947. *Tetrahedral Nickel*(II) *Complexes and the Factors Determining Their Formation. Part III.*[1] *Complexes with Triarylphosphines.*

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Tri-*p*-tolyl- and tri-*p*-methoxyphenyl-phosphine are shown to form complexes of the type L_2NiX_2 (L = phosphine, and X = Cl, Br, I, and SCN). The halogeno-complexes are paramagnetic and have been assigned pseudo-tetrahedral structure in the solid state; the thiocyanato-complexes are diamagnetic and are probably planar. Spectral evidence indicates that in benzene solutions of the chloro- and bromo-complexes there are small amounts of diamagnetic species in equilibrium with paramagnetic species. The increases in dipole moment on replacement of chloride by bromide and iodide are attributed to expansion of the PNiX bond angles.

In Part I of this series one of us reported the preparation and properties of some complexes of nickel(II) with triphenylphosphine of the type $(Ph_3P)_2NiX_2$, and it was suggested that the halogeno-complexes of this series had tetrahedral structures.

Table 1.

Colour, decomposition points and electric and magnetic dipole moments of triarylphosphine complexes of nickel and cobalt.

Compound ‡	Colour	Decomp. pt.	μ (D)	$\mu_{eff.}$ (B.M.)
$(p\text{-}Tol_3P)_2NiCl_2$	Olive-green	203—205°	6·2	3·27
$(p\text{-}Tol_3P)_2NiBr_2$	Dark green	236—238	8·6	3·28
$(p\text{-}Tol_3P)_2NiI_2$	Dark brown	230—232	9·8	3·23
$(p\text{-}Tol_3P)_2Ni(SCN)_2$	Red	207—210	2·3	Diamag.
$(p\text{-}Anis_3P)_2NiCl_2$	Brown	165—167	7·4	3·27
$(p\text{-}Anis_3P)_2NiBr_2$	Red-brown	185—187	9·0	3·26
$(p\text{-}Anis_3P)_2NiI_2$	Dark brown	159—160	9·2	3·22
$(p\text{-}Anis_3P)_2Ni(SCN)_2$	Red	187—190	—*	Diamag.
$(p\text{-}Anis_3P)_2Ni(NO_3)_2$	Green	185—189	—*	3·24
$\{(p\text{-}Cl{\cdot}C_6H_4)_3P\}_2Ni(SCN)_2$	Red	190—195	—*	Diamag.
$(Ph_3P)_2CoCl_2$	Blue	231—232	—†	4·51
$(Ph_3P)_2CoBr_2$	Green	218—219	7·6	4·57
$(Ph_3P)_2CoI_2$	Brown	232—233	9·6	4·73

* Not measured. † Insoluble in benzene. ‡ Tol = C_6H_4Me; Anis = $MeO{\cdot}C_6H_4$.

The dipole moments of $(Ph_3P)_2NiX_2$ (X = Br and I) were determined again and found to be 6·8 and 9·0 D, respectively.

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[1] Parts I and II, *J.*, 1958, 719; 1961, 2705.

We report here the preparation of complexes of nickel(II) with tri-*p*-tolyl- and tri-*p*-methoxyphenyl-phosphine by the method used for the isolation of the triphenylphosphine analogues. Tri-*p*-chlorophenylphosphine gave only a pure thiocyanate complex and an impure iodo-complex. The complexes now prepared and characterized are listed in Table 1, with their properties.

TABLE 2.

Magnetic susceptibilities of phosphine complexes of nickel.

