Alkyl- and Aryl-fluorophosphines as Ligands in Transition-metal Complexes with Metals in Positive Oxidation States. Part I. Nickel(II) and Cobalt(II) Halide Complexes of Di-(t-butyl)fluorophosphine

By **Othmar Stelzer** * and **Eugen Unger**, Lehrstuhl B für Anorganische Chemie der Technischen Universität, 33 Braunschweig, Pockelsstrasse 4, Germany

Di-(t-butyl)fluorophosphine forms stable complexes of the type NiX_2L_2 and CoX_2L_2 (where X = Cl, Br, or I and L = $Bu^t{}_2PF$) with nickel(II) and cobalt(II) halides. The structure of these compounds, elucidated by n.m.r., i.r., and u.v. spectra as well as by magnetic measurements is *trans*-square planar in the case of NiX_2L_2 and tetrahedral for the complexes CoX_2L_2. For $NiCl_2(Bu^t{}_2PF)_2$ a *cis–trans*-equilibrium is likely to exist in solution. The low-temperature ^{19}F n.m.r. spectrum of the latter compound is explained by the presence of different rotamers with respect to the Ni–P axis.

THE co-ordination chemistry of alkyl- and aryl-fluorophosphines has been investigated only in a very few examples.[1-4] Complexes of these ligands with transition metals in positive oxidation states have not been so far synthesised. During a systematic investigation of the reactivity of co-ordinated ligands, it seemed interesting to prepare complexes of fluorophosphines with metals in a positive oxidation state. Di-(t-butyl)fluorophosphine[5] in contrast to other dialkylfluorophosphines is stable with respect to the redox disproportionation[6,7] (1). For

$$3R_2PF \longrightarrow R_2PF_3 + R_2P\text{-}PR_2 \qquad (1)$$

that reason we first evaluated di-(t-butyl)fluorophosphine with regard to its ligand properties towards metals in positive oxidation states.

EXPERIMENTAL

All experiments were conducted in a dry oxygen-free atmosphere of nitrogen or argon, purified over a BASF BTS catalyst. Methylene dichloride, 1,2-dichloroethane, and acetone were dried by repeated distillation over P_4O_{10}. Benzene and toluene were distilled twice over lithium aluminium hydride. Molecular weights were determined cryoscopically on 10^{-2}—10^{-1}M solutions in benzene.

N.m.r. spectra were recorded on a Varian HA 60 A instrument at 60, 56·4, and 24·3 MHz for ^1H, ^{19}F, and ^{31}P, respectively, or on a Bruker HFX 90 at 84·67 MHz for ^{19}F. ^{19}F N.m.r. shifts are given relative to internal Cl_3CF or C_6F_6 standard, ^1H n.m.r. shift relative to CH_2Cl_2.

I.r. spectra were recorded on a Beckman IR 10 A instrument on Nujol mulls or methylene dichloride solutions by use of KBr or polyethylene cells. The i.r. spectra in the range from 250 to 70 cm^{-1} were run on a Beckman IR 11 instrument with polyethylene cells.

The u.v. spectra were obtained on a Beckman Acta III spectrophotometer on Nujol mulls or solutions in methylene dichloride or acetone. Quartz cells (0·1 or 1·0 cm) were used.

Magnetic moments in the solid state were determined by the Gouy method,[8] magnetic moments in solution were obtained by Evans' method[9] with methylene dichloride, benzene, or toluene as solvents and toluene as standard for the benzene and methylene dichloride solutions. The susceptibility of the halide ions and $Bu^t{}_2PF$ was calculated from Pascal's constants.[8]

Di-(t-butyl)fluorophosphine[5] and di-(t-butyl)chlorophosphine[10,11] were prepared by literature methods.

Anhydrous nickel(II) and cobalt(II) halides were obtained by conventional methods.[12]

Preparation of the Complexes NiX_2L_2 *and* CoX_2L_2 *from* $Bu^t{}_2PF$ *and Nickel*(II) *or Cobalt*(II) *Halides* (L = $Bu^t{}_2PF$; X = Cl, Br, I).—Di-(t-butyl)fluorophosphine (1·64 g, 0·01 mol) was added under nitrogen to the suspension of 0·015 mol anhydrous nickel or cobalt halide in acetone or benzene (50 ml) (saturated with argon). After 24 h stirring at room temperature the excess of the metal halide was filtered off and the solvent evaporated *in vacuo* (20 °C, 10 mmHg). The complexes obtained by this procedure are already quite pure but they can be recrystallised from methylene dichloride or toluene at −50 °C. The yields (see also Table 1) are as follows: $Cl_2Ni(Bu^t{}_2PF)_2$ (I), 1·60 g (70%), ruby-red;

