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Stereochemistry of 5-Co-ordinated Compounds

III. Some New Phosphine Complexes of Divalent Nickel and Cobalt

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In continuation of earlier work [1,2] some new phosphine complexes of divalent nickel and cobalt have been prepared (Tables 1 and 2). They serve as starting materials for the preparation of phosphine complexes of trivalent nickel and cobalt, to be described in the following paper.

In contrast to the complexes of higher phosphines, the trimethylphosphine complexes are oxidised to nickel(III) and cobalt(III) compounds by atmospheric oxygen and the nickel halides are able to take up more than two moles of the phosphine. The additional phosphine molecules are, however, very loosely bound and only the compounds of the type $[NiX_2(Me_3P)_2]$ could be prepared in the pure state.

The nitrites of the type $[Ni(NO_2)_2(R_3P)_2]$ resemble the halides and pseudohalides; they are diamagnetic and have zero dipole moment and therefore are *trans*-planar nitro-complexes (with Ni bound to N). Nickel salts of other oxo-acids form red complexes at low temperature, but at room temperature these turn green or yellow. The ultraviolet spectra of the red and green complexes differ fundamentally and it is supposed that quite generally diamagnetic, *trans*-planar nickel phosphine complexes with oxo-anions are only stable at low temperature and are transformed into paramagnetic, tetrahedral complexes at room temperature. All the cobalt phosphine complexes are analogous to the stable nickel complexes with oxo-anions and no transformation to another form occurs at low temperature.

The infra-red spectra of the phosphine complexes (Table 3) show no essential differences from the spectra of the free phosphines in the NaCl-range.

The red, square-planar nickel complexes of the type $[NiX_2(R_3P)_2]$ are oxidised by chlorine, bromine, chlorine dioxide, nitrogen dioxide and similar reagents to form intensely dark blue or dark green complexes containing trivalent nickel [1,3]. These are decomposed by water, but are extremely soluble in benzene, light petroleum and other organic solvents. They are rather instable, undergoing autoreduction to the divalent stage, but a closer examination of the bromide $[NiBr_3(Et_3P)_2]$ showed it to be monomolecular and to contain one unpaired electron[3]. We also found that it apparently possesses a finite but rather small dipole moment (2.5 D). This seems to rule out the trigonal bipyramidal configurations which should either have zero or a much larger dipole moment than 2.5 D, but is in accordance with a tetragonal pyramidal structure. However, considering the lability of the compound and the uncertainty of the correction for the atom polarisation this conclusion is not altogether definite, and so we have searched rather extensively for more stable compounds of this type, which would allow a more definite determination of the dipole moments and perhaps also an X-ray structure determination to be made.

In addition to the compounds of triethylphosphine, tripropylphosphine and tributylphosphine, studied in earlier papers[1-3], we have prepared compounds of trimethylphosphine, triisopropylphosphine, triisobutylphosphine, tri-*sec*-butylphosphine and tribenzylphosphine. After completion of this work some of these compounds have also been described by Giacometti and Turco[11] and by Venanzi *et al.*[8,21-23]. The tricyclohexylphosphine compounds[4,5] and triphenylphosphine compounds[6-8] studied by other workers in this field were also included in the investigation. Table 1 contains all the substances we have used for the oxidation experiments, whether new or known compounds.

The new nickel complexes of higher trialkylphosphines do not differ essentially from the triethylphosphine complexes. The trimethylphosphine compounds show, however, a rather different behaviour. The red solution formed by addition of trimethylphosphine to an ethanolic solution of nickel chloride or bromide is coloured violet-blue by an excess of trimethylphosphine, indicating the addition of more than two moles of trimethylphosphine. Probably compounds of the type $[NiX_2(Me_3P)_4]$ are formed. Trimethylphosphine is, however, given off very easily from these compounds, and in the case of the chloride, only the red compound $[NiCl_2(Me_3P)_2]$ could be isolated. In the case of the bromide, however, an almost black compound, soluble in benzene with dark blue colour was isolated, which according to the analysis contains 3 moles of trimethylphosphines but probably is a mixture of $[NiBr_2(Me_3P)_2]$ and $[NiBr_2(Me_3P)_4]$.