Compound	$10^6\chi_m$ * (uncorr.)	$10^6\chi_m$ (corr.)	Temp. (°K)	$\mu_{eff.}$ (corr.) B.M.
$(p\text{-Tol}_3P)_2NiCl_2$	3949	4417	292°	3·225
	3839	4307	292	3·185
	4097	4567	292	3·28
	4292	4760	299	3·38
	8100	8568	153	
	11,500	11,968	103	
				Mean 3·27
$(p\text{-Tol}_3P)_2NiBr_2$	4073	4561	292	3·28
	4696	5184	241	
	5853	6341	199	
	6387	6875	176	
	7460	7948	145	
$(p\text{-Tol}_3P)_2NiI_2$	3957	4477	293	3·25
	3761	4281	298	3·21
				Mean 3·23
$(p\text{-Anis}_3P)_2NiCl_2$	4309	4805	292	3·36
	3906	4401	292	3·22
	4007	4502	293	3·26
	4213	4708	293	3·33
	4159	4654	293	3·32
	6719	7714	189	
	10,950	11,445	117	
				Mean 3·27
$(p\text{-Anis}_3P)_2NiBr_2$	3982	4497	293	3·26
	4506	5021	247	
	5170	5685	217	
	6147	6662	176	
	7492	8007	142	
$(p\text{-Anis}_3P)_2NiI_2$	3968	4515	294	3·27
	3720	4267	293	3·18
	5978	6525	180	
	10,310	30,857	117	
				Mean 3·22
$(p\text{-Anis}_3P)_2Ni(SCN)_2$	−479	34	292	Diamag.
	−350	163	219	
	−239	274	199	
	−386	126	173	
	−386	126	148	
$(p\text{-Anis}_3P)_2Ni(NO_3)_2$	4007	4490	290	3·24
	4527	5010	249	
	5199	5682	217	
	6484	6967	133	
	8441	8924	172	
$\{(p\text{-Cl}\cdot C_6H_4)_3P\}_2Ni(SCN)_2$	−312	187·5	291	Diamag.
	−338	161·5	203	
	−293	207	151	

* Braces indicate groups of figures used for plots of temperature dependence.

Thus, the two new series of complexes appear to be similar to their triphenylphosphine analogues.

Their molecular weights could not be determined because the molar solubilities are low in non-donor solvents suitable for such measurements. They were non-electrolytes in nitrobenzene.

The magnetic susceptibility of the paramagnetic complexes follows the Curie–Weiss law over the range 150—290° K (see Table 2). The diamagnetic complexes, however, show the small, temperature-independent paramagnetism found in the compounds of similar type described in Part II.[1] The values of the magnetic moments of the compounds described in the present communication are very similar to those of the corresponding triphenylphosphine complexes, $(Ph_3P)_2NiX_2$ (X = Cl, Br, and I), for which values of $\mu_{eff.}$ of 3·41, 3·27, and 3·28 have been reported.[2]

The visible and ultraviolet spectra of benzene solutions of the triphenyl, tri-*p*-tolyl, and tri-*p*-methoxyphenyl derivatives in the region 300—1000 mμ are recorded in Table 3. They are all very similar, the spectra of the tri-*p*-tolylphosphine complexes being typical, (see Fig. 1).

TABLE 3.

Electronic absorption spectra of the triarylphosphine complexes of nickel.

	Solution		Solid	
Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	"Absorbency"
$(Ph_3P)_2NiCl_2$	400	3000	400	1·57
	525—575	sh	570	0·87
	875	76	930	0·92
$(Ph_3P)_2NiBr_2$	425	5200	450	1·65
	570	300	600	1·11
	920	160	950	1·18
$(Ph_3P)_2NiI_2$	425	3200	450	1·70
	475	sh	525—575	sh
	990	400	650—750	sh
			⩾1000	⩾1·25
$(Ph_3P)_2Ni(SCN)_2$	425	2600	460	1·57
			550	sh
$(p\text{-}Tol_3P)_2NiCl_2$	410	2120	440	1·48
	535	205	560	0·82
	900	108	900	0·84
$(p\text{-}Tol_3P)_2NiBr_2$	435	10,000	440	1·58
	580	225	600	1·25
	920	270	960	1·27
$(p\text{-}Tol_3P)_2NiI_2$	460	6100	480	1·8
	975	570	625—675	1·06
			⩾1000	⩾1·22
$(p\text{-}Tol_3P)_2Ni(SCN)_2$	420	8500	400—420	1·74
			475—525	sh
$(p\text{-}Anis_3P)_2NiCl_2$	440	7400	350	1·55
	550	194	460	1·65
	890	158	540—580	sh
			900	0·875
$(p\text{-}Anis_3P)_2NiBr_2$	465	5000	340	1·61
	585	200	480	1·79
	900	255	575—625	sh
			935	0·92
$(p\text{-}Anis_3P)_2NiI_2$	475	4700	350	1·65
	650—700	sh	515	1·86
	960	520	625—675	sh
			⩾1000	⩾1·19
$(p\text{-}Anis_3P)_2Ni(SCN)_2$	420	14,680	330	1·46
			400	1·43

