276. *Reactions of Tertiary Diphosphines with Nickel and Nickel Carbonyl.*

By J. Chatt and F. A. Hart.

Nickel carbonyl treated with the diphosphines $o\text{-}C_6H_4(PR_2)_2$ and $C_2H_4(PR'_2)_2$ (where R = Me, Et, and Ph, and R′ = Et and Ph) readily forms derivatives of the type [Ni(CO)$_2$diphosphine]. The aromatic diphosphines $C_2H_4(PPh_2)_2$, $o\text{-}C_6H_4(PEt_2)_2$, and $o\text{-}C_6H_4(PPh_2)_2$, also displace all of the carbon monoxide to form compounds of the type [Ni(diphosphine)$_2$]. These are also formed by the direct reaction of the aromatic diphosphines with Raney nickel.

The infrared spectra and dipole moments of the dicarbonyl derivatives, their arsenic analogues, and related compounds have been examined and interpreted to show that the P–Ni and As–Ni bonds in these nickel(0) compounds have essentially the same bond order. From the bond dipole moments of about 3·3 D this is estimated to lie between 1·4 and 1·7.

The much more ready replacement of carbon monoxide by the tertiary phosphines than by the tertiary arsines must reside in the greater overall affinity of the phosphines for metals with filled *d*-orbitals and not only in the supposedly greater capacity of the phosphines to form stronger d_π–d_π-bonds.

During the last five years the replacement of carbon monoxide in metal carbonyls by other ligands has aroused considerable interest. In general it is possible to replace only about half of it. Rarely can all of it be replaced. This limitation has been attributed variously to kinetic factors and to insufficient double-bonding capacity of the ligand atoms in the substituting ligands.

Recently we have prepared a number of organic diphosphines of the types $C_2H_4(PR_2)_2$ and $o\text{-}C_6H_4(PR_2)_2$. Excepting ligands based on carbon as ligand atoms (*e.g.*, CO, CNR,

C_6H_6, etc.), we expect these ligands to have a stronger affinity than any others for metal atoms in low-valent states and with filled orbitals of d_ϵ or d_{xy}-type, such as occur in the metal carbonyls. We have, therefore, started to investigate their reactions with various metal carbonyls to see (*a*) how far substitution will go and (*b*) whether we can get any information about the extent of double bonding between the metal and phosphorus atoms in the substitution products.

In this paper we describe the reactions of the ditertiary phosphines with nickel carbonyl and with metallic nickel, record the relevant physical properties of the products, and compare them with those of their arsenic analogues. It will be shown that, unlike the purely aliphatic diphosphines, some chelating tertiary aromatic diphosphines readily displace all of the carbon monoxide from nickel carbonyl, and also dissolve finely divided nickel to form compounds of the type [Ni(chelate)$_2$]. The partially substituted products [Ni(chelate)(CO)$_2$] have dipole moments of about 5 D, and tentatively the bond orders of the P–Ni and As–Ni bonds are estimated to lie in the range 1·4—1·7.

Common ligands, such as ammonia, amines, ethers, sulphides, and the halide ions, if they react with nickel carbonyl, usually give intractable substitution products too unstable to be isolated and characterised. It appears that the ligand must be capable of more than a certain minimum amount of π-bonding to the metal in order to form isolable substitution products, and only a limited number of ligands do this. Even fewer are capable of replacing all the carbon monoxide from nickel carbonyl. As a summary of the present development, we list the well-characterised substitution products in Table 1. Only two ligands, carbon monoxide and methyldichlorophosphine are known to react with metallic nickel to produce complexes containing nickel(0).

TABLE 1. *Simple substitution products of nickel carbonyl.*

Degree of substitution	Ligands L *
Monosubstituted [$Ni(CO)_3L$]	PPh_3,[a] P(*p*-$MeC_6H_4)_3$,[b] P(*p*-$ClC_6H_4O)_3$,[c] $P(CF_3)_3$,[d] $AsPh_3$,[b] $SbCl_3$,[e] $SbPh_3$ [a]
Disubstituted [$Ni(CO)_2L_2$] ...	PPh_3,[a] PBu_3,[a] $P(OMe)_3$,[f] $P(OPh)_3$,[f] P(*p*-X·C_6H_4·O)$_3$ (X = F, Cl and NO_2),[c] $P(CF_3)_3$,[d,g] CN^-,†[h] *o*-$C_6H_4(AsMe_2)_2$,[i] dipyridyl,[j] *o*-phenanthroline [k]
Trisubstituted [$Ni(CO)L_3$] ...	$P(OEt)_3$,[c] $P(OPh)_3$,[c] P(*p*-X·C_6H_4·O)$_3$ (X = OMe, F and Cl),[c] MeNC [l]
Tetrasubstituted [NiL_4]	$PMeCl_2$,[m] $PPhCl_2$,[c] PF_3,†[e] PCl_3,[n] PBr_3,†[e] PhNC,[l,o] *p*-EtO·C_6H_4·NC,[o] CN^-,†[p] *o*-$C_6H_4(AsMe_2)_2$,[q] $P(NCO)_3$,[r] $P(NCS)_3$ [r]

* L_2 may be one, and L_4 two bidentate ligands. † Not obtained by direct substitution.

[a] Reppe and Schweckendiek, *Annalen*, 1948, **560**, 104; Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, 1949, p. 260. [b] Yamamoto and Kunizaki, Jap. P. 5087/1954. [c] Malatesta and Sacco, *Ann. Chim.*, 1954, **44**, 134. [d] Eméleus and Smith, *J.*, 1958, 527. [e] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5502. [f] Reed, *J.*, 1954, 1931. [g] Burg and Mahler, *J. Amer. Chem. Soc.*, 1958, **80**, 2334. [h] Nast and Roos, *Z. anorg. Chem.*, 1953, **272**, 242. [i] Nyholm, *J.*, 1952, 2906. [j] Nyholm and Short, *J.*, 1953, 2670. [k] Hieber, Mühlbauer, and Ehmann, *Ber.*, 1932, **65**, 1090. [l] Hieber and Böckly, *Z. anorg. Chem.*, 1950, **262**, 344. [m] Quin, *J. Amer. Chem. Soc.*, 1957, **79**, 3681. [n] Wilkinson and Irvine, *Science*, 1951, **113**, 742. [o] Klages and Mönkemeyer, *Chem. Ber.*, 1950, **83**, 501. [p] Easres and Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1189. [q] Nyholm and Rao, personal communication. [r] Wilkinson, *Z. Naturforsch.*, 1954, **9**b, 446.

In addition to the simple substitution products listed in Table 1, inseparable mixtures of substitution products $Ni(CO)_n(PF_3)_{4-n}$ [1] and $K_{4-n}Ni(CN)_{4-n}(CO)_n$ (n = 2 or 3) [2] are obtained by the reaction of trifluorophosphine and potassium cyanide respectively with nickel carbonyl; also certain perfluoromethylpolyphosphines [3] $(CF_3)_2P{\cdot}P(CF_3)_2$ and $(CF_3)_4P_4$ have afforded polynuclear substitution products of nickel carbonyl, and pyridine an unstable substance $Ni_2(CO)_3py_2$.[4] Our present study has afforded further examples of partial substitution, complete substitution, a binuclear complex, and ligands capable of direct addition to metallic nickel.