TABLE 1

Analytical data (%) and molecular weights[a]

	C	H	P	F	*M*
$Cl_2Ni(Bu^t{}_2PF)_2$ (I)	41·4	8·3	13·9	8·5	480
	(41·9)	(7·9)	(13·5)	(8·3)	(458·0)
$Br_2Ni(Bu^t{}_2PF)_2$ (II)	34·9	6·8	11·4	7·0	560
	(35·1)	(6·6)	(11·3)	(6·9)	(546·9)
$I_2Ni(Bu^t{}_2PF)_2$ (III)	30·1	5·8	9·7	5·9	610
	(30·0)	(5·7)	(9·7)	(5·9)	(640·9)
$Cl_2Co(Bu^t{}_2PF)_2$ (IV)	41·8	7·8	13·5	8·0	475
	(41·9)	(7·9)	(13·5)	(8·3)	(458·2)
$Br_2Co(Bu^t{}_2PF)_2$ (V)	35·3	6·8	11·3	6·7	533
	(35·1)	(6·6)	(11·3)	(6·9)	(574·1)
$Br_2Ni(Bu^t{}_2PHO)_2$ (VI)[b]	35·2	7·0	11·4		
	(35·1)	(6·6)	(11·3)		
$I_2Ni(Bu^t{}_2PHO)_2$ (VII)[b]	29·7	6·0	9·5		
	(30·0)	(5·7)	(9·7)		

[a] Calculated values in parentheses. [b] It was impossible to determine the molecular weight cryoscopically in benzene, because the solutions slowly decomposed with separation of nickel(II) bromide or iodide.

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$Br_2Ni(Bu^t{}_2PF)_2$ (II), 2·10 g (77%), brown-red; $I_2Ni(Bu^t{}_2PF)_2$ (III), 2·82 g (88%), violet; $Cl_2Co(Bu^t{}_2PF)_2$ (IV), 1·85 g (81%), blue; and $Br_2Co(Bu^t{}_2PF)_2$ (V), 2·25 g (82%), blue-green. By the reaction of CoI_2 with $Bu^t{}_2PF$ we could not obtain pure products of the composition $CoI_2(Bu^t{}_2PF)_2$.

Synthesis of Complexes (I) *and* (II) *from* NiX_2 (X = Cl, Br), $Bu^t{}_2PCl$, *and* NaF.—To the suspension of NaF (0·63 g; 0·015 mol) and $NiCl_2$ (1·30 g; 0·01 mol) or $NiBr_2$ (2·2 g; 0·01 mol) in acetone (50 ml), $Bu^t{}_2PCl$ (1·80 g, 0·01 mol) was added with stirring. After 72 h the excess of nickel halide and sodium fluoride was filtered off and about three quarters of the solvent was evaporated *in vacuo* (20 °C, 25 mmHg). After filtration under nitrogen through a sintered glass funnel, and washing with 20 ml pentane, the compounds (I) and (II) were obtained in good yields: (I), 1·55 g (68%); (II), 2·00 g (73%).

TABLE 2

^{19}F and ^{31}P N.m.r. data for the complexes (I) and (II) in methylene dichloride solution (coupling constants in Hz, chemical shift values in p.p.m.) relative to C_6F_6 as internal standard

	^{19}F n.m.r.						^{31}P n.m.r.	
	t/°C	δ_F	$\lvert {}^3J_{PF} + {}^1J_{PF} \rvert$	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	δ_P	$^1J_{PF}$
trans-$Cl_2Ni(Bu^t{}_2PF)_2$ (I)	+80	$+19·5 \pm 2$ [a]	925	945 ± 10 [b]	18 ± 10 [b]	425 ± 10 [b]		
	+30	$+23·5 \pm 2$					−176	~920
	−20	$+25·8 \pm 0·5$ [c]	908	917 ± 5	10 ± 5	425 ± 5		
		$+23·5 \pm 0·5$ [c]	903	915 ± 5	13 ± 5	425 ± 5		
cis-$Cl_2Ni(Bu^t{}_2PF)_2$ (I)		$-5·3 \pm 0·5$	900			<90		
trans-$Br_2Ni(Bu^t{}_2PF)_2$ (II)	+30	$+12·3 \pm 2$					−175	~900

[a] Relative to C_6F_6 as internal standard in 1,2-dichloroethane. [b] In trichloroethylene solutions. [c] Values for two isomers (see text).