All the paramagnetic complexes show absorption bands at about 900 mμ, characteristic of high-spin complexes of this type, as discussed in Part II.[1] The bands at about 600 mμ in the paramagnetic complexes have extinction coefficients, $\varepsilon_{max.}$, of about 200, while in the diamagnetic complexes, *e.g.*, $(Et_3P)_2NiX_2$, these bands have extinction coefficients of about 600. The absorption spectra of $(Ph_3P)_2NiCl_2$ and of $(Ph_3P)_2Ni(SCN)_2$ in benzene solution are to be taken as being indicative only: the compounds are sparingly soluble in the solvent and thus the extinction coefficients may be in error by a factor of two. The

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[2] Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

spectra of the triarylphosphine derivatives differ from those of their butyldiphenylphosphine analogues in that no major shifts of absorption bands are observed in going from benzene solutions to solids (see Table 3).

In Part II it was observed that, for a given anionic ligand, a change from trialkyl- to dialkylphenyl- to alkyldiphenyl-phosphine caused small shifts in the absorption bands of the diamagnetic complexes. Large shifts were observed when either the change of phosphine or the change in physical state was accompanied by a change in magnetic susceptibility. Thus major band shifts were observed on comparing the solid complexes $(Bu^n{}_2PhP)_2NiX_2$, which are diamagnetic, with the solid complexes $(Bu^nPh_2P)_2NiX_2$, which are paramagnetic. Band shifts were also observed between the solid complexes $(Bu^nPh_2P)_2NiX_2$ and their benzene solutions and it was shown that these shifts could be associated with the presence in solution of the equilibrium:

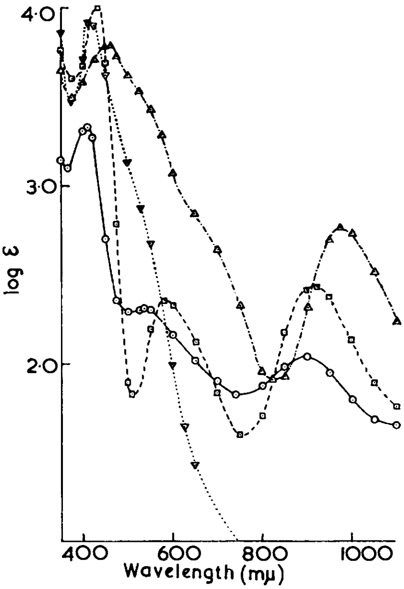

FIG. 1. Spectra of $(p\text{-}Tol_3P)_2NiX_2$ in benzene solution.

—○—○— X = Cl. -□--□- X = Br. -·△-·-△·- X = I. ···▽···▽··· X = SCN.