Reactions of Nickel Carbonyl with Diphosphines.—The diphosphines $C_2H_4(PR_2)_2$ (R = Et and Ph) and *o*-$C_6H_4(PEt_2)_2$ have been prepared in sufficient quantity for a

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[1] Chatt and Williams, *J.*, 1951, 3061.

[2] Burg and Dayton, *J. Amer. Chem. Soc.*, 1949, **71**, 3233.

[3] Burg and Mahler, *J. Amer. Chem. Soc.*, 1958, **80**, 2334.

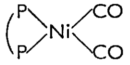
[4] Hieber, *Angew. Chem.*, 1952, **64**, 465.

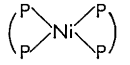
complete study of their substitution reactions, but o-$C_6H_4(PR_2)_2$ (R = Me and Ph) have been obtained in such small yields that only their simplest derivatives could be studied. These five diphosphines react very readily with nickel carbonyl in an organic solvent at room temperature to give complexes of type (I). They are crystalline solids, ranging in colour from white to pale yellow, and have fair thermal stability. They are non-electrolytes in nitrobenzene solution and stable in dry air but slowly decompose in air.

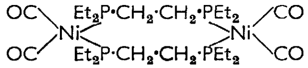
The aromatic diphosphines displace carbon monoxide from the appropriate compounds of type (I) at 150—200° in an atmosphere of nitrogen, to form compounds of type (II). $C_2H_4(PPh_2)_2$ causes rather less ready displacement than o-$C_6H_4(PEt_2)_2$ or o-$C_6H_4(PPh_2)_2$. The products (II) are red to orange crystalline complexes, readily attacked by air, but having good thermal stability. Neither o-$C_6H_4(AsMe_2)_2$ nor o-$C_6H_4(AsPh_2)_2$ displaces carbon monoxide under the above conditions, but recently Nyholm and Rao, by repeated application of an excess of the diarsine *in vacuo* at an elevated temperature, have been able to prepare $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ from $[Ni{\cdot}(CO)_2o\text{-}C_6H_4(AsMe_2)_2]$.[5]

The aliphatic diphosphine $C_2H_4(PEt_2)_2$, under the same conditions as the aromatic diphosphines, caused substantial replacement of carbon monoxide from $[Ni(CO)_2C_2H_4(PEt_2)_2]$, but gave no identifiable product. The only solid product was colourless and still retained some carbon monoxide, as shown by bands at 1883 and 1910 cm.$^{-1}$ in its infrared spectrum. Similar attempts to replace carbon monoxide from $[Ni(CO)_2(PPh_3)_2]$ by reaction with triphenylphosphine were unsuccessful.

A dimeric complex, tetracarbonyl-μμ′-di-1,2-bisdiethylphosphinoethanedinickel (III), is also obtained as a by-product in the preparation of the corresponding monomer of type (I).


(I)


(II)



(III)

($\left(\begin{smallmatrix}P\\P\end{smallmatrix}\right.$ = a diphosphine of the type $R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ or o-$C_6H_4(PR_2)_2$.

This was assigned the structure (III) because its infrared spectrum indicates the presence only of terminal carbonyl groups, and its electric dipole moment is very small. In boiling solvent it rearranges to the corresponding complex of type (I).

These substitution products, together with similar compounds, whose physical constants we have measured, are listed in Table 2.

Reaction of Nickel with the Diphosphines.—The aromatic diphosphines o-$C_6H_4(PEt_2)_2$ and $C_2H_4(PPh_2)_2$ slowly dissolve Raney nickel at 160° under nitrogen to give products of type (II), but neither the purely aliphatic diphosphine, $C_2H_4(PEt_2)_2$, nor the diarsines, o-$C_6H_4(AsR_2)_2$ (R = Me and Ph), react in this manner.

Reactions of Halogens with $[Ni(CO)_2o\text{-}C_6H_4(PEt_2)_2]$.—Nyholm[6] reported that the reactions of halogens (X_2) with $[Ni(CO)_2o\text{-}C_6H_4(AsMe_2)_2]$ gave unstable dihalides $[NiX_2o\text{-}C_6H_4(AsMe_2)_2]$. Only the di-iodide was sufficiently stable to be isolated and purified. Similarly the above diphosphine gave dihalides $[NiX_2o\text{-}C_6H_4(PEt_2)_2]$ but these have extraordinary stability and high melting points (dichloride, m. p. 338—341°). Their thermal stability decreases in the order Cl > Br > I, the reverse of the order observed in the diarsine series. These dihalides are presumably planar, being diamagnetic and non-conductors in nitrobenzene solution. Their colours range from brown (dichloride) to dark red (iodide).

The dibromide $[NiBr_2o\text{-}C_6H_4(PEt_2)_2]$, m. p. 332—335°, undergoes a remarkable change of phase at about 215°. Each bronze-coloured crystal becomes dark red as a sharp boundary between the two colours moves rapidly across it. The crystals slowly regain their original colour on cooling. The dichloride and di-iodide also undergo reversible darkening of colour on heating, but slowly and with no sharp boundary between the light and the dark parts of each individual crystal.

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[5] R. S. Nyholm and R. Rao, personal communication.

[6] Nyholm, *J.*, 1952, 2906.

TABLE 2. *Some physical properties of nickel carbonyl and its substitution products.*

Compound	M. p.	Colour	CO frequencies [b] (cm.$^{-1}$)	Dipole moment [f]	Ni–ligand group moments [g]	(P, As)–Ni bond moment
$[Ni(CO)_4]$	—	White	2050, 2043 [c]			
$[Ni(CO)_3AsPh_3]$	—	,,	(2072, 1995, 2041) [d]	3·59	3·09	3·1
$[Ni(CO)_3PPh_3]$	—	,,	2063, 1987	3·84	3·34	3·35
$[Ni(CO)_2o\text{-}C_6H_4(AsPh_2)_2]$ [a]	182—190°	,,	2002, 1941	5·14	4·56	3·2
$[Ni(CO)_2Ph_2As(CH_2)_2AsPh_2]$ [a]	140—144	Cream	2002, 1939	5·07	—	—
$[Ni(CO)_2o\text{-}C_6H_4(PPh_2)_2]$ [a]	225—228 *	Pale yellow	1999, 1939	5·39	4·81	3·4
$[Ni(CO)_2Ph_2P{\cdot}(CH_2)_2{\cdot}PPh_2]$ [a]	138·5—140	White	1997, 1936	4·81	—	—
$[Ni(CO)_2o\text{-}C_6H_4(AsMe_2)_2]$	—	,,	1996, 1931	5·13	4·55	3·2
$[Ni(CO)_2o\text{-}C_6H_4(PMe_2)_2]$ [a]	121—125	,,	1996, 1931	5·40	4·82	3·4
$[Ni(CO)_2(AsPh_3)_2]$	—	Cream	1995, 1941, 2072	3·34	2·76	2·4 [h]
$[Ni(CO)_2(PPh_3)_2]$	—	,,	1994, 1933	3·82	3·24	2·8 [h]
$[Ni(CO)_2o\text{-}C_6H_4(PEt_2)_2]$ [a]	65	White	1986, 1925	5·48	4·90	3·5
$[Ni(CO)_2C_2H_4(PEt_2)_2]$ [a]	12—13·5	,,	1984, 1920			
$[Ni_2(CO)_4\{C_2H_4(PEt_2)_2\}_2]$ [a]	116—117	,,	1978, 1915	1·6		
$[Ni(CO)_2dipyl]$	—	Red	1950, 1861 [e]			
$[Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ [a]	241—243	,,	—			
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}_2]$ [a]	dec. <350	,,	—			
$[Ni\{C_2H_4(PPh_2)_2\}_2]$ [a]	253·5—256·5 *	Orange	—			