Hydrolysis of the Complexes (I)—(III) *in Acetone–Water Mixtures*.—$Cl_2Ni(Bu^t{}_2PF)_2$ (I). The solution of (I) (0·92 g; 2 mmol) in methylene dichloride (5 ml) was added slowly under stirring to acetone (7·2 ml) with 1% water (4 mmol H_2O). A yellow precipitate was formed (0·240 g; 1·85 mmol). It was separated by centrifuging and identified by a Debye–Scherrer photograph as $NiCl_2$. The solvent in the centrifugate was removed *in vacuo*, an oily hygroscopic liquid was obtained which was identified by n.m.r. and i.r. to be di-(t-butyl)phosphine oxide, $Bu^t{}_2PHO$;[13] ^1H n.m.r.: δ_H 215 Hz (relative to CH_2Cl_2), $^3J_{PH}$ 15 Hz, i.r. (cm^{-1}): 2950s, 2290m, 1470s, 1394w, 1370m, 1142s, 918m, 815s (P–Bu^t), and 656s.

$Br_2Ni(Bu^t{}_2PF)_2$, (II) *and* $I_2Ni(Bu^t{}_2PF)_2$ (III). These experiments were carried out in an analogous manner to the hydrolysis of (I). The complexes (II) (1·10 g; 2 mmol) and (III) (1·28 g) were used. Intense green solutions were obtained in both cases. After removal of the solvent *in vacuo* we obtained green products which were soluble in benzene, toluene, and methylene dichloride; yield: 1·0 g (VI) (91%) and 1·2 g (VII) (94%). It was, however, quite difficult to obtain (VII) completely dry. Only after drying *in vacuo* over P_4O_{10} were we able to obtain a product which contained only small quantities of water (according to the i.r. absorptions in the 3500 cm^{-1} region).

RESULTS AND DISCUSSION

In acetone or benzene suspensions di-(t-butyl)fluorophosphine readily forms stable complexes with nickel(II) and cobalt(II) halides of the type $MX_2(Bu^t{}_2PF)_2$ [M = Co, X = Cl, Br (IV), (V); M = Ni, X = Cl, Br, I (I), (II), (III)]. Analogous cobalt and nickel complexes with neutral phosphine (or other) ligands have been known for a long time.[14-17] They are still being intensely investigated by different spectroscopic methods.[18-20]

The compounds $Cl_2Ni(Bu^t{}_2PF)_2$ (I) and $Br_2Ni(Bu^t{}_2PF)_2$ (II) can also be synthesised indirectly by the reaction of di-(t-butyl)chlorophosphine with a suspension of nickel(II) bromide and sodium fluoride in acetone.

The compounds (I)—(V) are obtained as intensely coloured crystalline solids which are soluble in organic solvents such as methylene dichloride, benzene, dibutyl ether, acetone, and acetonitrile. They are stable to hydrolysis in the solid state. The solutions, however, can be very easily hydrolysed. By careful hydrolysis in acetone–water mixtures complexes of di-(t-butyl)phosphine oxide are obtained which have been characterised by elemental analysis, i.r., and u.v. spectra. According to magnetic measurements in acetone solution (see the corresponding sections) these complexes have a pseudo-tetrahedral arrangement of the ligands $Bu^t{}_2PHO$ and X round the central nickel atom [$\mu_{eff} = 5·20$ for (VI) and 4·56 for (VII)].

In the case of $Cl_2Ni(Bu^t{}_2PF)_2$ (I) hydrolysis under these conditions leads to nickel chloride and di-(t-butyl)phosphine oxide.

By none of these reactions have we been able to synthesise complexes of $Bu^t{}_2P$–O–H. Barium salts of hydroxyphosphines could be obtained by hydrolysis of, *e.g.*, $Ni(PF_3)_4$ with $Ba(OH)_2$.[21] A nucleophilic displacement of one fluorine atom followed by a deprotonation under these conditions led to complexes containing the interesting ligand PF_2O^-.

^1H *N.m.r. Spectra*.—The ^1H n.m.r. spectra of the

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[20] G. N. La Mar, E. O. Sherman, and G. A. Fuchs, *J. Co-ordination Chem.*, 1971, **1**, 289; G. N. La Mar, *J. Amer. Chem. Soc.*, 1965, **87**, 3567.