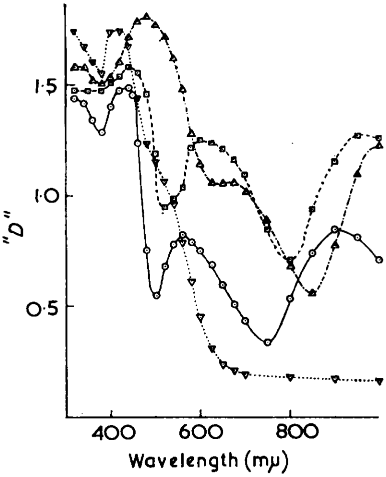

FIG. 2. Reflection spectra of $(p\text{-}Tol_3P)_2NiX_2$.

—○—○— X = Cl. -□--□- X = Br. -·△-·-△·-X = I. ···▽···▽··· X = SCN.

$$\underset{\text{Diamagnetic}}{(Bu^nPh_2P)_2NiX_2} \rightleftharpoons \underset{\text{Paramagnetic}}{(Bu^nPh_2P)_2NiX_2}$$

From magnetic-susceptibility measurements the benzene solutions of $(Bu^nPh_2P)_2NiX_2$, where X = Cl, Br, or I, appear to contain 90%, 40%, and 10%, respectively, of diamagnetic species, and the ratio of the intensities of the band at *ca.* 600 mμ (which is the superimposition of the bands of the diamagnetic and the paramagnetic complex in this region) and that at about 900 mμ (which is characterisic of the paramagnetic species) are in good agreement with the figures quoted above.[1]

The spectroscopic evidence presented here indicates that equilibria of the above type are set up in the triarylphosphine complexes. This hypothesis is supported by the relative intensities of the bands at about 600 and 900 mμ. In the spectra of the solid complexes $(Bu^nPh_2P)_2NiX_2$ and $(Ar_3P)_2NiX_2$ (X = Cl, Br, or I), which are fully paramagnetic, the two bands have intensities which are roughly equal. The intensities of the 600 and the 900 mμ bands of the triarylphosphine complexes in benzene solution differ slightly, indicating that small amounts of diamagnetic species may be present in solutions of the chloro- and possibly even of the bromo-complexes (compare Figs. 1 and 2). Confirmation of these conclusions, by measuring the magnetic susceptibility of benzene solutions, is being undertaken by Dr. R. J. P. Williams and co-workers.

There are no apparent shifts in absorption bands of the nickel complexes caused by the substituents in the benzene rings. Thus, the expected changes of strength of the crystal field produced by the operation of the inductive and mesomeric effects of the substituents introduced in *para*-position to the phosphorus atom are very small.

Dipole Moments.—The values of the dipole moments of the triphenylphosphine complexes and of the other triaryl derivatives investigated are given in Table 1. The dipole moments of the chloro-complexes of triphenylphosphine could not be measured because of their low solubility in benzene.

The dipole moments of the thiocyanate complexes are around 2—3 D: these are similar to the values found for the diamagnetic halide and thiocyanate complexes of dibutylphenylphosphine, and it is suggested that they also have a square-planar structure. The larger dipole moments of the paramagnetic halide complexes are in accord with a tetrahedral structure. It is interesting that, contrary to expectation, the dipole moment of the molecule increases with increasing atomic weight of the halogen atom.[3] Two interpretations of this observation are possible: (*a*) an equilibrium is set up in solution between the tetrahedral paramagnetic form and a *trans*-square-planar diamagnetic form which varies as the halide changes from chloride, through bromide, to iodide; (*b*) the complex has a single, distorted tetrahedral structure in solution and the bond angle PNiX increases as X changes from Cl to Br to I. Possible variations in magnetism are explained in the second case by the existence of a paramagnetic ground state and a diamagnetic excited state, separated by only a small energy gap.[1]

The presence of some diamagnetic form in solution, previously suggested on the basis of spectral data for the chloro-complexes and possibly for some bromo-complexes, fits both interpretations. The crystallographic work of Garton *et al.*[4] supports the second: they find that in crystalline $(Ph_3P)_2NiCl_2$ the bond angles are: $\angle PNiP = 116\frac{1}{2}^\circ$, $\angle ClNiCl = 123\frac{1}{2}^\circ$, and $\angle PNiCl = 104^\circ$ and 105°: the structure is thus that of a flattened tetrahedron.[4] If this structure persists in solution then an increase in the size of the halogen atoms will increase the angle PNiX, which is small, and the structure will approach that of a regular tetrahedron.