This difference in behaviour of the triethylphosphine and the trimethylphosphine compounds is also illustrated by the influence of an excess of the trialkylphosphine on the electric conductivity of ethanolic solutions of the complexes: An ethanolic solution of $[NiCl_2(Et_3P)_2]$ has a very small conductivity in accordance with the formulation of the compound as a non-electrolyte. On addition of triethylphosphine the conductivity falls almost to zero, probably because of depression of a slight dissociation of the compound into the phosphine and nickel chloride. Further addition of triethylphosphine causes a slight increase of the conductivity, but it remains very low, even on addition of a large excess of triethylphosphine. An ethanolic solution of the trimethylphosphine compound, $[NiCl_2(Me_3P)_2]$, has similarly a very small initial conductivity, but here the addition of trimethylphosphine at once causes a strong increase of the conductivity which reaches an almost constant value of about 25 $ohm^{-1} \cdot mole^{-1} \cdot cm^2$ at 20°C when a little more than 2 moles of trimethylphosphine have been added, in accordance with the assumption that the compound [$NiCl_2(Me_3P)_4$] is formed. From its solubility in such solvents as benzene and light petroleum this compound would not be expected to be an electrolyte, but the coordination of additional molecules of a phosphine to the central atom must diminish its positive charge and thus facilitate the solvation process:

$$[NiX_2(Me_3P)_4] + EtOH \rightleftharpoons [NiX(EtOH)(Me_3P)_4]^+ + X^-$$

This limiting conductivity is almost identical with the values found for uni-univalent electrolytes (NH_4Cl, LiCl) in ethanol.

Another difference between the nickel complexes of trimethylphosphine and the higher trialkylphosphine is that the former (especially the bromide and iodide) are oxidised by atmospheric oxygen to compounds with trivalent nickel. These in turn undergo a dismutation to nickel(II) halogenide and trimethylphosphine oxide. Whereas samples of the compounds of triethyl-, tripropyl- and tributylphosphine, prepared in 1936, are still unchanged, the trimethylphosphine complexes were decomposed within a few months, as shown by the change of their dark red or dark blue colour to light green.

The cause of this difference between complexes of trimethylphosphine and the higher phosphines is probably the smaller size of the methyl group. This would explain that only in the case of trimethylphosphine is it possible to accomodate more than two phosphine molecules near the nickel atom. That the steric requirement of the phosphine molecule may have a very marked influence on the properties of phosphine complexes is also evident from some interesting papers by Turco *et al.*[5] and Venanzi *et al.*[8,22–24]. The reason for the greater ease of oxidation of the trimethylphosphine compounds compared with the compounds of higher phosphines may be that the smaller size of the trimethylphosphine molecule leads to a shortening of the nickel-halogen bond. An X-ray crystallographic determination of the Ni—Br bond length in [$NiBr_2(Me_3P)_2$] and comparison with the known length [9] of this bond in [$NiBr_2(Et_3P)_2$] would clearly be of interest.

The compounds of tribenzylphosphine are very similar to the trialkylphosphine compounds. The triphenylphosphine complexes of the type [$NiX_2(Ph_3P)_2$], except the red thiocyanate, are however rather different. The chloride is blue-green and the bromide dark green and soluble in benzene with a green colour. As found by Venanzi [8] these compounds are paramagnetic, probably because a tetrahedral arrangement is forced by the steric requirement of the ligands. The iodide, although brown and soluble in benzene with a red-brown colour, is similar to the chloride and bromide. The red complexes of trialkylphosphines on the contrary have generally been found to be diamagnetic (Asmussen [10], Venanzi *et al.*[21] and own measurements).