[21] T. Kruck, M. Höfler, K. Baur, P. Jukes, and K. Glinka, *Chem. Ber.*, 1968, **101**, 3827.

cobalt complexes (IV) and (V) in methylene dichloride show only one broad signal at δ_H 242 ± 2 Hz (relative to CH_2Cl_2 as internal standard), the line-width at half-height being *ca.* 50 and 75 Hz, respectively. The nickel complexes (I)—(III) in CH_2Cl_2 solutions show at room temperature only a slightly broadened singlet at δ_H 222 Hz. On heating toluene solutions (δ_H 46 Hz relative to the CH_3 resonance of toluene) to 80 or 100 °C the line shapes and positions of these singlets are not altered distinctly. Upon cooling the methylene dichloride solutions the singlet is broadened and split into a doublet and a singlet with almost the same chemical shift (see Figure 1). The area under the singlet decreases as the temperature decreases. This process is reversible. This observation is generally true for all nickel complexes (I)—(III), although the limited solubility of (II) and even more of (III) makes it quite difficult to observe n.m.r. spectra below —20 °C.

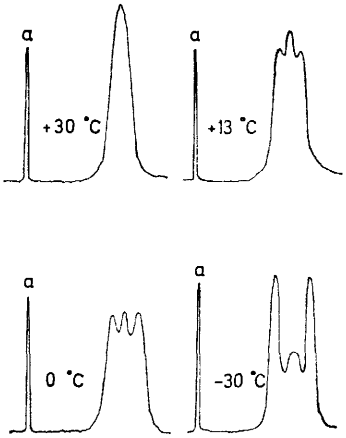

FIGURE 1 Temperature-dependence of the ^1H n.m.r. spectrum of compound (I) in methylene dichloride solution containing *ca.* 5% toluene. The peak marked a is the reference signal (protons of the methyl group in toluene)

The ^1H n.m.r. spectra of compounds (I)—(III) in methylene dichloride containing *ca.* 10% Bu^t_2PF show at room temperature, besides the singlets of the protons in (I)—(III), the well resolved doublet of doublets for Bu^t_2PF at 252 ± 2 Hz ($^3J_{PH}$ 13·0 Hz, $^4J_{FH}$ 1·5 Hz).[5] On cooling, the singlets of (I) and (II) undergo the same changes in shape as in CH_2Cl_2 solutions without the free ligand. The chemical shift for the protons in Bu^t_2PF and (I) with respect to (II) are constant within ±2 Hz. The integration ratio (*ca.* 3 : 2 for complex : Bu^t_2PF) is constant as well (±5% deviation) within the temperature range +40 to —40 °C. From this we conclude that there is no fast exchange between free and complexed Bu^t_2PF in (I) or (II). The formation of a penta-co-ordinated species in appreciable amounts in an equilibrium (2) can also be excluded. This should alter

$$Bu^t_2PF + (Bu^t_2PF)_2NiX_2 \rightleftharpoons (Bu^t_2PF)_3NiX_2 \quad (2)$$

the integration ratio of complex (I), (II), or (III) with respect to free Bu^t_2PF. If 1,2-dichloroethane is employed as a solvent instead of methylene dichloride the ^1H n.m.r. spectra of the $X_2Ni(Bu^t_2PF)_2$ (X = Cl, Br) solutions containing *ca.* 10% Bu^t_2PF at 30 °C are identical to those mentioned above (shifts measured relative to an internal CH_2Cl_2 standard) for methylene dichloride solutions. The chemical shift of the singlet for the protons of (I) and (II) (deviation ±2 Hz) and integration ratio (within ±5%) remain constant. It must be noted, however, that the ^1H n.m.r. spectrum of the Bu^t_2PF added to the 1,2-dichloroethane solutions of (I) changes within the temperature range from +30 to 80 °C. At 50 °C the doublet according to ^{19}F–^1H coupling collapses and one gets a simple doublet. At +60 °C this doublet also collapses giving a broad singlet. The ^1H n.m.r. signal of the protons in (I), however, is not shifted within the observed temperature range (+30 to 80 °C), the line shape remains unchanged. Mixtures of (II) and Bu^t_2PF in 1,2-dichloroethane must be heated to +80 °C until collapse of the doublet of doublets to a simple doublet in the ^1H n.m.r. spectrum is observed, the chemical shift of the singlet for the proton in (II) being constant.

The u.v. spectra of the diluted n.m.r. samples of Bu^t_2PF–(I) and Bu^t_2PF–(II) in 1,2-dichloroethane showed very weak absorptions at 975 and 980 nm. The intensity of these peaks increased after contact of the solutions with air. In the case of the mixture of (II) with Bu^t_2PF the position of the two absorptions in the u.v. spectrum is the same as for the hydrolysis product (see Table 4).

