134. *Tetrahedral Complexes of Nickel*(II) *and the Factors Determining Their Formation. Part IV.* Complexes with Tribenzyl-, Dibenzylphenyl-, Benzyldiphenyl-, and Allyldiphenyl-phosphine.*

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The preparation and properties are described of complexes of the type L_2NiX_2 where

$L = (Ph{\cdot}CH_2)_3P$, $(Ph{\cdot}CH_2)_2PPh$, $Ph{\cdot}CH_2{\cdot}PPh_2$, or $CH_2{:}CH{\cdot}CH_2{\cdot}PPh_2$,

and X = Cl, Br, I, or SCN. Benzene solutions of the alkyldiphenylphosphine complexes contain mixtures of diamagnetic and paramagnetic forms which, in many cases, can be obtained pure in the solid state. The changes in magnetic susceptibility with changes of phosphine are discussed.

The series of complexes of the type L_2NiX_2 (where L is $Bu^n{}_2PhP$, Bu^nPh_2P, or Ar_3P, and X is Cl, Br, I, SCN, or NO_3) show some interesting changes in magnetic properties as the number of phenyl groups in the phosphine molecule increases. The halide complexes of trialkyl- and dialkylphenyl-phosphines are diamagnetic in solution and in the solid state,[1] but those of the triarylphosphines are paramagnetic in the solid state and almost completely paramagnetic in solution,[2] while the complexes of alkyldiphenylphosphines take an intermediate position, being paramagnetic in the solid state and forming an equilibrium between diamagnetic and paramagnetic forms in solution.[1]

In order to investigate the factors responsible for these changes we have prepared four new series of complexes, those of tribenzyl-, dibenzylphenyl-, benzyldiphenyl-, and allyldiphenyl-phosphine, with nickel chloride, bromide, iodide, and thiocyanate. The complexes of tribenzyl- and dibenzylphenyl-phosphine were prepared by mixing hot ethanolic solutions of the solid phosphine and the nickel salt, and separated either immediately or on cooling. The complexes of benzyldiphenyl- and allyldiphenyl-phosphine

Table 1.

Colour, decomposition point, electric dipole moment, magnetic moment, and molecular weight of phosphine complexes of nickel.

					Mol. wt.	
Compound *	Colour	Dec. pt.	μ (D)	$\mu_{eff.}$ (B.M.)	Found	Calc.
$(By_3P)_2NiCl_2$	Red	125—126°	1·35	Diamag.	653	738
$(By_3P)_2NiBr_2$	Brown	134—137	1·77	,,	732	827
$(By_3P)_2NiI_2$	Brown	134—137	3·69	,,	868	921
$(By_3P)_2Ni(SCN)_2$	Orange	182—183	2·73	,,	—	—
$(By_2PhP)_2NiCl_2$	Red	216—219	1·69	,,	631	710
$(By_2PhP)_2NiBr_2$	Light brown	223—225	2·14	,,	790	799
$(By_2PhP)_2NiI_2$	Brown	180—185	3·2	,,	805	890
$(By_2PhP)_2Ni(SCN)_2$	Orange	235—236	—	,,	—	—
$(ByPh_2P)_2NiCl_2$	Blue-green	190—215	2·4	3·23	—	—
	Red	190—215	1·2	Diamag.	—	—
$(ByPh_2P)_2NiBr_2$	Green	192—193	2·7	2·70	—	—
	Red	192—193	—	Diamag.	—	—
$(ByPh_2P)_2NiI_2$	Dark red	150—151	7·7	2·61	—	—
	Dark red	140—141	—	Diamag.	—	—
$(ByPh_2P)_2Ni(SCN)_2$	Orange-red	192—193	—	,,	—	—
$(AllPh_2P)_2NiCl_2$	Red	142—143	—	,,	—	—
$(AllPh_2P)_2NiBr_2$	Green	118—123	—	3·31	—	—
	Purple	114—115	—	Diamag.	—	—
$(AllPh_2P)_2NiI_2$	Dark brown	121—122	—	3·19	—	—
$(AllPh_2P)_2Ni(SCN)_2$	Orange-red	135—139	—	Diamag.	—	—

* By = benzyl. All = Allyl.

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* Part III, *J.*, 1961, 4816.

[1] Coussmaker, Hutchinson, Mellor, Sutton, and Venanzi, *J.*, 1961, 2705.

[2] Browning, Davies, Morgan, Sutton, and Venanzi, *J.*, 1961, 4816.

were prepared from the solid (or liquid) phosphine and the appropriate nickel salt, the solvent and conditions used varying somewhat. The complexes characterized are listed in Table 1, with some of their properties.

The complexes of tribenzyl- and of dibenzylphenyl-phosphine are non-electrolytes in nitrobenzene solution; the other complexes are insoluble in, or decomposed by, solvents suitable for conductivity.

TABLE 2.

Magnetic susceptibilities of phosphine complexes.

Complex	$10^6\chi_m$ (uncor-rec.)	$10^6\chi_m$ (corr.)	Temp. (K)	$\mu_{eff.}$ (B.M.)
$(By_3P)_2NiCl_2$	−395	63	293°	—
$(By_3P)_2NiBr_2$	−393	94	293	—
$(By_3P)_2NiI_2$	−80	440	293	—
$(By_3P)_2Ni(SCN)_2$	−210	275	293	—
$(By_2PhP)_2NiCl_2$	−302	141	293	—
$(By_2PhP)_2NiBr_2$	−326	238	293	—
$(By_2PhP)_2NiI_2$	−230	265 †	293	—
$(By_2PhP)_2Ni(SCN)_2$	−444	27	293	—
$(ByPh_2P)_2NiCl_2$				
(diamag. form)	−289 *	131	293	—
(paramag. form)	3830 *	4250	295	3·18
	4195	4615	289	3·28
	5702	6122	213	—
	8155	8575	151	—
$(ByPh_2P)_2NiBr_2$				
(diamag. form)	−188 *	252	293°	—
(paramag. form)	2511 *	2951	293	2·64
	2803	3243	290	2·75
	3709	4149	213	
	5229	5669	153	
$(ByPh_2P)_2NiI_2$				
(diamag. form)	−558	−86	293	—
(paramag. form)	2409	2881	292	2·61
	3205	3679	219	
	4882	5354	154	
$(ByPh_2P)_2Ni(SCN)_2$	−444	27	293	—
$(AllPh_2P)_2NiCl_2$	−210 *	141	293	—
$(AllPh_2P)_2NiBr_2$				
(diamag. form)	−95 *	276	293	—
(paramag. form)	4257 *	4629	293	3·31
$(AllPh_2P)_2NiI_2$	3894 *	4298	293	3·19
$(AllPh_2P)_2Ni(SCN)_2$	−179	191	293	—