One of the Referees suggested that the changes in dipole moments observed in the set of compounds $(p\text{-}Tol_3P)_2NiX_2$ cannot be accounted for only on the basis of changes of bond angles and invited us to express our views on this point. We suggest that part of the change might be attributed to increases in bond moments Ni–X in the order $Cl < Br < I$, due to an increase in polarizability of metal–halogen bonds. A rough calculation, with bond polarizabilities derived from group and atom refractions, and covalent atomic radii with tetrahedral angles, gives the induced moment along the main axis of the molecule caused by the phosphorus–metal dipole acting upon the polarizable metal–halogen bonds. We made one further assumption that the mean dielectric constant of the space between the inducing dipole and the polarizable material was equal to that of benzene. This assumption is scarcely justifiable, though it is probably less bad than assuming a vacuum. The result of this calculation is as follows: for every unit of 1 D in the phosphorus–metal bond, 0·6 D is induced along the main axis between the two metal–halogen bonds, in the case of the bromides (with nickel as the metal); for the iodides the figure is 1·0 D. Of course, to obtain a gross moment we should have to add to this both the values of the unperturbed bond moments and the back-polarization of the phosphorus–metal bond. In view of the crudity of the assumptions, it seems valueless to refine this

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[3] Smyth, "Dielectric Behaviour and Structure," McGraw Hill, New York, 1955, p. 244.

[4] Garton, Henn, Powell, and Venanzi, unpublished work.

calculation: nevertheless, it does appear that the observed differences might—in part at least—be explained by this effect.

The dipole moments of two cobalt complexes investigated (which are expected to have tetrahedral structure) are given in Table 1; they show the same increase on replacement of bromide by iodide as the nickel complexes do. Cobalt(II) complexes of this type are not expected to show magnetic variations similar to those of the nickel complexes and so interpretation (*a*) cannot apply here. By analogy it seems likely that the variation in bond angles proposed in (*b*) occurs in the nickel complexes as well as in the cobalt complexes.

The increment in dipole moment produced by the replacement of triphenylphosphine by tri-*p*-tolylphosphine, 1·8 D in L_2NiBr_2 and 0·8 D in L_2NiI_2, calls for comment. A calculation, in which the group moment of the methyl group and regular tetrahedral angles at the phosphorus and nickel atoms are used, predicts an increment in dipole moment of about 0·6 D. Thus, in view of the approximations used in this calculation, the observed and the calculated increment in dipole moment due to the methyl group in the iodide complex are in good agreement. The observed further increment in the bromo-complexes can be explained by assuming that the equilibrium of $(Tol_3P)_2NiBr_2$ in benzene solution contains almost entirely the paramagnetic form while that of $(Ph_3P)_2NiBr_2$ contains some of the diamagnetic form. This is supported by the spectra of the benzene solutions of the two complexes (see Table 3): the ratio of the intensities of the absorption bands at about 600 and 900 mμ are 1 : 1·12 and 1 : 0·55, respectively; ratios of the order 1 : 1 to 1 : 1·2 are normal for fully paramagnetic complexes.

EXPERIMENTAL

Preparation of the Phosphines.—Tri-*p*-tolyl-, tri-*p*-methoxyphenyl-, and tri-*p*-chlorophenylphosphine were prepared by Mann and Chaplin's method.[5] In the preparation of the methoxy-derivative it was preferable to use tetrahydrofuran as solvent.