[a] New compounds. [b] In ethylene dichloride at 20°. [c] In the vapour phase (Crawford and Cross, *J. Chem. Phys.*, 1938, **6**, 525). [d] Disproportionation probable. [e] In the solid phase (Nyholm and Short, *J.*, 1953, 2670). [f] In Debye units. [g] This is the molecular moment less the resultant of the Ni–C–O moments. [h] These low values are explained in the text. * With decomp.

Reaction of Bromine with Compounds of Type (II).—$[Ni\{o\text{-}C_6H_4(PEt_2)_2\}_2]$ is oxidised by an equimolecular proportion of bromine in cold benzene to give a small quantity of $[NiBr_2o\text{-}C_6H_4(PEt_2)_2]$ and a dark red substance of the formula $[NiBr_2\{o\text{-}C_6H_4(PEt_2)_2\}_2]$. The latter product can also be prepared by the direct reaction of the diphosphine with aqueous-alcoholic nickel chloride, the product being treated with potassium bromide. In nitrobenzene it conducts as a uni-univalent electrolyte, and may dissolve as $[NiBr\{o\text{-}C_6H_4(PEt_2)_2\}_2]Br$. In the solid state it is more likely to have an elongated octahedral co-ordination with abnormally long Ni–Br bonds and to be similar in configuration to the corresponding compounds of $o\text{-}C_6H_4(AsMe_2)_2$ with nickel(II), palladium(II), and platinum(II).[7] It is unusual in crystallising from water as a yellow octahydrate; both the anhydrous and the hydrated form are diamagnetic.

Possible Causes of the Effectiveness of Ditertiary Phosphines in replacing Carbon Monoxide.—The ditertiary phosphines, especially those containing aromatic groups, are much more effective in replacing carbon monoxide from nickel carbonyl than are the corresponding diarsines, or any other bidentate ligands so far investigated. It is commonly considered that stable complexes of metals in their zerovalent states are formed only by ligands capable of forming strong double bonds with the metal.[8] For poor electron donors such as carbon monoxide the formation of a co-ordinate bond of considerable double-bond character is considered to be essential for the formation of stable complexes. There is now a fair body of evidence that double bonding to suitable metals is slightly greater with phosphines as ligands than with arsines, sulphides, and other similar donors.[9] We have therefore sought in this the cause of the relative ease of formation and the stability of our diphosphine derivatives of nickel carbonyl, but without success.

If the Ni–P and Ni–As bond orders differed markedly in the substituted nickel carbonyls we should expect to detect this and get some rough estimate of its magnitude by measuring the differences between (*a*) the C–O stretching frequencies (ν_{CO}), and (*b*) the dipole moments of analogous phosphine- and arsine-substituted nickel carbonyls.

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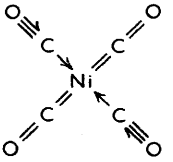
[7] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

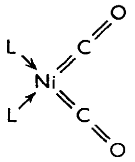
[8] See Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

[9] (*a*) Chatt and Wilkins, *J.*, 1952, 4300; (*b*) Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; (*c*) 1958, 3203; (*d*) Chatt, Gamlen, and Orgel, *J.*, 1959, 1047.

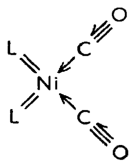
Infrared Spectra.—In a tetrahedrally co-ordinated metal such as in nickel carbonyl the *d*-orbitals are arranged so that only two strong and two weak π-type bonds can be formed to the ligands.[10] Thus the Ni–C bond will be intermediate between the single-bonded form, $\mathrm{Ni{-}C}\overset{\leftarrow}{\equiv}\mathrm{O}$, and double-bonded form, Ni=C=O; and if we ignore the possibility



(IV)



(Va)



(Vb)

of weak π-bonding the nickel carbonyl molecule can be represented as a resonance hybrid of canonical forms of the type (IV). When the carbon monoxide is replaced by less strongly double-bonding ligands L, as in (V), the canonical form (Va) with single metal-to-ligand bonds, and double carbon-to-ligand bonds, should make the greater contribution to the structure. So, on passing from form (IV) to (V) the bond order of the C–O bond and ν_{CO} would be expected to decrease. A decrease of ν_{CO} has already been observed in previous studies of this kind and explained in this manner.[11,12]

However, the substituting ligands under comparison have often contained ligand atoms of widely differing electronegativities, *e.g.*, nitrogen and arsenic, or have been attached to groups of widely differing electronegativities. Inductive effects are also transmitted across metal atoms,[9b,9c,13] and the effects observed might, therefore, be caused by differences in electronegativity, *i.e.*, inductive effects, as well as by differences in π-bonding, *i.e.*, mesomeric effects. However, in the phosphine and arsine derivatives the ligand atoms have almost identical electronegativities and any marked difference between double-bonding capacities of the ligand atoms should appear as a difference in the C–O stretching frequencies (ν_{CO}) of their analogous substituted carbonyls.

In Table 2 the compounds are arranged in order of decreasing ν_{CO} and so, on the basis of the above arguments, in order of decreasing tendency for the substituting chelate ligands to form double bonds to the metal. It will be noted that the phosphorus and the arsenic derivatives do not fall into separate groups but that an arsenic derivative usually occurs slightly higher in the Table than its phosphorus analogue. Indeed, ν_{CO} is much more affected by the organic parts of the chelate ligands than by whether the ligand atom is phosphorus or arsenic.

We should expect that the more electronegative the organic parts of the ligands the greater will be the value of ν_{CO}, because the more electronegative ligands would induce greater mesomeric and inductive withdrawal of electrons from the nickel atoms. This would slightly favour the triple bonded form: $\longleftarrow\overset{\curvearrowleft}{\mathrm{Ni}{=}}\overset{\curvearrowleft}{\mathrm{C}{=}}\mathrm{O}\rightarrow\longleftarrow\mathrm{Ni}\leftarrow\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O}$. Thus of similar chelating ligands the more aromatic derivatives should appear at the top of the Table 2 followed by methyl and ethyl derivatives. This is found in both the phosphorus and the arsenic series of substitution products. The apparently greater double-bonding properties of the aromatic than of the aliphatic diphosphines may account for their more ready displacement of carbon monoxide from nickel carbonyl and their greater reactivity towards metallic nickel, especially since they are weaker bases and should have

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[10] Kimball, *J. Chem. Phys.*, 1940, **8**, 194.