For that reason we believe that the observed change in the ^1H n.m.r. spectrum of Bu^t_2PF in these solutions is probably due to a rapid ligand exchange involving small amounts of hydrolysis products and free ligand Bu^t_2PF.

The ^1H n.m.r. spectra of the compounds (VI) and (VII) in concentrated methylene dichloride solutions show for the t-butyl protons a singlet at δ_H 123 Hz and δ_H 281 Hz, respectively. Only very concentrated solutions in methylene dichloride or benzene are stable. On dilution the dissociation equilibrium (3) is shifted to

$$X_2Ni(Bu^t_2PHO)_2 \rightleftharpoons X_2Ni + 2Bu^t_2PHO \quad (3)$$

the side of the decomposition products and nickel halide is precipitated from the solutions. Acetone solutions are stable even for very low concentrations (10^{-3}—10^{-4}M).

No ^1H n.m.r. signal corresponding to the P–H protons in the complexes (VI) and (VII) could be observed. This may be explained by a rapid proton exchange between different sites (*e.g.*, solvent and other complex molecules) and the effect of the paramagnetic central atom.[22]

^{19}F *N.m.r. Spectra.*—The complexes (I) and (II) show relatively broad doublets at δ_F 23·5 p.p.m. and δ_F 12·3 p.p.m., respectively. Because of the low solubility of (III) in most of the inert organic solvents we could not obtain ^{19}F n.m.r. spectra. The methylene dichloride

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solutions of the tetrahedrally co-ordinated cobalt complexes (IV) and (V) showed no ^{19}F n.m.r. signals. This is probably due to the limited solubility of (IV) and (V) and the line broadening by contact interaction with the paramagnetic central atom.[22]

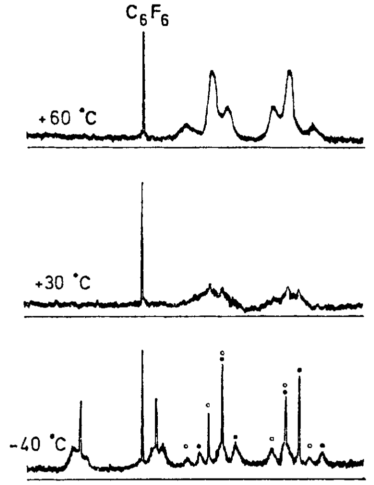


FIGURE 2 Temperature-dependence of the ^{19}F n.m.r. spectrum of compound (I) in methylene dichloride solution. The signs ○ and ● indicate the different lines of the two $[AX]_2$ spin systems

For $Cl_2Ni(Bu^t{}_2PF)_2$ the temperature-dependence of the ^{19}F n.m.r. spectrum has been studied in the range between −50 and +80 °C by use of methylene dichloride, 1,2-dichloroethane, or trichloroethylene solutions (see Figure 2).

The ^{19}F n.m.r. spectra of trichloroethylene solutions at 32 °C show a relatively broad doublet at δ_F 23·0 p.p.m., with some irregular spikes at the top of the doublet signals. At +80 °C the typical six-line pattern for an $[AX]_2$ spin system[23] with $J_{XX'}$ *ca.* 0 can be observed (see Figure 2). The signals are relatively broad (line-width in half-height 70—90 Hz). Methylene dichloride solutions at −20 °C show an additional 'doublet' with δ_F −5·3 p.p.m. and in the place of the broad doublet at room temperature a system of ten signals with differing intensities in the 56·4 MHz spectrum or 11 in the 84·67 MHz spectrum. These spectra can be constructed by superimposing two sets of six lines corresponding to two $[AX]_2$ spin systems with a shift difference for the centres of *ca.* 2 p.p.m. (see Figure 3).

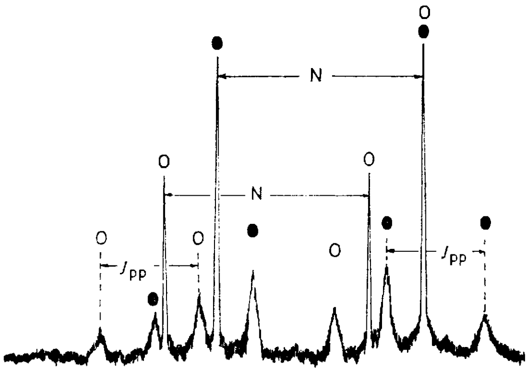
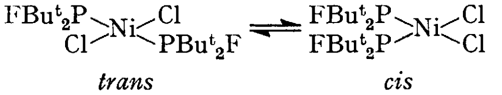


FIGURE 3 84·67 MHz ^{19}F n.m.r. spectrum of compound (I) in methylene dichloride solution at −20 °C. The signs ○ and ● assign the observed lines to one of the two $[AX]_2$ spin systems

The magnetic volume susceptibility of CH_2Cl_2 solutions is almost constant within the observed temperature range (+40 to −50 °C), and the solutions are diamagnetic (partially hydrolysed solutions are weakly paramagnetic). Therefore, an equilibrium between the square planar and tetrahedral form of (I) can probably be excluded.