Preparation of the Complexes.—*Bis(trimethylphosphine)dichloronickel.* The method described in Part I was improved as follows: nickel chloride hexahydrate (2·38 g.) was refluxed for 30 min. with glacial acetic acid (50 c.c.), dehydration being accompanied by a change from green to yellow. The acetic acid was decanted and the residue washed twice with butan-1-ol. A solution of triphenylphosphine (7·80 g.) in butan-1-ol (75 c.c.) was then added to the solid, and the mixture boiled under reflux. The resulting deep blue solution was filtered and, on cooling, the product separated in 86% yield (Found: Ni, 9·0. Calc. for $C_{36}H_{30}Cl_2NiP_2$: Ni, 9·0%).

The following were prepared and purified as described in Part I:

Bis(triphenylphosphine)dibromonickel (Found: Ni, 7·9. Calc. for $C_{36}H_{30}Br_2NiP_2$: Ni, 7·9%). *Bis(triphenylphosphine)di-iodonickel* (Found: Ni, 6·9. Calc. for $C_{36}H_{30}I_2NiP_2$: Ni, 7·0%). *Bis(triphenylphosphine)dithiocyanatonickel* (Found: Ni, 8·4. Calc. for $C_{38}H_{30}N_2NiP_2S_2$: Ni, 8·3%). The tri-*p*-tolyl- and tri-*p*-methoxyphenyl-phosphine complexes were prepared analogously to the corresponding triphenylphosphine complexes. Butan-1-ol was used as a solvent for recrystallization of the complexes unless otherwise specified.

Bis(tri-p-tolylphosphine)dichloronickel (86%) (Found: Ni, 7·95. $C_{42}H_{42}Cl_2NiP_2$ requires Ni, 8·0%). *Bis(tri-p-tolylphosphine)dibromonickel* (55%) (Found: Ni, 6·9. $C_{42}H_{42}Br_2NiP_2$ requires Ni, 7·1%). *Bis(tri-p-tolylphosphine)di-iodonickel* (67·5%) (Found: Ni, 6·5. $C_{42}H_{42}I_2NiP_2$ requires Ni, 6·4%). *Bis(tri-p-tolylphosphine)dithiocyanatonickel* (69%) (Found: Ni, 7·3. $C_{44}H_{42}N_2NiP_2S_2$ requires Ni, 7·5%). *Bis(tri-p-methoxyphenylphosphine)dichloronickel* (73%) (Found: Ni, 7·0. $C_{42}H_{42}Cl_2NiO_6P_2$ requires Ni, 7·0%). *Bis(tri-p-methoxyphenylphosphine)dibromonickel* (83·5%) (Found: Ni, 6·2. $C_{42}H_{42}Br_2NiO_6P_2$ requires Ni, 6·4%) *Bis(tri-p-methoxyphenylphosphine)di-iodonickel* (81%) (Found: Ni, 5·9. $C_{42}H_{42}I_2NiO_6P_2$ requires Ni, 5·8%). *Bis(tri-p-methoxyphenylphosphine)dithiocyanatonickel* (94%) (Found: Ni, 6·95. $C_{44}H_{42}N_2NiO_6P_2S_2$ requires Ni, 6·7%). *Bis(tri-p-methoxyphenylphosphine)dinitratonickel* (prepared in 50% yield analogously to the *p*-tolyl derivative) (Found: Ni, 6·55. $C_{42}H_{42}N_2NiO_{12}$ requires Ni, 6·6%). Bis(tri-*p*-chlorophenylphosphine)di-iodonickel (mauve

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[5] Mann and Chaplin, *J.*, 1937, 527.

crystals, contaminated with free phosphine) was obtained by the usual method; the mauve product decomposed on attempted recrystallization). *Bis*(*tri*-p-*chlorophenylphosphine*)*dithiocyanatonickel* (90%) (Found: Ni, 6·25. $C_{38}H_{24}Cl_6N_2NiP_2S_2$ requires Ni, 6·5%).