[11] Nyholm and Short, *J.*, 1953, 2670.

[12] L. S. Meriwether and M. L. Fiene, personal communication.

[13] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

poorer σ-bonding capacities. Nevertheless, no explanation of the markedly greater activity of the chelating diphosphines than of their diarsine analogues in replacing carbon monoxide from nickel carbonyl can be found in their relative double-bonding capacities as indicated by the values of ν_{CO} given in Table 2.

Dipole Moments.—Double bonding between a ligand atom and a metal such as nickel(0) can most readily be visualised as the result of donation of a lone pair of electrons from the ligand atom to the metal, together with a back-donation of electrons from *d*-orbitals of the metal into suitable orbitals on the ligand atom. Thus double bonding involves the neutralisation or partial neutralisation of the large dipole moment which is associated with single co-ordinate bonds.

The dipole moments of eleven substitution products of nickel carbonyl are listed in Table 2. From these we have estimated the P–Ni and As–Ni bond moments, and very tentatively, the corresponding bond orders.

To calculate the P–Ni and As–Ni bond moments we must know (*a*) the exact stereochemistry of the complex, (*b*) the Ni–CO group moment, and (*c*) the C_{ar}–P and C_{ar}–As bond moments.

We assume the substitution products of nickel carbonyl to have a tetrahedral configuration, with distortions imposed by the stereochemistry or bulk of the substituents.

In the compounds containing the *o*-phenylene chelate ligands, we expect the ligand to be negligibly distorted, while the ligand–metal–ligand bond angle would adjust itself to fit the relevant covalent radii. This has been shown to be so in certain tetrahedral gold(I) complexes,[14] and assuming it to be true in the nickel(0) complexes we estimate the P–Ni–P and As–Ni–As angles to be almost exactly 90°. Since the Ni–CO bond moment is small the value of the C–Ni–C bond angle is not critical for the calculation of Ni–P bond moments, and we have assumed that the CO groups remain tetrahedrally disposed with a C–Ni–C bond angle of 109°.

Molecular models of the complexes derived from $C_2H_4\{(P,As)R_2\}_2$ show that no reliable value can be assigned to the bond angles, owing to the absence of rigidity in the chelating ligand. These complexes have therefore been disregarded in the present calculations.

The dipole moments of metal–CO groups appear to be small, because the moment of *cis*-$[PtCl_2(CO)_2]$ (4·65 D) is little greater than that to be expected from the Pt–Cl bonds alone,[1] and Fischer estimates the combined Cr–C–O moments in $[Cr(CO)_3C_6H_6]$ to be 0·8 D.[15] We are therefore confident that the Ni–C–O group moment is close to 0·5 D.

With these assumptions, the moments of the nickel–organic ligand groups have been calculated (see Table 2).

To find the P–Ni and As–Ni bond moments a small correction should be made for the out-of-balance C–P and C–As moments in the Ni–ligand groups. Where group moments have been listed in Table 2 all the C–P and C–As moments are between aromatic groups and 4-co-ordinated phosphorus or arsenic atoms. In the absence of mesomeric effects and charge on these atoms the C_{ar}–P and C_{ar}–As moments would be of the order 0·5 D with the carbon atom negative (based on Pauling electronegativities).[16] However, the phosphorus and the arsenic atom carry appreciable positive charge due to the dipolar P–Ni and As–Ni bonds, and so electrons will be drawn both mesomerically (into *d*-orbitals) and inductively from the aromatic system. This effect will, however, be quite small, since Jaffe[17] was unable to detect any interaction between phenyl groups conjugated through a $\geqslant$PO group. Assuming that it is sufficient to reduce the small C_{ar}–P and C_{ar}–As moments expected on the basis of electronegativity to about zero, we have calculated the P–Ni and As–Ni bond moments given in Table 2. They agree so well that the assumptions made in the calculation appear to be justified. The compounds $[Ni(CO)_2(PPh_3)_2]$ and

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[14] Cochrane, Hart, and Mann, *J.*, 1957, 2816.

[15] Fischer, Internat. Conference on Co-ordination Chemistry, London, *Chem. Soc. Special Publ. No.* 13, 1959.

[16] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 60.

[17] Jaffe, *J. Chem. Phys.*, 1954, **22**, 1430.

$[Ni(CO)_2(AsPh_3)_2]$ give anomalously low results, but this is probably caused by distortion from the regular tetrahedral angle by the bulky phosphine and arsine ligands. The P–Ni and As–Ni bond moments therefore appear to be about 3·4 and 3·2 D respectively, but the difference between them is not significant in view of the assumptions made in their calculation. Again there is no evidence that bonds of phosphorus to nickel(0) are of markedly greater double-bond character than of arsenic.

It is not possible to get more than a very tentative value of bond order for the P–Ni or As–Ni bonds from this work, but since previous inference has been (*a*) from infrared data,[11] that the As–Ni bond order is 2, (*b*) from force constant data [18] that there is no evidence of P–Ni double bonding in $Ni(PF_3)_4$, and (*c*) from kinetic data [12] that the P–Ni bond has little double-bond character, it seems worth making some estimate, however crude, from the dipole moments.

If double bonding were complete, the P–Ni and As–Ni bonds would be almost non-dipolar, with moments corresponding to the difference in electronegativities of the atoms, say about 0·5 D with nickel positive. Obviously double bonding is far from complete.

If there were no double bonding the P–Ni and As–Ni bonds would presumably be comparable with the co-ordinate bonds $\colon N \longrightarrow B\colon$, $\colon P \longrightarrow B\colon$, $\colon O \longrightarrow B\colon$, and $\colon S \longrightarrow B\colon$ where double bonding is not possible, and the nickel atom would be negative. Here the bond moments correspond to the transfer of 0·41—0·58 of an electron from a donor to an acceptor atom.[19] If there is an electron transfer of 0·5 and bond lengths are about 2·25 Å for P–Ni and 2·33 Å for As–Ni, the moments of the P–Ni and As–Ni bonds would be 5·4 and 5·6 D respectively. This is 2·1—2·3 D greater than the observed 3·3 D, and if we attribute this difference to partial neutralisation of the moment due to the σ-co-ordinate bond (estimated at 5·5 D) by back-donation equal to a moment of 2·2 D in the π-bond, we might say that the P–Ni and As–Ni bond orders are about $\frac{5{\cdot}5 + 2{\cdot}2}{5{\cdot}5} = 1{\cdot}4$.

This, we think, represents a lower limit, because the back-donation of electrons from the nickel atom in the π-bond will cause further release of electrons in the σ-bond so that in this case 5·5 D is likely to be a low estimate for the charge transfer in the σ-bond. Some greater quantity $(5{\cdot}5 + y)$ is needed and the bond order becomes $[(5{\cdot}5 + y) + (2{\cdot}2 + y)]/(5{\cdot}5 + y)$. It is unlikely that the electron transfer in the σ-bond ever exceeds the theoretical 1·0 electron corresponding to $y = 5{\cdot}5$, so substituting $y = 5{\cdot}5$ we obtain an upper limit of 1·7 for the bond order.