Somewhat unexpectedly some of the trialkylphosphine nickel complexes were found to be *green*, but *diamagnetic*. Giacometti and Turco [11] have described the compound [$NiBr_2(sec\mathrm{Bu}_3P)_2$] as a red solid forming a green solution. We have only obtained this substance as dark green crystals (when recrystallised from acetone the crystals have a brownish tinge), but it is quite possible that both a red and a green form exist, since Venanzi *et al.*[23] in some cases were able to isolate two forms with benzyldiphenylphosphine or allyldiphenylphosphine. The complex of nickel iodide and tributylphosphine, [$NiI_2(Bu_3P)_2$]

forms green-black crystals, soluble in organic solvents with a dark green colour, whereas the corresponding bromide is red and forms red solutions. In contrast to all green phosphine nickel complexes hitherto described these two complexes were found to be diamagnetic. Their electric dipole moments, however, are definitely higher than zero, and it therefore seems that some distortion from the square-planar configuration takes place in solution, due to the steric requirements of the large iodide ion or the secondary alkyl groups. With reference to the results obtained with the Ni(III)-complexes (see the following paper), it is of interest that the above mentioned complexes were found to have finite dipole moments even in pentane solution.

We have also prepared nitrites of the type $[Ni(NO_2)_2(R_3P)_2]$ (with R = ethyl or propyl), which are yellow. Although their colour is rather different from that of the halides, they are of the same type. They have been found to be diamagnetic and to possess zero dipole moment. Accordingly they have a *trans*-planar configuration and are nitro-complexes (with Ni bound to N), not nitrito-complexes.

Table 1. Trialkyl (or -aryl)phosphine complexes of divalent nickel, $[NiX_2(R_3P)_2]$.

X	R	Colour	M.p., °C	Analyses					
				C		H		X or N	
				found	calc.	found	calc.	found	calc.
Cl	Methyl [a]	red	195–97	24.80	25.56	6.54	6.39	25.00	25.18
Cl	Ethyl [1]	red	112–13					19.37	19.38
Cl	Propyl [1]	red	92–93					15.73	15.77
Cl	Isopropyl [11]	red	185–87					15.48	15.77
Cl	Butyl [1]	red	48–49					13.25	13.28
Cl	Isobutyl	dark red	105–08	53.50	53.98	10.24	10.12	13.23	13.28
Cl	*sec*-Butyl [11]	dark red	103–05	53.35	53.98	9.97	10.12	12.77	13.28
Cl	Cyclohexyl [4,5]	red	226–27					12.63	12.70
Cl	Benzyl	red	124–25	68.05	68.32	5.96	5.73	9.35	9.61
Cl	Phenyl [6,7,8]	blue-green	ca. 200 [b]	66.15	66.09	4.47	4.54	10.72	10.89
Br	Ethyl [1]	red	106–07					35.08	35.15
Br	Butyl	red	51–53	46.35	46.30	8.72	8.75	25.62	25.70
Br	*sec*-Butyl [11]	dark green	104–05	45.68	46.30	8.64	8.75	25.40	25.70
Br	Benzyl	violet-brown	140–41	60.75	60.98	5.36	5.12	19.02	19.32
Br	Phenyl [6,7,8]	green	ca. 215 [b]	58.20	58.18	4.03	4.04	21.66	21.52
I	Ethyl [1]	dark brown	91–92	26.05	26.26	5.46	5.51	45.90	46.25
I	Butyl	green-black	32–33	40.00	40.23	7.45	7.60	35.78	35.50
I	Benzyl	dark brown	136–37	54.85	54.75	4.54	4.60	27.50	27.55
I	Phenyl [7,8]	red-brown	ca. 215 [b]	51.60	51.64	3.79	3.59	30.56	30.34
CN	Ethyl	yellow	156–57	48.10	48.44	8.35	8.72	8.08	8.07
SCN	Ethyl	orange	140–41	40.70	40.89	7.52	7.33	6.57	6.79
SCN	Phenyl [8]	red	ca. 205 [b]	65.20	65.18	4.38	4.29	3.89	4.00
NO_2	Ethyl	yellow	176–77	37.00	37.24	7.87	7.81	6.99	7.24
NO_2	Propyl	yellow	166–67	45.25	45.90	8.76	8.99	5.70	5.95
NO_3	Propyl	green	89–92	42.10	42.98	8.92	8.42	5.60	5.57

a) For other trimethylphosphine complexes see experimental part.

b) The melting points of the triphenylphosphine complexes are very dependent upon the heating rate and it seems impossible to determine a definite melting point.

A few thiocyanates and a cyanide were also prepared. They seem to be quite analogous to the halides.