* Measured by the Faraday-type balance; all the other measurements were done with a Gouy-type balance.

† Measurements with this compound were also carried out at lower temperatures; the value for the corrected molar susceptibility was constant.

TABLE 3.

Wavelength of maxima ($\lambda_{max.}$), maximum extinction coefficients (ε) of solutions, and absorbency of solids (" *D* "), in the absorption spectra of phosphine complexes of nickel(II).

	Benzene solution		Solid	
Complex	$\lambda_{max.}$	ε	$\lambda_{max.}$	" *D* "
$(By_3P)_2NiCl_2$	377	14,130	365	1·57
	500—510	556	390—410	sh
			470	0·99
$(By_3P)NiBr_2$	406	9560	400	1·57
	560—570	560	410—440	sh
			490—500	0·99
$(Bz_3P)_2NiI_2$	397	1990	380	1·47
	472	1660	490	1·53
	620	643	575—650	sh
$(By_3P)_2Ni(SCN)_2$	390	8860	375	1·38
	500—600	sh	460—540	sh
$(By_2PhP)_2NiCl_2$	385	9860	365	1·37
	485	620	380—420	sh
			480	0·88
$(By_2PhP)_2NiBr_2$	413	7280	400	1·36
	520	570	420—450	sh
			500	0·84
$(By_2PhP)_2NiI_2$	394	3460	390	1·42
	478	3170	490	1·43
	590	425	560—650	sh
$(By_2PhP)_2Ni(SCN)_2$	397	6850	380	1·39
	500—650	sh	480—530	sh
$ByPhP)_2NiCl_2$ (diamag. form)		*	375	1·61
			530	1·18
(paramag. form)	384	20,300	410	1·57
	500	6800	550	0·81
	850—950	sh	875	0·90

TABLE 3. (*Continued*).

Complex	Benzene solution λ		Solid	
	$\lambda_{max.}$	ε	$\lambda_{max.}$	" *D* "
$(ByPh_2P)_2NiBr_2$ (diamag. form)	*		405	1·70
			425—475	sh
			475—525	sh
			525—575	sh
(paramag. form)			395—400	1·58
	415	11,900	425—450	sh
	555	536	555—565	1·08
			625—675	sh
	885	22	860	1·02
$(ByPh_2P)_2NiI_2$ (diamag. form)	*		375—400	sh
			485	1·60
			600—650	sh
(paramag. form)	400—420	sh	350—400	1·60
	460—500	sh	465	1·66
			525—560	sh
	625	585	675—775	sh
	915	127	900	1·13
$(ByPh_2P)_2Ni(SCN)_2$	405	7060	390	1·51
	475—575	sh	500—550	sh
$(AllPh_2P)_2NiCl_2$	380	15,100	366	1·68
			385—410	sh
	490	667	475	1·18
			515—530	sh
	850	11		
$(AllPh_2P)_2NiBr_2$ (diamag. form)	*		400	1·55
			500—510	1·08
			550—600	sh
(paramag. form)	410	7400	400—420	1·51
	530	562	575	0·97
	880	69	900—925	1·11
$(AllPh_2P)_2NiI_2$	380—410	sh	440	1·70
	440—480	sh	500—550	sh
	580—650	sh	650—725	sh
	925	304	910	1·22
$(AllPh_2P)_2Ni(SCN)_2$	400	10,000	385	1·51
	475—550	sh	460—510	sh
	Acetone solution			
$(ByPh_2P)_2NiCl_2$	380	7650		
	500	445		
	850—875	25		
$(ByPh_2P)_2NiBr_2$	410	5740		
	565	316		
	890	47		
$(ByPh_2P)_2NiI_2$	410	2320		
	545	880		
	665	385		
	730	360		
	1000	283		

* The spectra of these forms are identical with those prepared from the other isomer.

Complexes of Tribenzylphosphine and of Dibenzylphenylphosphine.—These are very similar to those of the trialkylphosphines and to those of di-n-butylphenylphosphine:[1] the halogeno- and thiocyanato-complexes being monomeric and diamagnetic (see Tables 1 and 2). The small paramagnetic polarization, observed for the diamagnetic complexes of di-n-butylphenylphosphine, is observed for these complexes, and measurements on $(By_2PhP)_2NiI_2$ (where By = benzyl) indicate that, for this compound at least, the paramagnetism is temperature-independent. The electric dipole moments (see Table 1) are comparable with those of the di-n-butylphenylphosphine complexes.[1] The low values of μ_D, when compared with values of 7—10 D for the triarylphosphine complexes, indicate that these benzyl derivatives are essentially *trans*-planar in solution, though a small amount of the *cis*-isomer may be present.