The cobalt complexes were prepared in butan-1-ol solution and recrystallized from the same solvent. The method of preparation is that described for $(Ph_3P)_2NiBr_2$ and gave *bis*(*triphenylphosphine*)-*dichloro*- (74%) (Found: C, 65·8; H, 4·8. $C_{36}H_{30}Cl_2CoP_2$ requires C, 66·1; H, 4·6%), -*dibromo*- (77%) (Found: C, 58·4; H, 4·05. $C_{36}H_{30}Br_2CoP_2$ requires C, 58·2; H, 4·1%), and -*di-iodo-cobalt* (79%) (Found: C, 51·6; H, 3·9. $C_{36}H_{30}CoI_2P_2$ requires C, 51·6; H, 3·6%).

Analysis.—Analysis for nickel was carried out spectrophotometrically by measurement of the absorbance of solutions of the complex obtained by persulphate oxidation of bis(dimethylglyoxime)nickel(II) in the presence of sodium hydroxide, as described in Part II.[1]

Conductance Measurements.—These were carried out on a 0·001M-solution of the complex in nitrobenzene, with a Phillips P.R. 9500 conductivity bridge.

Magnetic Susceptibility Measurements.—These were performed on the finely powdered solids with a Gouy-type balance. The effective magnetic moments, $\mu_{\text{eff.}}$, were calculated from the susceptibilities at room temperature, correction being made for the diamagnetism of the component atoms. The susceptibility values are listed in Table 2.

Measurements of 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 reflection spectra of the finely powdered solids were measured over the range 320—1000 mμ on a Unicam S.P. 500 spectrophotometer fitted with a Unicam diffuse reflection attachment, S.P. 540, magnesium carbonate being the reference standard.

The values of $\lambda_{\text{max.}}$ and the corresponding extinction coefficients ε are listed in Table 3.

TABLE 4.

$(Ph_3P)_2NiBr_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
245	2·2768	1·14444
386	2·2777	1·14435
569	2·2792	1·14429

$\varepsilon_{12} = 2{\cdot}2750_0 + 7{\cdot}366w_2$
$v_{12} = 1{\cdot}14461 - 0{\cdot}536w_2$
${}_{\mathrm{T}}P_2 = 1120$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 205$ c.c.
$\mu = 6{\cdot}8 \pm 0{\cdot}2$ D

$(Ph_3P)_2NiI_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
350	2·2787	1·14435
442	2·2798	1·14431
476	2·2803	1·14431

$\varepsilon_{12} = 2{\cdot}2749_7 + 10{\cdot}972w_2$
$v_{12} = 1{\cdot}14459 - 0{\cdot}636w_2$
${}_{\mathrm{T}}P_2 = 1852$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 215$ c.c.
$\mu = 8{\cdot}95 \pm 0{\cdot}15$ D

$(p\text{-}Tol_3P)_2NiCl_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
501	2·2778	1·14432
642	2·2790	1·14426
691	2·2794	1·14423

$\varepsilon_{12} = 2{\cdot}2749_3 + 6{\cdot}258w_2$
$v_{12} = 1{\cdot}14459 - 0{\cdot}535w_2$
${}_{\mathrm{T}}P_2 = 1001$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 227$ c.c.
$\mu = 6{\cdot}2 \pm 0{\cdot}2$ D

$(p\text{-}Tol_3P)_2NiBr_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
288	2·2777	1·14444
692	2·2818	1·14438
828	2·2834	1·14426

$\varepsilon_{12} = 2{\cdot}2749_1 + 10{\cdot}107w_2$
$v_{12} = 1{\cdot}14458 - 0{\cdot}359w_2$
${}_{\mathrm{T}}P_2 = 1766$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 233$ c.c.
$\mu = 8{\cdot}6 \pm 0{\cdot}2$ D