The complexes of the oxo-anions other than the nitrites, on the other hand are very different from the halides. As found previously [1] an alcoholic solution of nickel nitrate first turns red on addition of triethylphosphine, but soon turns green, and only a green compound of the composition $[Ni(NO_3)_2(Et_3P)_2]$ could be isolated. This compound has a large dipole moment and is paramagnetic [1,10]. At low temperatures the red colour remains for a long time, but it was not possible to induce crystallisation of the red compound, even on cooling at $-80°C$. The other trialkylphosphines show a similar behaviour. The stereochemistry of the green nitrate has been quite extensively discussed [8,10,12–14] and it may be concluded from arguments based on the ligand field theory that the compound has a tetrahedral structure because the nickel-anion bond is too weak to cause spin-pairing and to force the molecule in a planar arrangement.

Other nickel salts of oxo-acids show a similar behaviour: Solutions of nickel acetate, perchlorate or chlorate in ethanol and nickel bromate or sulfate in methanol (these salts are almost insoluble in ethanol) when cooled at $-80°C$ give a red-brown to red-violet (permanganate-like) colour on addition of triethyl- or tripropylphosphine. On heating the colour changes over from brown to yellow (much like $Ni(CN)_4^{2-}$) or green and on cooling the colour turns red again. An ethanolic solution of the green nitrates similarly turns red on cooling. On standing at room temperature the solutions are as a rule changed irreversibly (because of reduction of the anion or solvolysis) and do not turn red again on cooling. No crystalline phosphine complexes with these anions could be isolated. Insoluble nickel salts do not as a rule react with ethanolic solutions of phosphines. Nickel carbonate remained unchanged, nickel sulfite gave a pink solution which became more intensely red on cooling and nickel hypophosphite gave a light yellow solution which similarly turned red on cooling; the solutions contained only traces of nickel compounds. Nickel cyanide showed a similar behaviour, but the cyanide $[Ni(CN)_2(Et_3P)_2]$ could be prepared by shaking a solution of $[NiBr_2(Et_3P)_2]$ with silver cyanide. This method could not be applied in other cases because silver salts generally destroy the nickel phosphine complexes by depriving them of the phosphine. In contrast to the other nickel phosphine complexes the cyanide is stable towards water. It does not react with cyanogen to form a tri-cyanide.

Although both the green nitrates and the green triphenylphosphine complexes are paramagnetic and probably tetrahedral the cause of the tetrahedral structure is different in the two cases. In the green trialkylphosphine complexes containing oxo-anionic ligands (NO_3^-, ClO_4^-) it is due to a predominant "ionic" character of the nickel-anion bond, in the triphenylphosphine complexes (and the other green paramagnetic halogeno-complexes) it is due to the steric requirement of the phosphine molecules without change of the "covalent" character of the nickel-halogen bond. This is borne out by the electronic absorption spectra of these compounds. The red compounds were found to have a very pronounced absorption maximum near 370 mμ (27 000 cm^{-1}); for the chlorides containing triethyl-, tripropyl- and tributylphosphine the maximum was found at 367 mμ, for the red diethylphenylphosphine compound [1],

$[NiCl_2(Et_2PhP)_2]$, it was found at 374 mμ. The spectrum of the green bromide $[NiBr_2(Ph_3P)_2]$ is very similar to the spectra of these red compounds, but the maximum has been displaced towards longer wave lengths and is now found to 423 mμ. Accordingly the conspicuous change of colour of these compounds is caused by a comparatively small shift of the absorption maximum without essential change of the spectrum. Spectroscopically therefore the green triphenylphosphine compounds belong to the "red series". This was also found to be the case with the yellow nitrites although the extinction of the band is much smaller in this case. The green nitrates, on the contrary, show no absorption in this region of the spectrum. The absorption spectrum of $[Ni(NO_3)_2(Et_3P)_2]$ has been discussed by Asmussen and Bostrup [14], and after the completion of our work the absorption spectra of nickel phosphine complexes have been more extensively studied by Giacometti and Turco [11] and by Venanzi *et al.*[21–23]. We shall therefore not enter into further details of our measurements.