The absorption spectra of the complexes in benzene solution are summarized in Table 3, and those of the dibenzylphenylphosphine complexes are shown in Fig. 1. They are essentially similar to those observed for the complexes of di-n-butylphenylphosphine,[1] showing (1) the sharp, intense absorption band near 400 mμ and (2) the broader crystal-field bands in the region 500—600 mμ. The absence of a band in the region of 900 mμ indicates that they are diamagnetic in solution, as well as in the solid state. The reflectance spectra were also recorded and are summarized in Table 3, and those of the dibenzylphenylphosphine complexes are shown in Fig. 2. These are analogous to the solution spectra, indicating that there is little or no change in structure with change of state.

Complexes of Benzyldiphenylphosphine.—The solid halogeno-complexes with this phosphine can be isolated in two isomeric forms, one paramagnetic and one diamagnetic. The magnetic moments of the paramagnetic form of the bromo- and iodo-complexes suggest that they are contaminated with some of the diamagnetic form. The temperature-dependence of the magnetic susceptibility of the three paramagnetic forms obeys the Curie–Weiss law over the temperature range 150—290°K. When the preparation of the chloro- and bromo-complexes is carried out in butan-1-ol, the product first formed is a mixture of paramagnetic and diamagnetic forms which, when kept in contact with the mother-liquor for 1—2 days gives pure isomeric forms: the chloro-complex gives the paramagnetic form; the bromo-complex gives the diamagnetic form. The paramagnetic form of the chloro-complex can be obtained by using glacial acetic acid as a solvent, and the paramagnetic form of the bromo-complex by using ethanol as a solvent, rapid precipitation and filtration of the complex being necessary in both cases to minimize the formation of the more stable isomer. A preparation of the iodo-complexes resulted in one instance in the formation of a paramagnetic form, yet all subsequent attempts by the same method yielded only a pure diamagnetic form. Changes of solvent failed to yield a paramagnetic form and, on recrystallization, the paramagnetic form gave the diamagnetic one.

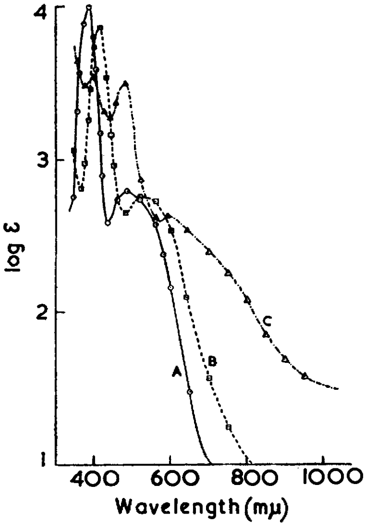

FIG. 1. Absorption spectra of benzene solutions of the complexes $(By_2PhP)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

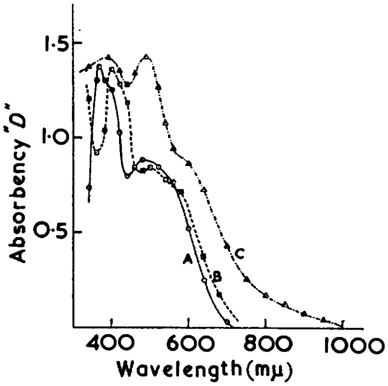

FIG. 2. Reflectance spectra of the complexes $(By_2PhP)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

Conversion of the chloro-complex from the diamagnetic into the paramagnetic form could be achieved by heating the sample to 114° for 2—3 hours. The diamagnetic bromo-complex showed no change on heating until the temperature was about 155°: then an impure green complex was obtained. The reflectance spectrum of this solid suggests that it contains some paramagnetic isomer, but its formation has been accompanied by partial decomposition.

The thiocyanato-complex is diamagnetic, like its n-butyldiphenylphosphine analogue.[1]

The reflectance spectra of the complexes of this series are summarized in Table 3. Those of the paramagnetic forms are similar to the spectra of the complexes n-butyldiphenylphosphine [1] (see Fig. 3) while those of the diamagnetic forms are similar to the spectra of the complexes of dibenzylphenylphosphine (compare Figs. 2 and 4).

The spectra of the fully diamagnetic complexes show no absorption at about 900 mμ, whereas the fully paramagnetic ones show a strong absorption band which, at least in the chloro-complex, is more intense than the composite band at about 500 mμ. (The relative intensities of the 900 and the 500 mμ bands in the bromo- and iodo-complexes are in agreement with their magnetic susceptibilities, which are lower than expected and have led us to believe that these " paramagnetic forms " contained small amounts of the diamagnetic isomer.) The crystal-field bands are at longer wavelength for the paramagnetic than for the diamagnetic complexes, showing, as might be expected, that the crystal-field splitting is larger in the diamagnetic complexes.

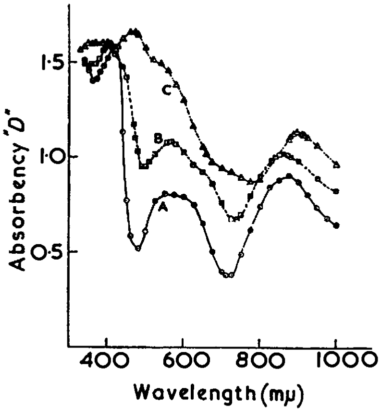

FIG. 3. Reflectance spectra of the paramagnetic forms of the complexes $(ByPh_2P)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

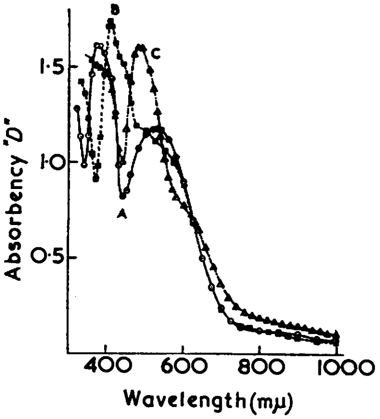

FIG. 4. Reflectance spectra of the diamagnetic forms of the complexes $(ByPh_2P)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

From the differences of magnetic susceptibilities and spectra it is evident that the two forms of each of the complexes are true isomers and not merely polymorphic crystalline forms. By analogy with the complexes of triphenylphosphine,[2] the paramagnetic complexes are assigned tetrahedral structures, whilst the diamagnetic forms, by analogy with the trialkylphosphine complexes,[1] are assigned *trans*-planar structure in the solid state.