We explain the temperature dependence of the ^{19}F and ^{1}H n.m.r. spectra by assuming (i) an equilibrium (4)



$$\begin{array}{c}\mathrm{FBu^t{}_2P}\\ \mathrm{Cl}\end{array}\!>\mathrm{Ni}<\!\begin{array}{c}\mathrm{Cl}\\ \mathrm{PBu^t{}_2F}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{FBu^t{}_2P}\\ \mathrm{FBu^t{}_2P}\end{array}\!>\mathrm{Ni}<\!\begin{array}{c}\mathrm{Cl}\\ \mathrm{Cl}\end{array} \qquad (4)$$

trans *cis*

between the *cis*- and *trans*-form of (I). The *cis*-form is more stable at low temperatures. We assign the additional 'doublet' with a broad weak line on the outer side of each of the two signals in the ^{19}F n.m.r. spectrum and the doublet in the ^{1}H n.m.r. spectrum, the area of which increases as the temperature decreases, to the *cis*-form of $Cl_2Ni(Bu^t{}_2PF)_2$. The similarity of the ^{1}H n.m.r. and ^{19}F n.m.r. spectrum of the complex *cis*-$Mo(CO)_4(Bu^t{}_2PF)_2$ (δ_F +9·8 p.p.m., $|^1J_{PF} + {}^3J_{PF}|$ 842 Hz, δ_H 234 Hz, relative to CH_2Cl_2, 'J_{PH}' 13·1 Hz) supports the assignment. A similar assignment seems to be reasonable for the bromo-complex $Br_2Ni(Bu^t{}_2PF)_2$.

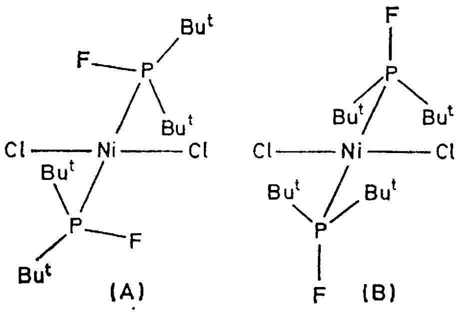


FIGURE 4 Suggested structures for the two rotamers of compound (I) at low temperature

(ii) The existence of two rotamers (A) and (B) different in energy for *trans*-$Cl_2Ni(Bu^t{}_2PF)_2$. The conformation (A) (see Figure 4) with the two fluorine atoms in (or almost in) the plane of the D_{2h} Cl_2NiP_2 skeleton is probably the stable one in the solid state of $Br_2Ni(Bu^t{}_2PF)_2$ according to *X*-ray data.[24] The conformer next to or comparable in energy with (A) is (B) with the bulky t-butyl groups in '*trans*' position as well. The different chemical environment of the fluorine atoms in the rotamers (A) and (B) explains the shift difference in the ^{19}F n.m.r. spectrum. At higher temperatures the rotation of the two $Bu^t{}_2PF$ ligands round the Ni–P axis

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[24] W. S. Sheldrick and O. Stelzer, *J.C.S. Dalton*, 1973, 926.

averages this difference and the spectrum of only *one* $[AX]_2$ spin system can be observed.

I.r. Spectra.—The metal–halogen, metal–phosphorus, and phosphorus–fluorine stretching frequencies are listed in Table **3** for the solid state of the compounds (I)—(V). The complexes (I)—(III) show only one Ni–X and Ni–P stretching frequency indicating the point group D_{2h} for the X_2NiP_2 skeleton with a *trans*-square planar arrangement of the ligands X and Bu^t_2PF round the Ni atom.