Thus on the basis of our dipole-moment measurements we estimate that the P–Ni and As–Ni bond orders in the substituted carbonyls are about equal and lie within the limits 1·4—1·7. In a preliminary communication [20] of this work, based on many fewer measurements, we estimated a much lower bond order in agreement with Meriwether and Fiene,[12] but the dipole moments undoubtedly indicate the greater double bonding quoted above.

We still have to explain why the organic phosphines replace carbon monoxide from nickel carbonyl more readily than do their arsenic analogues. We have shown that it is not due to a greater double-bonding capacity of phosphorus and so it must be due to the much greater general overall affinity of phosphorus for metals with filled *d*-orbitals, *i.e.*, to stronger σ- and π-bonding. The order of the relative affinities of phosphines and arsines for silver(I) [which is isoelectronic with nickel(0) in the valency shell] is shown by the first stability constants of $1{\cdot}4 \times 10^8$ and $2{\cdot}3 \times 10^5$ respectively for the reaction of silver ion with a monosulphonated triphenylphosphine and trisulphonated triphenylarsine in aqueous solution.[21] In the case of nickel(0) where the central atom is uncharged the difference between the affinities may well be very much greater.[22]

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[18] Woodward and Hall, *Nature*, 1958, **181**, 831.

[19] Phillips, Hunter, and Sutton, *J.*, 1945, 146.

[20] Chatt and Hart, *Chem. and Ind.*, 1958, 1474.

[21] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 276.

[22] Cf. Cd^{2+}: Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 1403.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney, and Miss S. Lathwell of these laboratories. M. p.s marked * were determined on the Kofler stage.

Preparation of Ditertiary Phosphines and Arsines.—These were all prepared in a nitrogen atmosphere.

1,2-*Bisdiethylphosphinoethane*, $Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2$, was prepared as described by Wymore,[23] or by hydrogenation of $Et_2P{\cdot}C{\equiv}C{\cdot}PEt_2$ as follows. Acetylene was passed at about 15 l./hr. for 3 hr. into the vigorously stirred Grignard reagent formed from ethyl bromide (175 g.) and magnesium (39·0 g., 1 mol.) in tetrahydrofuran (160 c.c.) at *ca.* 10°. Diethylchlorophosphine (200 g.) in tetrahydrofuran (70 c.c.) was added dropwise to the stirred solution, also at 10°, and the mixture was treated with saturated aqueous ammonium chloride (660 c.c.) and water (800 c.c.). The organic layer was separated and the aqueous layer washed with benzene (3 × 150 c.c.). The combined organic fractions were distilled, giving *bisdiethylphosphinoacetylene*, b. p. 54°/0·07 mm., n_D^{20} 1·5332 (100 g.) (Found: C, 59·0; H, 9·9. $C_{10}H_{20}P_2$ requires C, 59·4; H, 10·0%).

The acetylene diphosphine (19·3 g.) in ethanol (50 c.c.) was shaken with Raney nickel (2 g.) and hydrogen for 19½ hr., 2730 c.c. being absorbed. More Raney nickel (2 g.) and ethanol (20 c.c.) were added; shaking continued for a further 6½ hr., a further 1625 c.c. being absorbed. The product was filtered from nickel and distilled, giving 1,2-bisdiethylphosphinoethane, b. p. 56—57°/0·001 mm. after refractionation, n_D^{20} 1·5100 (10·1 g.) (Found: C, 58·2; H, 11·5. Calc. for $C_{10}H_{24}P_2$: C, 58·2; H, 11·7%).

1,2-*Bisdiphenylphosphinoethane.* We are indebted to Dr. H. R. Watson for our first samples of this diphosphine. He obtained it as follows: Diphenylphosphine (46·5 g., 2 mols.) in ether (30 c.c.) was added dropwise with stirring to a solution of sodium (5·75 g., 2 atom-equiv.) in liquid ammonia (*ca.* 250 c.c.), and after a further 30 min. ethylene dichloride (12·35 g., 1 mol.) in ether (25 c.c.) was added dropwise to the stirred mixture. After 30 min. more, enough ethylene dichloride (*ca.* 0·5 c.c.) was added to remove the remaining orange colour. The ammonia was removed and the residue extracted with water (150 c.c.) and benzene (700 c.c.). The organic layer was separated, washed with water (3 × 100 c.c.), and taken to dryness on a water-bath. Recrystallisation of the crystalline residue from benzene gave 40·0 g. (80·5%) of the *diphosphine*, m. p. 140—142°; raised to 143·5—144° by two further recrystallisations (Found: C, 78·3; H, 6·3%; *M*, 393. $C_{26}H_{24}P_2$ requires C, 78·4; H, 6·1%; *M*, 398). The *dimethiodide*, prepared in boiling nitromethane and recrystallised from methanol, had m. p. 306—307° (Found: C, 49·0; H, 4·6. $C_{28}H_{30}I_2P_2$ requires C, 49·3; H, 4·4%).

This diphosphine was also prepared from triphenylphosphine as follows. Lithium foil (10·6 g., 2 atom-equivs.) was dissolved by stirring (1 hr.) in a solution of triphenylphosphine (200 g.) in tetrahydrofuran (1 l.) (temp. rise to 48°). The mixture was then cooled in ice-water, and ethylene dichloride (60 c.c., 1 mol.) in tetrahydrofuran (100 c.c.) was added during 1 hr. The solution was boiled for 20 min. and cooled; methanol (1·5 l.) was added, and then slowly with stirring sufficient water to precipitate the crystalline diphosphine, which was recrystallised from light petroleum (yield 70%).

Preparation of the o-*phenylenediphosphines*, o-$C_6H_4(PR_2)_2$, *where* R = Me, Et, *and* Ph. These are much more difficult to prepare than their ethylene analogues and will form the subject of a later communication.

(i) *o*-Phenylenebisdimethylarsine was prepared as by Chatt and Mann.[24]

(ii) *o*-Phenylenebisdiphenylarsine (preparation by Mr. P. F. TODD). *o*-Phenylenebisdichloroarsine [24] (10 g., 1 mol.) in ether (100 c.c.) was added dropwise at −5° to the stirred Grignard reagent formed from bromobenzene (25·6 g., 6 mols.) and magnesium (3·97 g., 6 atom-equiv.) in ether (175 c.c.). The mixture was stirred for 1½ hr. at 20°, cooled, and treated with aqueous ammonium chloride (33 g. in 400 c.c.). The ether was removed by warming the mixture, and the solid *diarsine* filtered off from the remaining aqueous layer. Crystallised from ethyl carbonate, it had m. p. 199—201° (8·1 g.) (Found: C, 67·6; H, 4·7. $C_{30}H_{24}As_2$ requires C, 67·4; H, 4·5%).

Preparation and Purification of the Substitution Products of Nickel Carbonyl.—These were

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[23] Wymore, Ph.D. Thesis, University of Illinois, 1956.