Benzene solutions of para- and dia-magnetic forms of a given complex have identical spectra. These indicate the presence of equilibrium mixtures of the two forms, the paramagnetic form increasing in the order Cl $<$ Br $<$ I (see Table 3 and Fig. 5). The equilibria are set up quite rapidly and an examination of the spectra of solutions of the para- and dia-magnetic chloro-complexes over a period of time from 2 to 120 minutes shows no gradual attainment of equilibrium between the two forms. When changes of spectra were observed, they could be attributed to decomposition of the complexes.

Dipole-moment measurements in benzene solution indicate that the chloro- and bromo-complexes have low and the iodo-complex high polarities. The difference in dipole moments observed for solutions made up from the paramagnetic and the diamagnetic form of the chloro-complex are probably to be attributed to decomposition.

From the magnetic susceptibilities of the benzene solutions the following approximate percentages of the paramagnetic form present in solution were obtained: $(ByPh_2P)_2NiCl_2$ 6%; $(ByPh_2P)_2NiBr_2$ 33%; $(ByPh_2P)_2NiI_2$ 59%.

Thus, solutions of the benzyl derivatives, at parity of halogen, appear to contain less of the paramagnetic form than the butyl derivative: $(BuPh_2P)_2NiCl_2$ 12%; $(BuPh_2)_2NiBr_2$ 49%; $(BuPh_2P)_2NiI_2$ 64%. This is confirmed by the solution spectra and the dipole moments.

The spectra of the halogeno-complexes of benzyldiphenylphosphine were also recorded for acetone solutions. The main changes observed were: (1) the relative intensities of the 500 and 900 mμ bands indicate that in acetone the amount of paramagnetic form is larger than in benzene; (2) while the 900 mμ bands are not significantly shifted by the change of solvent, the shapes of the 500 mμ bands show greater intensity towards longer wavelength in acetone (compare Figs. 5 and 6). This supports the view that these bands result from the overlap of bands due to the diamagnetic and those due to the paramagnetic forms, the latter being at longer wavelengths.

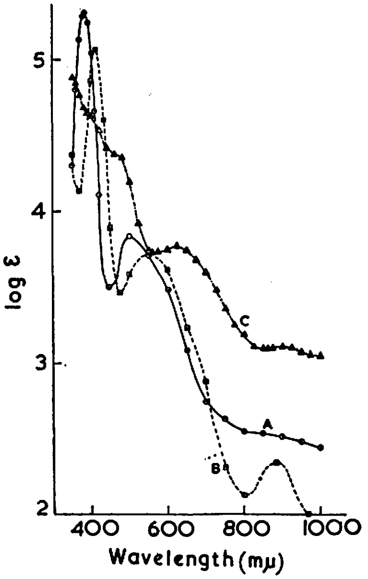

FIG. 5. Absorption spectra of benzene solutions of the complexes $(ByPh_2P)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

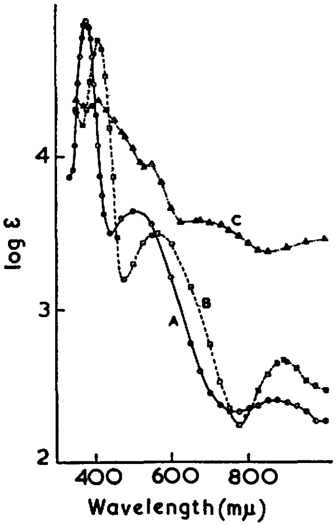

FIG. 6. Absorption spectra of acetone solutions of the complexes $(ByPh_2P)_2NiX_2$: X = (A) Cl, (B) Br, (C) I.

Complexes of Allyldiphenylphosphine.—The halogeno- and thiocyanato-complexes are described here. In this series isomeric solids were isolated only in the case of the bromo-derivative. The chloro-complex could be isolated only in the diamagnetic form and, despite the wide variation of preparative conditions, we found no evidence for the existence of a solid paramagnetic form. The paramagnetic form of the bromo-complex was prepared in, and recrystallized from, glacial acetic acid, while the diamagnetic isomer was formed in ethanol solution and recrystallized from butan-1-ol. The iodo-complex is paramagnetic, and no diamagnetic form could be obtained. The thiocyanato-complex is diamagnetic, as usual.

The reflectance spectra of the diamagnetic solids are similar to those of their benzyl analogues (see Fig. 7). In the spectra of the paramagnetic complexes, the 900 mμ band is more intense than the 500 mμ band, as expected from the large paramagnetic susceptibility of the solid complexes (see Tables 1 and 2). The 500 mμ band of the paramagnetic form of the bromo-complex is at longer wavelength than that of the diamagnetic form, as observed for the complexes of benzyldiphenylphosphine.

The absorption spectra of benzene solutions of the allyl complexes (see Table 3 and Fig. 8) show bands of varying intensities in the 900 mμ region, indicating that the proportion of paramagnetic form in solution increases in the order Cl $<$ Br $<$ I. If the relative intensities of the 900 and 500 mμ bands are taken to indicate the proportions of the two forms present in solution, the relative amounts are approximately the same as in benzene solutions of the benzyl complexes.

Discussion.—In Part II [1] it was proposed that the formation of diamagnetic complexes of the type $(R_3P)_2NiX_2$ is more dependent on the π-acceptor capacity than on the σ-donor capacity of the phosphorus atom, and the experiments now described were designed to test this view. The relative importance of these two factors is best studied in the series of complexes with alkyldiphenylphosphines, as solutions of these complexes contain both forms in equilibrium. The groups chosen for this study were benzyl and allyl, which could be compared with the n-butyl analogues investigated earlier.