Table 3

I.r. data of the complexes (I)—(VII) in the solid state (Nujol mulls; values in cm^{-1}) [a]

	ν(P–F)		Δν [b]		ν(M–X)		ν(M–P)		X-Sensitive vibrations	ν(P–O)	ν(P–H)
$Cl_2Ni(Bu^t_2PF)_2$ (I)	815		63		414		255		124		
	817 [c]		65		414 [c]						
$Br_2Ni(Bu^t_2PF)_2$ (II)	797		45		343		245		107		
	801 [c]		49		342 [c]						
$I_2Ni(Bu^t_2PF)_2$ (III)	789		37		290 [f]		237		97		
	793 [c]										
$Cl_2Co(Bu^t_2PF)_2$ (IV)	802	792	50	40	338	314	189 [f]	170	118		
$Br_2Co(Bu^t_2PF)_2$ (V)	795		43		273	244	192 [f]	172	99		
$Br_2Ni(Bu^t_2PHO)_2$ (VI)					255					1127	2366
					220						2340
$I_2Ni(Bu^t_2PHO)_2$ (VII)					215					1120	2365
					195 [f]						2343
Bu^t_2PF [d]	752										
Bu^t_2PHO [e]										1142	2290

[a] Maximum error ±2 cm^{-1}. [b] $\Delta\nu = \nu(P-F)_{Bu^t_2PF} - \nu(P-F)_{complex}$. [c] In CH_2Cl_2 solutions. [d] I.r. spectrum (1500—200 cm^{-1}, neat): 1472s, 1388m, 1366s, 1200m, 1178m, 1065w, 1022m, 1015m, 1007w, 942w, 932w, 870vw, 850vw, 830vw, 804s, 752s, 686w, 651w, 610s, 586s, 482s, 422s, 390m, 310m (s = strong, m = medium, w = weak, vw = very weak). [e] See ref. 13. [f] The assignment is ambiguous.

Taking into account the results of the i.r. and magnetic measurements in the solid state (see below) we attribute a C_{2v} pseudo-tetrahedral co-ordination of the two X and fluorophosphine ligands to the complexes $X_2Co(Bu^t_2PF)_2$. The assignment of the metal–halogen and metal–phosphorus stretching frequencies has been achieved by (i) comparison of the i.r. spectrum of the ligand Bu^t_2PF with that of the complexes (see Table 3, footnote *d*); (ii) comparison of corresponding values for M–X and M–P stretching frequencies in complexes X_2MP_2 (M = Co, Ni; X = Cl, Br, I) reported in the literature;[25,26] (iii) comparison of the i.r. spectra within the homologous series $X_2M(Bu^t_2PF)_2$ (X = Cl, Br, I; M = Co, Ni). The value of ν(NiCl) is almost the same in methylene dichloride solutions (410 cm^{-1}) as in the solid state (414 cm^{-1}). We therefore have in solution the *trans*-square planar form of $NiCl_2(Bu^t_2PF)_2$ (see n.m.r. discussion).

In the i.r. spectra of the compounds (I)—(V) there are two intense and relatively broad bands below 200 cm^{-1} (see Table 3). The position of one of these is quite sensitive to changes in the atomic weights of the halogen (' X-sensitive '). We tentatively assign this band to the Ni–X skeletal bending mode.

The phosphorus–fluorine stretching frequency of the free ligand (752 cm^{-1}) is shifted 40—50 cm^{-1} to higher wavenumbers in co-ordination. One could interpret the higher values of ν(PF) for the complexes (I)—(V) in Table **3** in terms of enhanced ($p \rightarrow d$) π-backbonding in the P–F bond caused by the metal in oxidation state 2. For various complexes of PF_3 the P–F stretching frequencies occur at higher wavenumbers compared with the ν(PF) in the free PF_3.[27]

On co-ordination of Bu^t_2PHO the values (in cm^{-1}) for the P–O stretching frequency decrease while those for the P–H stretching frequency increase (see Table 3). In accordance with a pseudo-tetrahedral structure for the complexes (VI) and (VII) there are two Ni–Br and Ni–I stretching frequencies relatively low-lying compared with the corresponding values in (II) and (III).

U.v. Spectra.—Table 4 lists the u.v. spectra of the complexes (I)—(V) for Nujol mulls and methylene dichloride solutions. The close agreement of the electronic spectra maxima in solution and in the solid state shows that the species in both states present must have the same structure (see discussion of the n.m.r. spectra). The lowest energy *d–d* bands in the compounds (I)—(III) which probably correspond to the $^1A_g \longrightarrow {}^1B_{1g}$ transitions[19] decrease along the series $Cl_2NiL_2 > Br_2NiL_2 > I_2NiL_2$ (L = Bu^t_2PF). Bu^t_2PF as ligand causes a ligand-field splitting comparable with that of Me_2PCF_3[28] (see Table 4).