Both the complexes of the "red series" and the green complexes of oxo-anions containing trialkylphosphines (but not those containing triphenylphosphine) are oxidised by bromine, nitrogen dioxide *etc.* (not by iodine, cyanogen or thiocyanogen) to strongly coloured nickel(III) complexes. The triphenylphosphine complexes are decomposed by these reagents, the phosphine being oxidised. $[NiI_2(Ph_3P)_2]$ reacted with iodine in chloroform solution to form a black tri-iodide, $[Ni(I_3)_2(Ph_3P)_2]$.

A number of cobalt complexes of trialkylphosphines were also prepared (Table 2). As found previously [2] the cobalt complex $[CoCl_2(Et_3P)_2]$ has a large dipole moment (8.7 D) and a paramagnetism corresponding to 3 spins and not, as would be expected for a planar complex, to 1 spin. Similar values have now been found for the dipole moment and the magnetic moment of the corresponding bromide, and undoubtedly this applies to all the cobalt-phosphine

Table 2. Trialkyl (or -aryl)phosphine complexes of divalent cobalt, $[CoX_2(R_3P)_2]$.

X	R	Colour	M.p., °C	Analyses					
				C		H		X	
				found	calc.	found	calc.	found	calc.
Cl	Methyl [a]	green	130–32	23.35	25.56	6.40	6.39	22.80	25.18
Cl	Ethyl [2]	blue	101–02					19.44	19.37
Cl	Propyl [2]	blue	81–83					15.71	15.75
Cl	Phenyl	blue	ca. 225 [b]	65.85	66.09	4.48	4.54		
Br	Methyl [a]	green	89–90	18.65	19.43	4.95	4.84	39.20	43.12
Br	Ethyl	blue-green	118–20	31.65	31.65	6.66	6.60	35.03	35.14
Br	Phenyl	dark green	ca. 225 [b]	57.95	58.18	3.97	4.04	21.48	21.52
I	Ethyl	green	118–20	26.10	26.24	5.46	5.47	46.10	46.25
I	Phenyl	brown	ca. 230 [b]	51.35	51.64	3.72	3.59	30.82	30.34

a) The trimethylphosphine complexes could only be obtained approximately pure, see text.

b) The melting points of the triphenylphosphine complexes are very dependent upon the heating rate and it seems impossible to determine a definite melting point.

complexes which are all very similar. Accordingly the cobalt complexes are fundamentally different from the red nickel complexes. This is also evident from the spectra of the cobalt complexes, from which the very intense band at 367 mμ, found in the spectra of the nickel complexes, is missing. Instead they have two weaker bands in the visible region. The spectrum of $[CoCl_2(Et_3P)_2]$ in benzene solution shows a broad band with two peaks at 610 and 624 mμ and a rather narrow band at 734 mμ. It is intended to discuss the absorption spectra of these cobalt complexes in another paper.

With the exception of the trimethylphosphine complexes of cobalt, which like the corresponding nickel complexes are oxidised to cobalt(III) complexes

Table 3. Infra-red spectra of trialkylphosphine complexes.

Me_3P (gas) [16]	$[NiCl_2(Me_3P)_2]$	$[NiBr_2(Me_3P)_2]$	$[CoCl_2(Me_3P)_2]$	$[CoBr_2(Me_3P)_2]$
667 vw 672 vw	672 m	669 m	666 w	665 w
707 vs, 715 vs	738 s	732 s	716 w, 746 m	713 w sh, 752 m br
826 w, 838 w				
852 w	854 m	856 m br	864 m	864 m
938 vs, 947 vs	945 vs br	945 vs br	945 vs br	947 vs br
960 vs, 970 s,				
1033 m, 1067 s,				
1113 w, 1132 m				
1143 s	1147 m br	1149 m br	1146 s	1141 m sh
1282 vs	1285 s	1281 s	1286 s	1286 s
1298 vs	1300 m	1301 m	1299 s	1299 s
1310 vs, 1323 s				
1348 m, 1360 w				
1417 vs, 1430 vs,				
1440 vs	1422 m br	1426 m	1414 m br	1418 m br
2850 vs, 2920 vs	2920 w	2920 w	2920 w	2915 w
2970 vs	2980 w	2985 w	2955 w	2985 w