$(p\text{-}Tol_3P)_2NiI_2$

—	2·2750	1·14460
382	2·2798	1·14444
508	2·2818	1·14441
738	2·2835	1·14423

$\varepsilon_{12} = 2{\cdot}2752_2 + 11{\cdot}818w_2$
$v_{12} = 1{\cdot}14462 - 0{\cdot}481w_2$
${}_{\mathrm{T}}P_2 = 2278$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 243$ c.c.
$\mu = 9{\cdot}8 \pm 0{\cdot}3$ D

$(p\text{-}Tol_3P)_2Ni(SCN)_2$

—	2·2750	1·14460
376	2·2756	1·14444
450	2·2758	1·14444
1450	2·2771	1·14406

$\varepsilon_{12} = 2{\cdot}2750_9 + 1{\cdot}424w_2$
$v_{12} = 1{\cdot}14460 - 0{\cdot}372w_2$
${}_{\mathrm{T}}P_2 = 469$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 242$ c.c.
$\mu = 2{\cdot}3 \pm 0{\cdot}2$ D

$(p\text{-}Anis_3P)_2NiCl_2$

—	2·2750	1·14460
577	2·2795	1·14438
863	2·2818	1·14432
1047	2·2833	1·4423

$\varepsilon_{12} = 2{\cdot}2749_5 + 7{\cdot}936w_2$
$v_{12} = 1{\cdot}14459 - 0{\cdot}343w_2$
${}_{\mathrm{T}}P_2 = 1360$ c.c.
${}_{\mathrm{E}}P_2$ (calc. $= 232$ c.c.
$\mu = 7{\cdot}4 \pm 0{\cdot}2$ D

$(p\text{-}Anis_3P)_2NiBr_2$

—	2·2750	1·14460
121	2·2662	1·14454
400	2·2785	1·14445
528	2·2808	1·14439

$\varepsilon_{12} = 2{\cdot}2749_0 + 10{\cdot}411w_2$
$v_{12} = 1{\cdot}14458 - 0{\cdot}381w_2$
${}_{\mathrm{T}}P_2 = 1911$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 238$ c.c.
$\mu = 9{\cdot}0 \pm 0{\cdot}3$ D

$(p\text{-}Anis_3P)_2NiI_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14460
117	2·2763	1·14454
230	2·2773	1·14451
685	2·2818	1·14423

$\varepsilon_{12} = 2{\cdot}2750_6 + 9{\cdot}853w_2$
$v_{12} = 1{\cdot}14460 - 0{\cdot}545w_2$
${}_{\mathrm{T}}P_2 = 1968$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 248$ c.c.
$\mu = 9{\cdot}2 \pm 0{\cdot}1$ D

$(Ph_3P)_2CoBr_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14463
200	2·2767	1·14446
295	2·2776	1·14442
357	2·2781	1·14439
759	2·2818	1·14414

$\varepsilon_{12} = 2{\cdot}2749_4 + 8{\cdot}990_5w_2$
$v_{12} = 1{\cdot}1445_8 - 0{\cdot}519w_2$
${}_{\mathrm{T}}P_2 = 1394$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 205$ c.c.
$\mu = 7{\cdot}6 \pm 0{\cdot}1$ D

$(Ph_3P)_2CoI_2$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14454
200	2·2773	1·14447
355	2·2791	1·14429
361	2·2793	1·14433
476	2·2807	1·14426

$\varepsilon_{12} = 2{\cdot}2749_7 + 11{\cdot}91w_2$
$v_{12} = 1{\cdot}1445_6 - 0{\cdot}638w_2$
${}_{\mathrm{T}}P_2 = 2083$ c.c.
${}_{\mathrm{E}}P_2$ (calc.) $= 215$ c.c.
$\mu = 9{\cdot}6 \pm 0{\cdot}1$ D

The intensity of absorption in the reflection spectra is given on an arbitrary scale, " *D*," which may vary from compound to compound.

Dipole-moment Measurements.—These were carried out in benzene solution, and calculated as described in Part I. The experimental data are listed in Table 4.

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