[24] Chatt and Mann, *J.*, 1939, 610.

carried out entirely under nitrogen. Careful recrystallisation was often attended by considerable loss. All the new complexes are non-conductors in nitrobenzene solution except where stated. Molecular weights were determined ebullioscopically in benzene solution except where otherwise stated.

*Dicarbonyl-*o*-phenylenebisdiethylphosphinenickel,* $[Ni(CO)_2o\text{-}C_6H_4(PEt_2)_2]$. Nickel carbonyl (0·285 c.c.) in methanol (5 c.c.) was treated with the diphosphine (0·559 g., 1 mol.) at 15°. Effervescence had almost ceased after 20 min., and after 35 min. the mixture was cooled in carbon dioxide and acetone. The colourless product (0·53 g.) was filtered off and washed with chilled alcohol; it sublimed at 80°/0·1 mm. in good yield and the *complex* then had m. p.* 65° (Found: C, 52·3; H, 6·7%; *M*, in 0·77% solution, 374; in 1·40% solution, 365. $C_{16}H_{24}O_2P_2Ni$ requires C, 52·1; H, 6·6%; *M*, 369). The powdered compound is diamagnetic with $\chi_g = -0{\cdot}47 \times 10^{-6}$ at 23°.

*Dicarbonyl-*o*-phenylenebisdimethylphosphinenickel,* $[Ni(CO)_2o\text{-}C_6H_4(PMe_2)_2]$, was prepared and purified in the same way as the preceding complex; it had m. p.* 121—125° (Found: C, 45·7; H, 5·1. $C_{12}H_{16}O_2P_2Ni$ requires C, 46·05; H, 5·2%).

*Dicarbonyl-*1,2-*bisdiphenylphosphinoethanenickel,* $[Ni(CO)_2C_2H_4(PPh_2)_2]$. Nickel carbonyl (0·33 c.c.) was added to a solution of the diphosphine (1 g., 1 mol.) in benzene (10 c.c.). After 3 min. the solution was boiled for 5 min., and the solvent was removed at 12 mm. The *product* (1·29 g.), m. p.* 135—138°, was washed with methanol and thrice recrystallised from ethanol, then having m. p.* 138—140° (0·15 g.) (Found: C, 65·3; H, 4·8%; *M*, in 0·485% solution, 509. $C_{28}H_{24}O_2P_2Ni$ requires C, 65·5; H, 4·7%; *M*, 513).

*Dicarbonyl-*1,2-*bisdiphenylarsinoethanenickel,* $[Ni(CO)_2C_2H_4(AsPh_2)_2]$. Nickel carbonyl (0·67 c.c.) was added to a solution of the diarsine (2·5 g., 1 mol.) in benzene (10 c.c.) and after 17 hr. the solvent was removed at 12 mm., and the product washed with methanol and collected (2·40 g.). The *complex,* thrice recrystallised from dimethylformamide–methanol, had m. p. 140—144° *in vacuo* (Found: C, 56·3; H, 4·1%; *M*, in 0·522% solution, 644; in 1·30% solution, 620; in 1·74% solution, 626. $C_{28}H_{24}O_2As_2Ni$ requires C, 55·95; H, 4·0%; *M*, 601).

*Dicarbonyl-*o*-phenylenebisdiphenylarsinenickel,* $[Ni(CO)_2o\text{-}C_6H_4(AsPh_2)_2]$. Nickel carbonyl (0·65 c.c.) was added to a solution of the diarsine (3·0 g., 1 mol.) in benzene (30 c.c.). After 3 min. the mixture was warmed to the b. p., then cooled, and the product was precipitated with alcohol (70 c.c.). The *complex,* twice recrystallised from ethyl methyl ketone, had m. p. 196—198° *in vacuo* (1·2 g.) (Found: C, 59·4; H, 4·0%; *M*, in 1·07% solution, 675. $C_{32}H_{24}O_2As_2Ni$ requires C, 59·3; H, 3·7%; *M*, 648).

*Dicarbonyl-*o*-phenylenebisdiphenylphosphinenickel,* $[Ni(CO)_2o\text{-}C_6H_4(PPh_2)_2]$, was prepared and purified in the same way as the preceding complex (30% yield); it decomposed at 225—228° *in vacuo* (Found: C, 68·85; H, 4·4. $C_{32}H_{24}O_2P_2Ni$ requires C, 68·5; H, 4·3%).

*Dicarbonyl-*1,2-*bisdiethylphosphinoethanenickel,* $[Ni(CO)_2C_2H_4(PEt_2)_2]$. Nickel carbonyl (1·51 c.c.) was added to a solution of 1,2-bisdiethylphosphinoethane (2·28 g., 1 mol.) in methanol (50 c.c.). After 25 min., the solution was boiled for 30 min., and the solvent, except for about 10 ml., was removed at 12 mm. The solution was cooled in carbon dioxide and alcohol, and the needles formed were filtered off under cold carbon dioxide. The *dicarbonyl* was recrystallised from methanol (8 c.c.) cooled in carbon dioxide and alcohol and washed with methanol at −50°. When dried at 0·05 mm. at 0° for 5 hr., it had m. p. 12—13·5° (1·7 g.) (Found: C, 45·1; H, 7·6%; *M*, in 1·91% solution, 339; in 2·36% solution, 342. $C_{12}H_{24}O_2Ni$ requires C, 44·9; H, 7·5%; *M*, 321).

*Tetracarbonyl-*μμ′*-di-*1,2-*bisdiethylphosphinoethanedinickel,* $[Ni_2(CO)_4\{C_2H_4(PEt_2)_2\}_2]$ is formed in small quantity as a by-product of the above reaction and can be isolated if the experiment is done on a larger scale. The ethane diphosphine (13·6 g.) in methanol (400 c.c.) and nickel carbonyl (8·55 c.c., 1 mol.) were allowed to react as before. The initial product (18·95 g.) was dissolved in warm methanol (60 c.c.); the solution, on cooling to 0°, deposited the *tetracarbonyl compound* (1·87 g.), m. p. 116—117° (from alcohol) (Found: C, 44·6; H, 7·5%; *M*, in 1·09% solution, 602; in 1·55% solution, 687. $C_{24}H_{48}O_4Ni_2$ requires C, 44·9; H, 7·5%; *M*, 642). The elevation of the b. p. in the molecular-weight determination increased with time, until after about 16 minutes' boiling, it was steady and corresponded to the monomer (Found: *M*, 298, 288 for the solutions quoted). The values for the dimer were obtained by extrapolation to zero time.

Action of 1,2-*bisdiethylphosphinoethane on dicarbonyl-*1,2-*bisdiethylphosphinoethanenickel.*

1,2-Bisdiethylphosphinoethane (0·88 g., 1·33 mols.) and the dicarbonyl compound (1·02 g.) were heated at 150° for 1 hr.; by then the initial effervescence had ceased. On cooling, an oil was obtained, but this gave cream-coloured prisms when kept for 16 hr. with methanol (10 ml.). These (0·17 g.) were very easily decomposed by air and, recrystallised from methanol, had m. p. 102·5—104° *in vacuo* (Found: C, 47·2, 47·2; H, 9·15, 9·1; Ni, 13·5%; *M*, in 1·16% solution, 630; in 1·75% solution, 646). The infrared spectrum of a Nujol mull of this compound showed absorption bands at 1883 and 1910 cm.$^{-1}$.

