(5)
		$\chi=Br^-$ (ν_2)		
Nujol	10,800	11,360	—	—
C_6H_6	10,900(160)	11,200(40)	10,800(6)	10,300(4)
$CHCl_3$	10,900(130)	11,400(140)	11,030(22)	10,260(10)
		$\chi=Cl^-$ (Square-planar transition)		
Nujol	—	18,500(sh)	20,400	20,400
C_6H_6	*a*	19,150(650)	20,200(520)	19,200(420)
$CHCl_3$	*a*	19,250(sh)	20,400(sh)	18,000(250)

[a] Extensive decomposition observed.

Table IV. Magnetic moments in Solution[a].

Compound	C_6H_6 μ_{eff} (B.M.)	N_T[b]	$CHCl_3$ μ_{eff} (B.M.)	N_T[b]	CH_2Cl_2 μ_{eff} (B.M.)	N_T[b]
$Ni(PPh_3)_2Cl_2$	*c*		*c*		3.30[d]	1.0
$Ni(PPh_2Cy)_2Cl_2$	1.54	.22	2.56	.60	2.47	.56
$Ni(PPhCy_2)_2Cl_2$	.76	.05	1.67	.26	1.42	.19
$Ni(PCy_3)_2Cl_2$	.55	.03	1.39	.19	1.17	.13
$Ni(PPh)_3)_2Br_2$	*c*		3.19	1.0	*c*	
$Ni(PPh_2Cy)_2Br_2$	1.77	.31	3.04	.9	2.84	.79
$Ni(PPhCy_2)_2Br_2$	1.06	.11	1.95	.37	1.76	.30
$Ni(PCy_3)_2Br_2$	.98	.09	1.86	.34	1.81	.32
$Ni(PPh_3)_2I_2$	3.26	1.0	3.26	1.0		
	2.90	.77	2.84	.74	2.78	.71
e						

[a] All measurements were taken at 37°C. [b] N_T (The mole fraction of tetrahedral isomer) - μ^2_{OBS}/μ^2_T. The following values were used for μ_T: 3.27 B.M. for $X = Cl^-$; 3.19 B.M. for $X = Br^-$; 4.26 B.M. for $X = I^-$. For example, see Ref. 12. [c] Readily decomposed. [d] Some decomposition noticeable. [e] The values for the other iodides were irreproducible due to decomposition.

spectrophotometer. Thus, we were unable to obtain the electronic spectra of this compound. However, based on its diamagnetism and the spectra of the isomerized form, we suggest that the red compound is the square-planar isomer of $Ni(PPh_3)_2Cl_2$.

Discussion

In 1962, Hayter demonstrated that in complexes of the type L_2NiX_2 (L=ethyldiphenylphosphine; $X=Cl^-, Br^-, I^-$), planar ⇆ tetrahedral isomerization take place both in solution and in the solid state and that the interconversion between the two structures depends on the halide ion.[13] This phenomenon had also been investigated by Coussmaker[14] and co-workers who showed that for a given halide there is a change in structure from square-planar to tetrahedral as alkyl groups in the tertiary phosphine are successively replaced by phenyl. Thus, whereas the complex $Ni(PPhBu_2)_2Cl_2$ is diamagnetic, the complex $Ni(PPh_2Bu)Cl_2$ is paramagnetic with an effective magnetic moment of 3.35 B. M. These investigations coupled with the recent study by Pignolet *et al.*[12] clearly suggest that the planar⇆tetrahedral isomerization is determined by both steric and electronic factors. Thus, bulky ligands favor the tetrahedral configuration whereas strong field ligands favor the square-planar isomer.

The electronic absorption spectra of the thiocyanate complexes reported here exhibit the first « *d—d* » spin allowed transition as a shoulder on the low energy side of the first charge transfer band. The observed shifts in these bands (*vide supra*) as a function of the phosphine ligand clearly places these ligands in the following spectrochemical order

$$PCy_3 > PPhCy_2 > PPh_2Cy > PPh_3$$

It is interesting to note that the increase in energy of the electronic absorption bands in going from PPh_3 to PPh_2Cy is about twice as large as in going from $PPh_2Cy \rightarrow PPhCy_2$ and $PPhCy_2 \rightarrow PCy_3$.

All the halo complexes in solution exhibit the well known planar⇆tetrahedral equilibrium. The equilibrium constants appear to depend on three factors: the polarity of the solvent, the halide ions, and the

---

(13) R.G. Hayter, F.S. Humier, *Inorg. Chem.*, *12*, 1701 (1965).
(14) C.R.C. Coussmaker, H. Hely Hutchinson, J.R. Mellor, L.E. Sutton, and L.M. Venanzi, *J. Chem. Soc.*, *1961*, 2705.
(15) M.C. Browning, R.F.B. Davies, D.J. Morgan, L.E. Sutton, and L.M. Venanzi, *J. Chem. Soc.*, *1961*, 4816.

phosphine ligands. Since weak field ligands favor the tetrahedral configuration, the amount of this isomer in solution will be expected to follow the order $I^- > Br^- > Cl^-$ for a given phosphine and $PPh_3 > PPh_2Cy > PPhCy_2 > PCy_3$ for a given halide. This behavior is indeed followed in both benzene solution, which in general favors the less polar square-planar isomer, and in $CHCl_3$ which favors the more polar tetrahedral isomer, as can be seen from the solution moments of these complexes.

The electronic absorption spectra of the tetrahedral isomers, however, follow a somewhat unexpected behavior. For a given halide, the ν_2 band shifts to higher energy in going from PPh_3 to PPh_2Cy, but upon further substitution of cyclohexyl groups this band shifts to lower energy. The same behavior is also noted for the diamagnetic halo complexes, except that the position of the « *d–d* » band follows the order $PCy_3 < PPhCy_2 > PPh_2Cy$. This behavior is clearly opposite to expectation if we consider only the the ligand field strength of the phosphine ligand. It seems reasonable to suggest that this behavior stems from the fact that the increase in ligand field strength upon cyclohexyl substitution is offset by a slight weakening of the metal-ligand bonds due to increase in non-bonded repulsion of the bulkier phosphine ligands are closer to one another. This is indeed born out by fact that in the tetrahedral complexes ν_2 shifts to lower energy in going from $PPh_2Cy \rightarrow PPhCy_2$, whereas in the planar complexes this shift occurs in going from $PPhCy_2, \rightarrow PCy_3$. Another explanation for similar behavior, which is based on differences in interaction between the different phosphine ligands and the *d* orbitals of the metal, has been suggested by Pignolet *et al.*[12] Unfortunately, on the basis of our data we canont distinguish between these two possibilities. We must note, however, that the expansion of the coordination sphere, if operative in these complexes, is probably small and is not expected to affect the observed magnetic moments.

Although our results are not conclusive, it is reasonable to suggest that with the ligands PC_3 and $PPhCy_2$ steric crowding is of considerable importance in determining the overall properties of the complexes studied. We find, for example, that the reaction of BH_4^- with the complexes NiL_2X_2 ($L = PPh_3$, PPh_2Cy) leads to immediate reduction of the metal whereas the reaction of BH_4^- with $Ni(PPhCy_2)_2Cl_2$ yields a complex analogous to $Ni(PCy_3)_2HCl$. To further investigate this point we are currently studying the effect of these ligands on the catalytic properties of certain metal complexes.