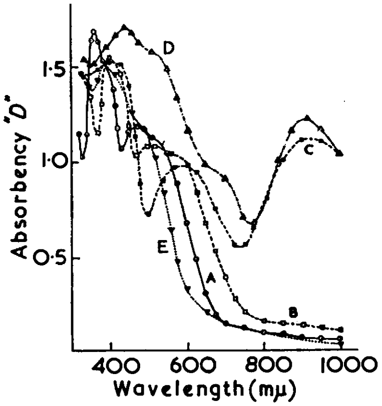

FIG. 7. Reflectance spectra of the complexes $(AllylPh_2P)_2NiX_2$: X = (A) Cl, (B) Br (diamag.), (C) Br (paramag.), (D) I, (E) SCN.

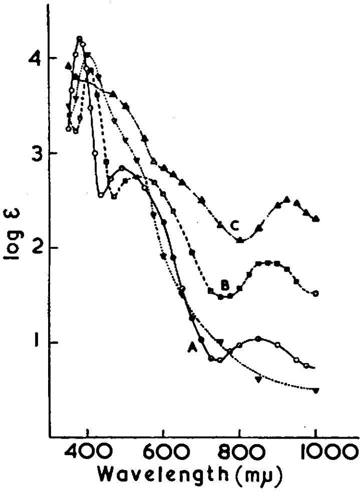

FIG. 8. Absorption spectra of benzene solutions of the complexes $(AllylPh_2P)_2NiX_2$: X = (A) Cl, (B) Br, (C) I, (D) SCN.

The benzyl group is more electron-attracting than the butyl group, as indicated by the acid dissociation constant of valeric acid (K_a $1{\cdot}38 \times 10^{-5}$) and phenylacetic acid (K_a $4{\cdot}88 \times 10^{-5}$).[3] Thus the replacement of an n-butyl group on phosphorus(III) by a benzyl group is expected to decrease the σ-donor capacity and increase the π-donor capacity of the donor atom. As we find that the amounts of diamagnetic form in solutions of the benzyl derivatives are greater than those in solutions of the corresponding n-butyl derivatives, we conclude that our interpretation is basically correct. Up to now, however, no account has been taken of steric factors, and it could be argued that the differences under discussion are caused by the different steric requirements of the n-butyl and the benzyl group. The study of solutions of the halogeno-complexes of allyldiphenylphosphine, however, shows that this is not the case. While from the steric point of view the allyl group is very similar to an n-butyl one, from the electronic point of view the allyl group is very similar to the benzyl group as shown by the acid dissociation constants

[3] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 734.

of phenylacetic (K_a 4·88 × 10^{-5}) and vinylacetic (but-3-enoic) acid (K_a 4·6 × 10^{-5}).[3] The observation that the amounts of paramagnetic form present in solutions of complexes of benzyl- and allyl-diphenylphosphine are practically identical is a clear indication that the changes under discussion are mainly of electronic origin.

The formation of para- and dia-magnetic species in solution has been discussed in earlier publications.[1,2] Two models have been put forward: (1) an equilibrium is set up in solution between a tetrahedral paramagnetic form and a *trans*-planar diamagnetic one, the equilibrium position changing with a change of halide; (2) the complexes exist in solution with distorted tetrahedral structures, the departure from planarity determining the multiplet separation and thus the paramagnetism of the complex. The changes of magnetic susceptibility with changes of halogen are then attributed to changes of the PNiX bond angles.

Our experiments do not allow a choice between these two models. In the past we have favoured the latter view, but the isolation of isomeric forms of the solid complexes might be taken as an indication that the former is more likely.

The larger amounts of paramagnetic forms present in solutions of polar (acetone) than in non-polar solvents (benzene) is in good agreement with our ideas on the nature of the paramagnetic species. These have high polarities and thus are expected to be favoured in solutions of polar solvents.

The isolation of isomeric forms of the solid complexes, on the other hand, must be attributed to a combination of steric and electronic factors. The magnetic equilibria established in solution indicate that the two forms have very similar energies. It is also expected that the lattice energies of these non-ionic complexes will not be very large and, thus, the differences in lattice energies between the two forms will be small. Further, the polarity of the paramagnetic species leads us to conclude that the lattice energies of these will be greater than those of the diamagnetic species. It follows that the balance between electronic and steric factors will be a very fine one, and it is likely that the nature of the solid isomer produced will depend on the relative solubility of the two forms in the solvent used.

In view of the results obtained with the complexes of benzyldiphenylphosphine, it is to be expected that the complexes of tribenzylphosphine and even those of dibenzylphenylphosphine should exist only in the diamagnetic form, as is the case.

EXPERIMENTAL

Preparation of the Phosphines.—All these preparations were carried out under nitrogen.

Tribenzylphosphine was prepared by slow addition of phosphorus trichloride (0·167 mole) in ether to benzylmagnesium chloride (0·5 mole) in ether at 0°. The mixture was stirred for a further 30 min., and the excess of Grignard reagent hydrolyzed with aqueous ammonium chloride. The ethereal layer was filtered, dried (Na_2SO_4), and evaporated. The phosphine crystallized on cooling (yield, 69% crude). Recrystallization from absolute ethanol, however, gave the phosphine oxide, m. p. 198·5—199·5° (decomp.) (see Hinton and Mann,[4] who describe both the pure phosphine and its oxide).

Dibenzylphenylphosphine was prepared as above, from dichlorophenylphosphine (0·2 mole) and benzylmagnesium chloride (0·4 mole), in 89% yield (crude). The product, recrystallized from ethanol, had m. p. 73° (decomp.). Mann, Millar, and Stewart [5] give m. p. 71—72°.