Et_3P (liq.) [17]	$[NiCl_2(Et_3P)_2]$	$[CoCl_2(Et_3P)_2]$	*cis*-$[PtCl_2(Et_3P)_2]$
655 m, 657 m			
670 m, 690 s	673 vw	687 vw, 699 vw	
717 m, 748 s	705 m, 720 s	727 m, 745 m	713 m, 723 m sh
765 s	763 vs	777 s	766 s
975 m	985 vw sh	987 m	983 vw
1003 m, 1023 m	1000 m, 1010 w	1007 m, 1019 m	1008 w
1043 s	1034 s	1049 m	1033 s
1098 vs, 1185 s			
1231 m, 1245 m sh	1240 w, 1248 w	1249 w	1240 w
1380 s	1375 w, 1383 vw	1388 w	1378 w
1423 m	1413 m, 1423 sh	1410 m	1414 m
1458 s, 1468 s	1453 m, 1460 m sh	1460 m br	1456 m
2845 m, 2900 s	2890 w, 2950 m	2920 m, 2940 m	2950 w
2998 s	2980 s	2975 m	2980 m

in the air, these cobalt complexes are not oxidised to cobalt(III) complexes even on addition of chlorine or bromine, which only decompose the complexes. The cobalt complexes show no change in colour or behaviour towards bromine on cooling to −80°C. As discussed in the following paper, however, cobalt(III) phosphine complexes could be prepared by treatment of the cobalt(II) complexes with nitrosyl chloride or bromide.

The infra-red spectra of some of these complexes have also been measured and compared with the known spectra of the free phosphines. As is seen from Table 3 the spectra of the complexes show fewer bands than the spectra of the phosphines, but no new bands. The only essential difference is that the P—C stretching frequencies of trimethylphosphine at 707 and 715 cm^{-1} are shifted a little to higher frequencies in the spectra of the complexes. For the triethylphosphine complexes the strong band at 760—770 cm^{-1}, which we assign to P—C stretching[15], is found at almost the same place in the spectrum of liquid triethylphosphine.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory by Albert Grossmann (1952—53), Walther Egger (1953—54), and Preben Hansen (since 1954).

Spectra in visible and ultraviolet were measured on a Cary Model 11 recording spectrophotometer.

Infra-red spectra were obtained on a Perkin Elmer model 21 double beam spectrometer with rock-salt prism, the KBr-disc technique being used.

Conductance measurements were carried out with a Type CDM 2d conductivity meter from Radiometer, Copenhagen.

Electric dipole moments were determined by measuring the dielectric constants of solutions of the complexes in benzene at 25°C with the apparatus Dipolmeter DM 01 from the Wissenschaftlich-Technische Werkstätten, Weilheim. Because of the intense colour of the solutions of the halogeno-complexes the determination of their refractive index is uncertain, therefore the electronic polarizations listed below have been equivalated to the molar refraction, R_D, calculated by addition of the appropriate atomic refractions (Ni = 18.8; Cl = 6.1; Br = 8.9; I = 13.9; P = 9.1; NO_2 = 8.4; C = 2.4; H = 1.1). For the atomic polarization our earlier results[1] indicate that it is reasonable to calculate with a value of *ca.* 30 cm^3. In the following table P, P_E, P_A, and P_O mean the total, electronic, atomic and orientation polarization of the solute at such low concentrations ($x = 0.002-0.004$) that there is no significant concentration dependency. Similar results were found for solutions of the complexes in pentane.