*Di-*o*-phenylenebisdiethylphosphinenickel*, [Ni{o-$C_6H_4(PEt_2)_2$}$_2$]. A mixture of *o*-phenylenebisdiethylphosphine (0·257 g.) and dicarbonyl-*o*-phenylenebisdiethylphosphinenickel (0·373 g., 1 mol.) was heated at 150° for 2 hr. There was effervescence and a red colour developed; at the end of the heating the product was a red crystalline mass. This mass is stable indefinitely; but, once briefly exposed to air, the crystals slowly develop yellow flecks and give low analytical values. The crystalline mass was extracted with 5 c.c. of cold methanol and quickly collected on a filter, giving scarlet crystals (0·37 g.), m. p. 241—243° *in vacuo*.. The *complex* was dried under a high vacuum for 30 min. and analysed at once (Found: C, 58·8; H, 8·6. $C_{28}H_{48}P_4Ni$ requires C, 59·3; H, 8·5%). The complex is stable in solution in benzene or petrol under nitrogen (Found: *M*, in 1·15% solution under nitrogen, 512; in 1·94% solution, 516. $C_{28}H_{48}P_4Ni$ requires *M*, 567). The powdered complex is diamagnetic with $\chi_g = -0{\cdot}64 \times 10^{-6}$ at 24°.

An alternative method of preparation is as follows. A mixture of the diphosphine (0·53 g., 2 mols.) and Raney nickel (0·18 g., 3 atom-equiv.) was stirred and heated at 160° for 8 hr. The product was extracted with benzene (5 ml.), then filtered from nickel. The benzene solution on evaporation in a stream of nitrogen gave the bis(diphosphine)nickel, 0·20 g., identical in infrared spectrum with the authentic material.

*Di-*o*-phenylenebisdiphenylphosphinenickel*, [Ni{o-$C_6H_4(PPh_2)_2$}$_2$]. A mixture of the diphosphine (0·12 g.) and dicarbonyl-*o*-phenylenebisdiphenylphosphinenickel (0·15 g., 1 mol.) was heated in an oil-bath. The mixture, on melting, became dark red and effervesced, but at once resolidified. It was heated at 200° for 10 min. The cooled product was extracted with boiling ethyl methyl ketone (10 ml.) to remove unchanged starting materials, giving 0·12 g. of red crystals. The *complex* was purified by slow precipitation as red crystals from benzene on addition of methanol; rather variable analytical results were, however, obtained (Found: C, 75·95, 74·6, 76·3; H, 5·6, 5·2, 5·3. $C_{60}H_{48}P_4Ni$ requires C, 75·7; H, 5·1%). When heated in an evacuated tube, it reversibly blackens at about 260°, but at about 350° the change ceases to be reversible.

*Di-*1,2*-bisdiphenylphosphinoethanenickel*, [Ni{$C_2H_4(PPh_2)_2$}$_2$]. The diphosphine (0·388 g.) and dicarbonyl-1,2-bisdiphenylphosphinoethanenickel (0·50 g., 1 mol.) were boiled in xylene (10 c.c.) for 8 hr. The colour became deep orange after 10 min. Methanol (20 c.c.) was added to the cooled solution in two portions, and orange crystals (0·51 g.) were collected. These had a small carbonyl band at 1908 cm.$^{-1}$. The substance was taken up in hot benzene (10 c.c.), and methanol (20 c.c.) was added; and the filtered solution deposited overnight 0·22 g. of crystals. These still had a very small carbonyl band. Repurification in the same way gave 0·10 g. of orange needles, m. p. (decomp.) 253—256·5° *in vacuo*. This substance had a negligibly small CO peak in its infrared spectrum, and was the required *complex* (Found: C, 72·4; H, 5·8%; *M*, in 0·804% solution, 843. $C_{52}H_{48}P_4Ni$ requires C, 73·0; H, 5·7%; *M*, 856). The somewhat low carbon value is presumably due to unremoved traces of carbonyl compounds.

A purer product, but in tiny yield, was obtained as follows. The diphosphine (1 g.) and Raney nickel (0·445 g., 1·5 atom-equiv.) were heated at 160° for 32 hr. with stirring. The cooled mass was broken up, taken up in xylene (15 c.c.), and filtered, and light petroleum (b. p. 40—60°) (50 c.c.) was added. After one month a few large orange prisms (*ca.* 0·05 g.) had been formed and were collected and washed with alcohol (Found: C, 72·8; H, 5·7%).

Action of Triphenylphosphine on Dicarbonylbistriphenylphosphinenickel. The phosphine (0·639 g., 2 mols.) was heated with the complex 0·524 g., 1 mol.) at 210° for 15 min. There was no effervescence. The mixture blackened at 225—230° without effervescence.

Action of o*-phenylenebisdiphenylarsine on dicarbonyl-*o*-phenylenebis diphenylarsinenickel.* An equimolecular mixture blackened at about 170° without effervescence.

*Dichloro-*o*-phenylenebisdiethylphosphinenickel*(II), [$NiCl_2$$o$-$C_6H_4(PEt_2)_2$]. A solution of chlorine (0·115 g.) in carbon tetrachloride (4·43 c.c.) was added dropwise with swirling to a solution of dicarbonyl-*o*-phenylenebisdiethylphosphinenickel (0·60 g., 1 mol.) in benzene (5 c.c.)

at 15° There was instantaneous formation of a dark yellow-green precipitate, and the solution became warm. After 30 minutes' shaking, a buff powder (0·63 g.) was collected. This, twice recrystallised from dimethylformamide, gave brown plates (0·32 g.) having m. p.* 338—341° (followed by decomposition) (Found: C, 44·0; H, 6·4. $C_{14}H_{24}Cl_2P_2Ni$ requires C, 43·8; H, 6·3%). The compound was too insoluble for a molecular-weight determination. It was diamagnetic as powder, $\chi_g = -1{\cdot}29 \times 10^{-6}$.

Dibromo-o-*phenylenebisdiethylphosphinenickel*(II), $[NiBr_2o\text{-}C_6H_4(PEt_2)_2]$. A solution of bromine (0·127 g.) in benzene (5·38 c.c.) was added dropwise with swirling to a solution of dicarbonyl-*o*-phenylenebisdiethylphosphinenickel (0·293 g., 1 mol.) in benzene (5 c.c.) at 15°. There was an immediate brown precipitate and slight effervescence. The *product* (0·36 g.) was twice recrystallised from dimethylformamide and then had m. p.* 332—335° (followed by decomposition) (0·22 g.) (Found: C, 35·5; H, 5·15%; *M*, ebullioscopically in 0·56% chloroform solution, 488; in 0·91% solution, 508. $C_{14}H_{24}Br_2P_2Ni$ requires C, 35·6; H, 5·1%; *M*, 473).