Benzyldichlorophosphine was prepared from dibenzylcadmium by Fox's method,[6] and from benzylzinc chloride as described by Weil *et al.*[7] Both methods gave a colourless liquid, b. p. 107—118°/7—8 mm., in 30% yield.

Benzyldiphenylphosphine was prepared from chlorodiphenylphosphine (0·113 mole) and

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[4] Hinton and Mann, *J.*, 1959, 2835.

[5] Mann, Millar, and Stewart, *J.*, 1954, 2832.

[6] Fox, *J. Amer. Chem. Soc.*, 1950, **72**, 4147.

[7] Weil, Prijs, and Erlenmeyer, *Helv. Chim. Acta*, 1953, **36**, 1314.

benzylmagnesium chloride (0·109 mole), and from benzyldichlorophosphine (0·26 mole) and phenylmagnesium bromide (0·52 mole). It crystallized from the reaction mixture after evaporation, and after two distillations, had b. p. 146—148°/0·15 mm., m. p. 142—143° (decomp.) (yield 54%).

Allyldiphenylphosphine, prepared from chlorodiphenylphosphine (0·25 mole) and allylmagnesium chloride (0·3 mole), was distilled from the reaction mixture (b. p. 114—130°/0·7 mm.; 18%). Redistillation gave a product of b. p. 102—103°/0·45 mm. which is easily oxidized in air and was assumed to be the desired phosphine.

Preparation of the Complexes.—Complexes of tribenzylphosphine were prepared by addition of a hot ethanolic solution of the crude phosphine to one of the appropriate nickel salt. The complexes crystallized on cooling and were recrystallized from butan-1-ol. The solution of nickel iodide (or thiocyanate) was prepared by dissolving sodium iodide (or potassium thiocyanate) in boiling ethanol, adding this solution to one containing the stoicheiometric amount of nickel nitrate in hot ethanol, cooling, and using the solution after filtration from the precipitate.

Thus were obtained: *Dichloro-* (32%) (Found: Ni, 8·1. $C_{42}H_{42}Cl_2NiP_2$ requires Ni, 8·0%), *dibromo-* (26%) (Found: 7·1. $C_{42}H_{42}$ Br_2NiP_2 requires Ni, 7·1%), *di-iodo-* (23%) (Found: Ni, 6·4. $C_{42}H_{42}I_2NiP_2$ requires Ni, 6·4%) and *dithiocyanato-bistribenzylphosphinenickel* (74%) (Found: Ni, 7·3. $C_{44}H_{42}N_2NiP_2S_2$ requires Ni, 7·5%).

The following complexes of dibenzylphenylphosphine were prepared analogously and were recrystallized from nitromethane: *dichloro-* (29%) (Found: Ni, 8·3. $C_{40}H_{38}Cl_2NiP_2$ requires Ni, 8·3%), *dibromo-* (39%) (Found: Ni, 7·3. $C_{40}H_{38}Br_2NiP_2$ requires Ni, 7·4%), *di-iodo-* (40%) (Found: Ni, 6·55. $C_{40}H_{38}I_2NiP_2$ requires Ni, 6·6%), and *dithiocyanato-bis(dibenzylphenylphosphine)nickel* (35%) (Found: Ni, 7·5. $C_{42}H_{38}N_2NiP_2$ requires Ni, 7·8%).

No general method of preparation was applicable to all the complexes of benzyl- and allyldiphenylphosphine. All these preparations were carried out in an atmosphere of nitrogen.

Dichlorobis(benzyldiphenylphosphine)nickel. (*a*) Red form. A solution of nickel chloride hexahydrate (0·3 g.) in water (1 c.c.) was diluted with acetic acid (10 c.c.), and a hot solution of the phosphine (0·7 g.) in glacial acetic acid (10 c.c.) was added. The resulting dark red solution was decanted from the mixture of red and blue crystals which separated immediately. The second crop of crystals (red *form*, needles) were filtered off after 15 min. (Found: Ni, 8·5. $C_{38}H_{34}Cl_2NiP_2$ requires Ni, 8·6%). (*b*) Blue form. A solution of the phosphine (1·38 g.) in warm ethanol (50 c.c.) was added to a solution of nickel chloride hexahydrate (0·6 g.) in boiling ethanol (30 c.c.). An immediate red coloration was observed, but after three days blue-green plates of the *complex* had formed (yield 20%) (Found: Ni, 8·55%).

Dibromobis(benzyldiphenylphosphine)nickel. (*a*) Green form. A solution of the phosphine (2·73 g.) in hot ethanol (25 c.c.) was added to one of nickel bromide trihydrate (1·35 g.) in hot ethanol (10 c.c.). Dark green crystals of *complex* (75%) which separated were filtered off at once (Found: Ni, 7·6. $C_{38}H_{34}Br_2NiP_2$ requires Ni, 7·6%). (*b*) Red form. Recrystallization of the finely powdered green form (0·3 g.) from butan-1-ol (30 c.c.) gave in 24 hr. the red *form* as plates (Found: Ni, 7·6%).

Di-iodobis(benzyldiphenylphosphine)nickel. (*a*) A nickel iodide solution [15 c.c., which had been prepared from nickel nitrate (15·5 g.) and sodium iodide (16·0 g.) in ethanol (40 c.c.)] gave, on addition of the phosphine (3·8 g.), a dark red paramagnetic *complex* (60%) (Found: Ni, 6·75. $C_{38}H_{34}I_2NiP_2$ requires Ni, 6·8%). Recrystallization of this product gave the diamagnetic *form* (see below). Subsequent attempts to prepare the paramagnetic form from another batch of phosphine gave only the diamagnetic form (80%) (Found: Ni, 6·8%).

Dithiocyanatobis(benzyldiphenylphosphine)nickel was prepared in the same way as its tribenzylphosphine analogue (yield 40%) (Found: Ni, 8·05. $C_{40}H_{34}N_2NiP_2S_2$ requires Ni, 8·05%).