	P	P_E(calc)	$P_A + P_O$	P_O	μ(D)
$[NiCl_2(Et_3P)_2]$	137	111	26	~0	0
$[NiBr_2(Bu_3P)_2]$	199	172	27	~0	0
$[NiBr_2(sec\text{-}Bu_3P)_2]$	334	172	162	132	2.5
$[NiI_2(Bu_3P)_2]$	262	182	80	50	1.6
$[Ni(NO_2)_2(Et_3P)_2]$	148	116	32	~0	0
$[Ni(NO_2)_2(Pr_3P)_2]$	176	144	32	~0	0

Magnetic susceptibility measurements were done with a Gouy-type balance at room temperature. The nickel compounds $[Ni(NO_2)_2(Et_3P)_2]$, $[Ni(NO_2)_2(Pr_3P)_2]$, $[NiBr_2(sec\text{-}Bu_3P)_2]$, $[NiBr_2(Bu_3P)_2]$ and $[NiI_2(Bu_3P)_2]$ were found to be diamagnetic. For the paramagnetic cobalt compounds $[CoCl_2(Et_3P)_2]$ and $[CoBr_2(Et_3P)_2]$ the following magnetic moments were found:

	T	$10^6\chi_M$	μ_{eff}(B.M.)
$[CoCl_2(Et_3P)_2]$	292	6017	3.76
$[CoBr_2(Et_3P)_2]$	293	8535	4.51

Preparation of the phosphines. Triethylphosphine and the higher aliphatic homologues were prepared by Grignard syntheses, mainly as described by Davies *et al.*[18] It should be noted that the best yields were obtained by using equimolar quantities of the Grignard reagent and the phosphorus trihalide, contrary to what has been recommended in the literature. Further it was found that the yields were not improved by replacing phosphorus trichloride by phosphorus tribromide. In the preparation of triethylphosphine it was found advantageous to decompose the Grignard complex by dilute hydrochloric acid instead of aqueous ammonium chloride. The phosphine then passes into the aqueous layer, and the troublesome colloidal matter, that appears on this point of the synthesis, is now found in the ethereal layer and thus easily removed. The aqueous layer is then made alkaline with aqueous ammonia and the phosphine extracted with ether. The separation of ether and the phosphine by distillation is then also facilitated, because it is not necessary to use so much ether to extract the phosphine. The aspects of the use of this method in the preparation of the higher homologues were not explored.

Attempts to prepare tri-*tert*-butylphosphine, which has not hitherto been described, were unsuccessful. The ether extracts gave neither colour nor precipitate with carbon disulfide or nickel chloride.

Tribenzylphosphine was prepared in the following way: A solution of 45 g of phosphorus trichloride in 50 ml of ether was added dropwise at 0° to a Grignard solution prepared from 32 g of magnesium and 152 g of benzyl chloride. After refluxing for 1 h a solution of 50 g of ammonium chloride in 300 ml of water was added and the ethereal layer was separated and dried. On evaporation of the ether the phosphine was left as a white crystalline product. It proved to be highly sensitive to air and was not recrystallised but dissolved into absolute ethanol and the solution used directly for the preparation of the complex compounds. (The pure compound has been described recently by Hinton and Mann [19]).

Tricyclohexylphosphine was prepared according to Issleib and Brack [4]; triphenylphosphine was a recrystallised, commercial product.

Trimethylphosphine is conveniently regenerated from the AgI-compound as indicated by Mann and Wells [20]. As the synthesis presents some difficulties and only few details are given in the relevant papers the procedure used is given here: A solution of 14 ml of phosphorus trichloride in 35 ml of ether was added dropwise (in the course of 3 h) to a vigourously stirred solution of methyl magnesium iodide (prepared from 24.3 g of Mg and 63 ml of methyl iodide in 300 ml of ether), which was cooled in an ice-salt bath and kept under nitrogen. After standing overnight at 0° the ethereal phosphine solution was distilled under nitrogen into a well cooled and vigourously stirred solution of 24 g AgI in a saturated aqueous KI-solution. When the temperature of the bath, in which the reaction flask was heated, had reached 200°C the distillation stopped. The aqueous solution was stirred for another 2 h and the white precipitate was filtered off and dried in a desiccator over $CaCl_2$; it is stable in air.

Trimethylphosphine was regenerated from this addition compound by heating in a nitrogen atmosphere. Decomposition begins at 100°C and melting of the solid begins at about 150°C bath temperature. It was, however, found convenient to use a small free flame during distillation to avoid excessive foaming when the phosphine is distilled off. The overall yield was 37 %.