The u.v. spectra in the range 200—1000 nm of the cobalt complexes (IV) and (V) and those reported for the

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pseudo-tetrahedral complexes $X_2Co(PPh_3)_2$ (X = Cl, Br, I) [14,29] show similar features. For the phosphine oxide complexes (VI) and (VII) a pseudo-tetrahedral ligand arrangement for the solid state may be assumed according to the u.v. spectra.[30]

TABLE 4

U.v. and visible spectra in the region 250—1000 nm for the complexes (I)—(III) [a] and for some analogous complexes of trifluoromethylphosphines [b]

$Cl_2Ni(Bu^t_2PF)_2$ (I)	460 (465) [c]	375 (4950)	290(sh)	250 (>10,000)
	465	365	260—290	225
$Br_2Ni(Bu^t_2PF)_2$ (II)	485 (485)	408 (5900)	315(sh)	250 (>10,000)
	475—520	415	310(sh)	250
$I_2Ni(Bu^t_2PF)_2$ (III)	575(sh, 610)	475 (1550), 375(sh)	310(sh)	263 (>10,000)
	575	475 370	320	260
$Cl_2Co(Bu^t_2PF)_2$ (IV)	721 (360)	644 (445)	585 (370)	260
	726	645	585	260
$Br_2Co(Bu^t_2PF)_2$ (V)	740(sh), 710 (435)	674 (530), 658, 635(sh)	606 (350)	268
	740 720(sh)	670 673(sh)	605(sh)	260
$Br_2Ni(Bu^t_2PHO)_2$ (VI)	975 (60), 950 (60)	670 (100), 620 (115)	585(sh)	410 (150)
	980	700	600	406
$I_2Ni(Bu^t_2PHO)_2$ (VII)	985 (16), 960 (16)	717 (19), 680 (18)	625(sh), 490 (35)	405 (202)
	>1000	750	650 508	
$Cl_2Ni(CF_3PMe_2)_2$ [b]	480	405	345	255
$Br_2Ni(CF_3PMe_2)_2$ [b]	487	395	262	240
$I_2Ni(CF_3PMe_2)_2$ [b]	375	355	314	228

[a] First line values for methylene dichloride, or for (VI) and (VII) in acetone solutions; second line spectral data of Nujol mulls. [b] Values taken from M. A. A. Beg and H. C. Clark, *Canad, J. Chem.*, 1961, **39**, 595. [c] All values in this Table in parentheses are the molar extinction coefficients.

TABLE 5

Magnetic data for the compounds (IV) and (V)

	$Cl_2Co(Bu^t_2PF)_2$ (IV)			$Br_2Co(Bu^t_2PF)_2$ (V)		
	$10^3 \times \chi_M$ [b]		μ [c]	$10^3 \times \chi_M$		μ
Methylene [a] dichloride	7·43		4·18	7·82		4·28
Toluene [a]	7·74		4·26	8·44		4·44
Benzene [a]	7·44		4·18	7·78		4·27
Solid state [d]		195 K			195 K	
	10·10 (0·11)		4·54 (0·05)	11·62 (0·12)		4·49 (0·07)
		297 K			298 K	
	7·87 (0·09)		4·65 (0·04)	8·31 (0·07)		4·61 (0·05)
		322 K			363 K	
	7·14 (0·04)		4·60 (0·03)	6·70 (0·06)		4·55 (0·04)
		363 K				
	6·43 (0·05)		4·60 (0·03)			

[a] Maximum error ±0·3 × 10^3. [b] χ_M Is the molar susceptibility in $cm^3\ mol^{-1}$. [c] μ Is the effective magnetic moment which has no dimension (see J. L. Hoppee, *J. Chem. Educ.*, 1972, **49**, 505), maximum error ±0·06. [d] The numbers in parentheses are the standard deviations.

Magnetic Measurements.—The complexes (I)—(III) are diamagnetic in the solid state. Toluene solutions are diamagnetic as well, while very concentrated solutions in methylene dichloride are very weakly paramagnetic. This is possibly due to interaction with the solvent.[31-33]

The cobalt complexes (IV) and (V) show only slightly different values for their magnetic moment in different solvents (see Table 5). These values indicate pseudo-tetrahedral ligand arrangement at the Co atom in solution. The magnetic behaviour of the complexes (IV) and (V) was studied in the temperature range 363—195 K. The complexes follow the Curie–Weiss law with θ = 45° ± 4° for (IV) and θ = 19° ± 6° for (V) (the regression value for the plot of $1/\chi_M$ the molar susceptibility, *viz.*, *T* being *ca.* 0·996). The values for μ_{eff} are typical for tetrahedral high-spin cobalt(II) complexes [34] and are consistent with the results obtained from detailed analysis of the u.v. and i.r. spectra.

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