Dichlorobis(allyldiphenylphosphine)nickel. The phosphine (2·46 g.) in warm ethanol (15 c.c.) was added to nickel chloride hexahydrate (1·33 g.) in hot ethanol (20 c.c.). The red solution, when cooled in ice, gave red crystals (47%). The *product* recrystallized from butan-1-ol (Found: Ni, 10·0. $C_{30}H_{30}Cl_2NiP_2$ requires Ni, 10·1%).

Dibromobis(allyldiphenylphosphine)nickel. (*a*) The phosphine (2 g.) in ethanol (25 c.c.) was added to nickel bromide trihydrate (1·3 g.) in hot ethanol (25 c.c.). The purple *product* crystallized on cooling in ice and was recrystallized from butan-1-ol (yield 64%) (Found: Ni, 8·65. $C_{30}H_{30}Br_2NiP_2$ requires Ni, 8·75%). (*b*) Nickel bromide trihydrate (0·13 g.) was dissolved in a few drops of water and glacial acetic acid (2 c.c.) added. The phosphine (0·3 g.) was added slowly, a dark green oil being formed. When the mixture was shaken and then set aside for 24 hr. a dark green *product* (34%) was obtained which recrystallized from glacial acetic acid (Found: Ni, 9·0%).

Di-iodobis(allyldiphenylphosphine)nickel. The phosphine (0·5 g.) in ethanol (10 c.c.) was added to a hot ethanolic solution of nickel iodide (9·0 c.c., prepared as described for the benzyldiphenylphosphine complex). On cooling, brown-black crystals of the *complex* were obtained and were recrystallized from butan-1-ol (yield 48%) (Found: Ni, 7·75. $C_{30}H_{30}I_2NiP_2$ requires Ni, 7·7%).

Dithiocyanatobis(allyldiphenylphosphine)nickel. A solution of nickel thiocyanate in butan-1-ol (8 c.c., containing 0·15 g. of the salt) was treated with the phosphine (0·1 g.) in hot butan-1-ol (2·0 c.c.). The *complex* (58%) crystallized on cooling (Found: Ni, 9·45. $C_{32}H_{30}N_2NiP_2S_2$ requires Ni, 9·4%).

TABLE 4.

Dipole moments of complexes.

$(By_3P)_2NiCl_2$ *

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
1998	2·2762	1·14410
2424	2·2764	1·14400
2961	2·2768	1·14360
3624	2·2771	1·14338

$\varepsilon_{12} = 2{\cdot}2750_1 + 0{\cdot}586w_2$.
$v_{12} = 1{\cdot}14465 - 0{\cdot}338w_2$.
${}_{\mathrm{T}}P_2 = 259$ c.c.
${}_{\mathrm{E}}P_2 = 227$ c.c. (calc.).
$\mu = 1{\cdot}35 \pm 0{\cdot}06$ D.

$(By_3P)_2NiBr_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
791	2·2754	1·14440
1520	2·2760	1·14407
3331	2·2771	1·14333
3444	2·2773	1·14330

$\varepsilon_{12} = 2{\cdot}2749_6 + 0{\cdot}662w_2$.
$v_{12} = 1{\cdot}14467 - 0{\cdot}397w_2$.
${}_{\mathrm{T}}P_2 = 287$ c.c.
${}_{\mathrm{E}}P_2 = 233$ c.c. (calc.).
$\mu = 1{\cdot}77 \pm 0{\cdot}10$ D.

$(By_3P)_2NiI_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
584	2·2758	1·14443
1668	2·2775	1·14404
3598	2·2809	1·14334
5445	2·2846	1·14267

$\varepsilon_{12} = 2{\cdot}2747_8 + 1{\cdot}765w_2$.
$v_{12} = 1{\cdot}14464 - 0{\cdot}362w_2$.
${}_{\mathrm{T}}P_2 = 521$ c.c.
${}_{\mathrm{E}}P_2 = 243$ c.c. (calc.).
$\mu = 3{\cdot}69 \pm 0{\cdot}06$ D.

$(By_3P)_2Ni(SCN)_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
271	2·2755	1·14448
494	2·2759	1·14432
711	2·2763	1·14416
985	2·2768	1·14407

$\varepsilon_{12} = 2{\cdot}2750_1 + 1{\cdot}765w_2$.
$v_{12} = 1{\cdot}14461 - 0{\cdot}570w_2$.
${}_{\mathrm{T}}P_2 = 503$ c.c.
${}_{\mathrm{E}}P_2 = 242$ c.c. (calc.).
$\mu = 2{\cdot}73 \pm 0{\cdot}10$ D

$(By_2PhP)_2NiCl_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
689	2·2757	1·14433
928	2·2759	1·14419
1237	2·2762	1·14406
1416	2·2763	1·14399

$\varepsilon_{12} = 2{\cdot}2750_1 + 0{\cdot}946w_2$.
$v_{12} = 1{\cdot}14460 - 0{\cdot}437w_2$.
${}_{\mathrm{T}}P_2 = 276$ c.c.
${}_{\mathrm{E}}P_2 = 218$ c.c. (calc.).
$\mu = 1{\cdot}69 \pm 0{\cdot}04$ D.

$(By_2PhP)_2NiBr_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
377	2·2753	1·14447
670	2·2757	1·14435
852	2·2758	1·14429
1281	2·2762	1·14410

$\varepsilon_{12} = 2{\cdot}2759_0 + 0{\cdot}913w_2$.
$v_{12} = 1{\cdot}14461 - 0{\cdot}389w_2$.
${}_{\mathrm{T}}P_2 = 317$ c.c.
${}_{\mathrm{E}}P_2 = 224$ c.c. (calc.).
$\mu = 2{\cdot}14 \pm 0{\cdot}07$ D.