Preparation of the complex compounds. The complex compounds of the trialkylphosphines — except the cyanide described below — were prepared by addition of the equivalent amount or a slight excess of the phosphine to a well cooled solution of the appropriate nickel or cobalt salt (0.01 mole; the hydrates may be used) in absolute ethanol (5—10 ml); a solution of nickel nitrite was prepared by shaking an ethanolic solution of nickel chloride with freshly precipitated silver nitrite until negative chloride reaction. The crystals which separated were filtered by suction, washed with a little ice-cold ethanol and dried in a vacuum desiccator over H_2SO_4. The yields depend upon the solubility of the compounds; in most cases 70—80 % could be obtained. The compounds are usually obtained pure directly. Recrystallisation from ethanol results in a decrease of the melting points. If necessary the compounds can be purified by recrystallisation from pentane or by dissolution in benzene and precipitation with pentane. The melting points of the trimethylphosphine compounds had to be determined in a sealed tube, as trimethylphosphine is given off upon heating.

The cyanide $[Ni(CN)_2(Et_3P)_2]$ was prepared by shaking an ethanolic solution of the corresponding chloride or bromide with silver cyanide until the colour had changed from red to light yellow. After filtering the solution was concentrated until crystallisation *in vacuo*. Yield 0.3 g from 0.5 g of the chloride. Methylene chloride could also be used as a solvent; in this case the solution was evaporated to dryness *in vacuo* and the residue extracted with pentane, in which the complex is insoluble.

The bis-trimethylphosphine compounds were only obtained reasonably pure in the case of the chlorides. The bromides and iodides contained an excess of trimethylphosphine which could not be removed. Nickel bromide and iodide gave compounds which contained approximately 3 moles of trimethylphosphine, but this may be a coincidence since the compound prepared from cobalt iodide contained approximately 2.5 moles of trimethylphosphine. It seems possible that we have to do with mixtures of bis- and tetrakis-trimethylphosphine compounds, but this question needs further examination. These compounds have the following properties:

$NiBr_2 \cdot 3Me_3P$, blue-black crystals, soluble in benzene with dark blue colour. (Found: C 23.95; H 6.01; Br 36.20. Calc.: C 24.2; H 6.1; Br 35.8).

$NiI_2 \cdot 3Me_3P$, violet-black crystals, soluble in methylene chloride with dark blue-green colour. (Found: C 18.5; H 5.2; I 45.2. Calc.: C 19.9; H 4.9; I 47.0).

$CoI_2 \cdot 2.5Me_3P$, violet-black crystals, soluble in methylene chloride with red-violet colour. (Found: C 17.8; H 4.7; I 50.0. Calc.: C 17.9; H 4.5; I 50.5).

The compound prepared from cobalt bromide contained approximately 2 moles of trimethylphosphine and has been listed in Table 2.

The freshly prepared nickel chloride compound also contains an excess of trimethylphosphine, as shown by a bluish tinge of the red crystals. On drying in a desiccator over H_2SO_4, the crystals lost the bluish tinge and the analyses corresponded well to the formula $NiCl_2 \cdot 2Me_3P$ (Table 1). From a solution containing 4 moles of trimethylphosphine on 1 mole of $NiCl_2$ deep blue crystals were isolated, but these turned red on drying over H_2SO_4 and were transformed into the red bis-trimethylphosphine compound.

Crystalline cobalt compounds could not be obtained from the butylphosphines. For example a deep blue oil separated on addition of tributylphosphine to an ethanolic solution of nickel iodide, and a blue oil was similarly obtained on addition of tributylphosphine to cobalt chloride, extraction with methylene chloride and evaporation of the solvent. These oily products were easily soluble in pentane; on evaporation or cooling they again separated as oils.

The cobalt-phosphine complexes are easily oxidised on lying in the air. For example the deep blue $[CoCl_2(Et_3P)_2]$ attains a lighter blue colour and becomes insoluble in pentane, being transformed into a complex compound of the phosphine oxide.

The triphenylphosphine compounds were prepared from the appropriate salts and triphenylphosphine in boiling ethanol or butanol, *cf.* Yamamoto [7] and Venanzi [8]. The solution should not be cooled below room temperature before filtering, otherwise the crystals may be contaminated by triphenylphosphine.

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