Di-iodo-o-*phenylenebisdiethylphosphinenickel*(II), $[NiI_2o\text{-}C_6H_4(PEt_2)_2]$. A solution of iodine (0·68 g.) in benzene (7 c.c.) was slowly added with swirling to a solution of dicarbonyl-*o*-phenylenebisdiethylphosphinenickel (0·90 g., 1 mol.) in benzene (5 c.c.) at 15°. The reddish-black crystalline precipitate (1·22 g.), recrystallised from 1 : 1 dimethylformamide–alcohol, had m. p.* 278—280° (decomp. 300—340°) (Found: C, 29·9; H, 4·4%; *M*, ebullioscopically in 0·63% chloroform solution, 626; in 1·03% solution, 594. $C_{14}H_{24}I_2P_2Ni$ requires C, 29·7; H, 4·3%; *M*, 567).

Di-o-*phenylenebisdiethylphosphinenickel*(II) *dibromide*. *o*-Phenylenebisdiethylphosphine (0·623 g., 2 mols.) was added to a solution of nickel chloride hexahydrate (0·292 g.) in water (4 c.c.) and ethanol (2 c.c.). The mixture was shaken, briefly boiled, and then cooled and allowed to evaporate to dryness in an evacuated desiccator. The residue, an orange-brown sticky solid, was dissolved in water (10 ml.), and to the filtered solution was slowly added an excess of aqueous sodium bromide solution with swirling. The yellow crystalline product (0·71 g.) was twice recrystallised from water. On the Kofler stage, it lost water and became dark red at *ca.* 70—80°, then darkened, decrepitated somewhat, half-melted, and resolidified from *ca.* 165—185°; it finally melted at 342—344°, having presumably lost diphosphine and become dibromodiphosphinenickel. The hydrate was air-dried and shown to be the *dibromide octahydrate* (Found: C, 38·5; H, 7·4. $C_{28}H_{48}Br_2P_4Ni,8H_2O$ requires C, 38·6; H, 7·4%). It loses water and becomes dark-red in a few minutes in a vacuum at room temperature. The anhydrous *dibromide* (which again became hydrated in air) was obtained by drying the octahydrate for 6 hr. at 60°/0·1 mm. (Found: C, 45·9; H, 6·8. $C_{28}H_{48}Br_2P_4Ni$ requires C, 46·25; H, 6·7%). The powdered dibromide (χ_g $-1{\cdot}36 \times 10^{-6}$) and dibromide octahydrate (χ_g $-1{\cdot}16 \times 10^{-6}$) were both diamagnetic. A $6{\cdot}32 \times 10^{-3}$M-solution of the dibromide in nitrobenzene had a molar conductivity of 22·75 mhos at 20°.

Action of bromine on di-o-*phenylenebisdiethylphosphinenickel*. A solution of bromine (0·016 g.) in benzene (1 c.c.) was added dropwise with swirling to a solution of di-*o*-phenylenebisdiethylphosphinenickel (0·057 g., 1 mol.) in benzene (5 c.c.) at 10°. The orange-red precipitate which was at once formed became yellow on addition of one drop of water and shaking, and was filtered off (0·069 g.). Recrystallisation from water gave di-*o*-phenylenebisdiethylphosphinenickel dibromide octahydrate (0·034 g.), identified by its characteristic behaviour on the Kofler stage. There was a small water-insoluble residue (0·0037 g.) of dibromo-*o*-phenylenebisdiethylphosphinenickel, identified by mixed m. p.

Action of chlorine on dicarbonyl-1,2-*bisdiethylphosphinoethanenickel*. The dicarbonyl compound (0·32 g.) was dissolved in benzene (10 c.c.), and the partly frozen solution was treated cautiously with chlorine diluted with much carbon dioxide until no more brown precipitate was formed. This (0·16 g.), filtered from the dark-brown mother-liquor, had m. p. 238—246°, raised to 246—254° by recrystallisation from dimethylformamide and sublimation at 225°/0·3 mm. (Found: C, 35·7; H, 7·3. Calc. for $C_{10}H_{24}Cl_2Ni$: C, 35·8; H, 7·2%). Wymore[23] gives 245° as the m. p. of this compound.

Dipole Moments.—The detailed results are shown in Table 3. These were obtained in benzene solution, the method and notation being as previously described.[25]

Values marked † were not constant and were determined by extrapolation to zero time. Estimated values are shown thus *. Errors are about ±0·1 D for moments greater than about 3·5 D.

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[25] Chatt and Shaw, *J.*, 1959, 705.

TABLE 3. *Dipole moments of nickel carbonyl substitution products.*

	10^3w	$\Delta\varepsilon/w$	$10^2\Delta n/w$	$-\Delta v/w$	$_{T}P$	$_{E}P$	$_{O}P$	μ
$Ni(CO)_3AsPh_3$	4·234	3·632 †						
	5·820	3·572 †						
	31·54		9·68					
	36·13		9·77					
				0·4 *	404	122	264	3·59
$Ni(CO)_3PPh_3$	4·745	4·494						
	4·807	4·465						
	26·17		10·9					
	46·46		10·7					
				0·4 *	432	113	302	3·84
$Ni(CO)_2Ph_2As{\cdot}CH_2{\cdot}CH_2{\cdot}AsPh_2$	3·512	5·210 †						
	4·845	5·248 †						
	39·19		12·6					
	40·39		12·8					
				0·4 *	726	174	525	5·07
$Ni(CO)_2Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$	2·150	5·541						
	2·590	5·561						
	35·15		14·7					
	35·77		15·0					
				0·4 *	651	155	472	4·81
$Ni(CO)_2$*o*-$C_6H_4(AsPh_2)_2$	2·583	5·055						
	2·834	5·071						
	25·58		14·4					
	34·71		14·4					
				0·4 *	763	194	540	5·14
$Ni(CO)_2$*o*-$C_6H_4(PPh_2)_2$	0·8602	6·276						
	0·9148	6·239						
	31·88		13·7					
	37·11		14·7					
				0·4 *	786	167	594	5·39
$Ni(CO)_2$*o*-$C_6H_4(AsMe_2)_2$	6·256	7·653						
				0·4 *	667	113 *	537	5·13
$Ni(CO)_2$*o*-$C_6H_4(PMe_2)_2$	1·623	10·604						
	2·395	10·605						
	50·91		10·4					
	51·07		9·50					
				0·4 *	695	86	596	5·40
$Ni(CO)_2(AsPh_3)_2$	4·207	2·247 †						
	4·627	2·168 †						
	19·87		11·1					
	40·85		11·9					
				0·4 *	464	206	228	3·34
$Ni(CO)_2(PPh_3)_2$	4·369	3·143						
	5·434	3·200						
	23·35		15·0					
	33·01		15·4					
	51·72		15·0					
	54·60		14·9					
	18·36			0·36				
	20·80			0·40	527	198	299	3·82
$Ni(CO)_2$*o*-$C_6H_4(PEt_2)_2$	4·254	9·272						
	36·94		8·13					
	32·87		7·82					
				0·4 *	727	97	615	5·48
$Ni(CO)_4(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)_2$	6·421	0·808						
	11·97		5·51					
	16·89		5·86					
				0·35 *	250	171	54	1·6

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