$(By_2PhP)_2NiI_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
549	2·2761	1·14432
805	2·2765	1·14419
936	2·2766	1·14416
1188	2·2769	1·14401

$\varepsilon_{12} = 2{\cdot}2750_9 + 1{\cdot}629w_2$.
$v_{12} = 1{\cdot}14460 - 0{\cdot}489w_2$.
${}_{\mathrm{T}}P_2 = 448$ c.c.
${}_{\mathrm{E}}P_2 = 234$ c.c. (calc.).
$\mu = 3{\cdot}2 \pm 0{\cdot}2$ D.

$(ByPh_2P)_2NiCl_2$: blue form

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
557	2·2757	1·14438
650	2·2758	1·14435
698	2·2758	1·14438
699	2·2762	1·14429

$\varepsilon_{12} = 2{\cdot}2749_8 + 1{\cdot}361w_2$.
$v_{12} = 1{\cdot}14460 - 0{\cdot}382w_2$.
${}_{\mathrm{T}}P_2 = 330$ c.c.
${}_{\mathrm{E}}P_2 = 209$ c.c. (calc.).
$\mu = 2{\cdot}4 \pm 0{\cdot}2$ D.

$(ByPh_2P)_2NiCl_2$: red form

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
888	2·2756	1·14410
990	2·2758	1·14400
1182	2·2762	1·14400

$\varepsilon_{12} = 2{\cdot}2749_5 + 0{\cdot}91w_2$.
$v_{12} = 1{\cdot}14464 - 0{\cdot}542w_2$.
${}_{\mathrm{T}}P_2 = 240$ c.c.
${}_{\mathrm{E}}P_2 = 209$ c.c. (calc.).
$\mu = 1{\cdot}2 \pm 0{\cdot}2$ D.

$(ByPh_2P)_2NiBr_2$: red form

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
480	2·2757	1·14444
854	2·2762	1·14426
1189	2·2765	1·14419
1772	2·2774	1·14394

$\varepsilon_{12} = 2{\cdot}2750_1 + 1{\cdot}331w_2$.
$v_{12} = 1{\cdot}14461 - 0{\cdot}370w_2$.
${}_{\mathrm{T}}P_2 = 371$ c.c.
${}_{\mathrm{E}}P_2 = 215$ c.c. (calc.).
$\mu = 2{\cdot}77 \pm 0{\cdot}08$ D.

$(ByPh_2P)_2NiI_2$: paramag. form

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
480	2·2782	1·14441
574	2·2784	1·14441
688	2·2795	1·14438
985	2·2822	1·14423

$\varepsilon_{12} = 2{\cdot}2746_0 + 7{\cdot}546w_2$.
$v_{12} = 1{\cdot}14461 - 0{\cdot}362w_2$.
${}_{\mathrm{T}}P_2 = 1163$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 225$ c.c.
$\mu = 7{\cdot}7 \pm 0{\cdot}3$ D.

* By = benzyl.

Analytical.—The nickel analyses were carried out spectrophotometrically as described in Part II.[1]

Determination of Molecular Weights.—These were determined cryoscopically in 1,2-dibromoethane, under dry nitrogen.

Conductance Measurements.—These were done with $\sim 10^{-3}$M-solutions in nitrobenzene, a Philips PR 9500 conductivity bridge being used. All the compounds investigated were non-electrolytes.

Magnetic-susceptibility Measurements.—Some of these measurements were carried out with a Gouy-type magnetic balance, and the others with a Faraday-type magnetic balance (see Table 2). The values of $\mu_{\text{eff.}}$ were calculated from the corrected molar susceptibilities at room temperature and the results are listed in Table 2. The solution measurements were done with a Quincke-type apparatus at about 18°. The values for the butyldiphenylphosphine complexes reported here differ from those given in Part II.[1] The earlier values of Mills and Williams were estimated by using as a standard value for the paramagnetism of the nickel ion that found in aqueous solution. The values reported here have been calculated as follows: benzene solutions of $[(p\text{-}C_6H_4Me)_3P]_2NiBr_2$ and $(By_3P)_2NiBr_2$ were used as paramagnetic and diamagnetic standards, respectively. It was assumed that the magnetic moments of the paramagnetic forms of the complexes with the alkyldiphenylphosphine were equal to those of tri-*p*-tolylphosphine, and the approximate percentages of paramagnetic form present in solution were estimated on this basis. Since in the present instance we are only interested in relative differences, the use of either standard will give comparable results.

Measurements of Visible and Ultraviolet Absorption Spectra.—The spectra of the complexes in benzene solution were measured at room temperature on a Beckman ratio-recording spectrophotometer (model DK-2) over the range 350—1000 mμ. The complete spectrum was obtained by using 10^{-3}M-solutions for the range 700—1000 mμ, and 10^{-4}M-solutions for the range 350—700 mμ.

The reflectance spectra of the finely powdered solids were measured over the range 320—1000 mμ on a Unicam S.P. spectrophotometer fitted with a Unicam diffuse reflectance attachment, S.P. 540; magnesium carbonate was the reference standard.

The values of $\lambda_{\text{max.}}$ and the corresponding extinction coefficients ε are listed in Table 3. The intensity of absorption in the reflectance spectra is given on an arbitrary scale, "*D*", which may vary from compound to compound.

Measurements of Infrared Spectra.—Since, in most cases, the complexes were prepared from the crude phosphines, the infrared spectra of the complexes were examined to ensure that the products obtained were not derivatives of phosphine oxides. None of the complexes showed bands attributable to P–O vibrations (see Cotton, Barnes, and Bannister[8]). The spectra were recorded on a Perkin-Elmer spectrophotometer for Nujol mulls.

Dipole-moment Measurements.—These were carried out for benzene solutions and calculated as described in Part I,[9] except that the dielectric constant of benzene was taken as 2·2750.[10] Results are listed in Table 4.

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