345. *Alkyls and Aryls of Transition Metals. Part III.** *Nickel*(II) *Derivatives.*

By J. Chatt and B. L. Shaw.

Series of stable organonickel complexes of the types [$(PR'_3)_2NiRX$] and [$(PR'_3)_2NiR_2$] have been prepared, where R is an *ortho*-substituted aryl group or an ethynyl or substituted ethynyl group. Similar alkylnickel(II) complexes could not be isolated and, although phenyl-, and *meta*- or *para*-substituted aryl-nickel complexes were more stable, they decomposed in solution or in air and were only obtained in an impure state. An explanation for the enhanced stability of *ortho*-substituted arylnickel complexes and for the stability of the nickel acetylide complexes is offered.

Some reactions of these organonickel complexes are given, including halogenation to deep blue compounds, probably of nickel(IV), and also a reaction with a tertiary phosphine, whereby a quinque-co-ordinate nickel(II) complex, [$(PPhEt_2)_3Ni(C{\equiv}CPh)_2$] is formed.

Alkyl and aryl derivatives of nickel are unknown, the closest approach to such compounds being the complex acetylides $K_2Ni(C{\equiv}CR)_4$ and $K_4Ni(C{\equiv}CR)_4$ described by

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* Part II, *J.*, 1959, 4020.

Nast and his co-workers[1,2] and the cyclopentadienyl derivatives, *e.g.*, $Ni(C_5H_5)_2$ and $NO{\cdot}NiC_5H_5$.[3,4]

Following on the preparation of very stable complex platinum(II) and palladium(II) organometallic complexes of the types $[L_2MRX]$ and $[L_2MR_2]$ (R = alkyl, aryl, or substituted ethynyl radicals; L = tertiary phosphine, arsine, or sulphide),[5,6] we have now prepared similar compounds of nickel(II). These are especially interesting, because as a class they are just on the limits of stability: some can even be sublimed in air but others decompose on attempted isolation. It is thus possible to make a rapid qualitative survey of structural factors affecting their stability.

In general, the organometallic complexes were prepared in the same way as their platinum(II) analogues, *i.e.*, by reaction of Grignard reagents or lithium or sodium compounds with complexes of the type $[(PR_3)_2NiX_2]$ (X = Cl, Br). The products were hydrolysed (usually with dilute halogen acid) and isolated from the organic layer:

$$[(PR_3)_2NiBr_2] + RMgBr \longrightarrow [(PR_3)_2NiRBr] + MgBr_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$[(PR_3)_2NiBr_2] + 2RMgBr \longrightarrow [(PR_3)_2NiR_2] + 2MgBr_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Alkylnickel(II) *Derivatives.*—The addition of *trans*-$[(PEt_3)_2NiBr_2]$ to methylmagnesium bromide discharged the red colour of the nickel halide complex, giving a yellow solution, which probably contained a methylnickel derivative. However, in attempts to isolate this in the usual manner the ether solution rapidly deposited greenish decomposition products and no definite organometallic compound could be isolated. Benzyl and other alkyl Grignard reagents and triphenylmethylsodium behaved similarly.

Arylnickel(II) *Derivatives.*—Phenylmagnesium bromide reacted with $[(PR_3)_2NiBr_2]$ to form phenyl derivatives. They were very pale yellow crystalline complexes, which were soluble in organic solvents, but could not be isolated in a pure state. Analysis indicated a probable formula $[(PR_3)_2NiPh_2]$, but they decomposed in solution and in air. Attempts to prepare derivatives of *meta*- and *para*-substituted phenyls and of 2-naphthyl gave similar products. However, *ortho*-substituted phenyls, 1-naphthyl, 9-phenanthryl, and 9-anthryl all form surprisingly stable compounds of the types *trans*-$[(PR_3)_2NiArX]$ and also, in some cases, *trans*-$[(PR_3)_2NiAr_2]$. These complexes were, with a few exceptions, stable in boiling ethyl alcohol and benzene solution and appear to be stable indefinitely in the solid state (some of them have remained unchanged after more than a year's storage in air at room temperature). The mesityl derivatives are particularly stable; for instance, the complex *trans*-$[(PEt_3)_2Ni(mesityl)Cl]$ sublimes in air at 150°/1 atm. on a Kofler block without decomposition.

Ethynylnickel(II) *Derivatives.*—These are of the type *trans*-$[(PR_3)_2Ni(C{\equiv}CR')_2]$ and can be prepared from $[(PR_3)_2NiBr_2]$ and $R'C{\equiv}C{\cdot}MgBr$ but the yields are not good. Nevertheless, all nickel acetylides of this type are readily prepared from the nickel halide complex and $R'C{\equiv}CNa$ reacting in liquid ammonia. Thus the complexes $[(PPr^n_3)_2Ni(C{\equiv}CPh)_2]$ and $[(PEt_nPh_{3-n})_2Ni(C{\equiv}CR')_2]$ (n = 0—3; R′ = H, Me, or Ph) were prepared as stable, pale yellow, highly crystalline complexes. They have strong infrared absorption bands at *ca.* 2000 cm.$^{-1}$, characteristic of a dipolar acetylenic linkage, and the complex $[(PEt_3)_2Ni(C{\equiv}CH)_2]$ also had a strong band at 3229 cm.$^{-1}$ characteristic of an ethynyl hydrogen.

The stable organonickel complexes isolated in this work are listed in Table 1 together with their melting points, colours, and method of preparation. They are diamagnetic, and those of type $[(PR_3)_2NiR'_2]$ have very small or zero electric dipole moments. They therefore have a *trans*-planar arrangement of groups around the nickel atom. The mixed

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[1] Nast, Vester, and Griesshammer, *Chem. Ber.*, 1957, **90**, 2678.
[2] Nast and Kasperl, *Z. anorg. Chem.*, 1958, **295**, 227.
[3] Fischer and Jira, *Z. Naturforsch.*, 1953, **8b**, 217.
[4] Fischer and Jira, *Z. Naturforsch.*, 1954, **9b**, 618.
[5] Parts I and II, Chatt and Shaw, *J.*, 1959, 705; 1959, 4020.
[6] Calvin and Coates, *Chem. and Ind.*, 1958, 160.

complexes [(PR$_3$)$_2$NiR′X] also have a *trans*-configuration as indicated from the dipole moments of a few typical examples. Although the complexes [(PPh$_3$)$_2$Ni(C$\equiv$CPh)$_2$] and [(PPh$_3$)$_2$Ni(1-naphthyl)Br] are yellow, *trans*-planar, and diamagnetic, the halide from which they were prepared, *viz.*, [(PPh$_3$)$_2$NiBr$_2$], is green, paramagnetic, and has a distorted tetrahedral configuration.[7] The complex [(PEtPh$_2$)$_2$NiBr$_2$] is also dark green and paramagnetic in the solid state but yields a yellow, diamagnetic acetylide [(PEtPh$_2$)$_2$Ni(C$\equiv$CPh)$_2$] of *trans*-planar configuration. The compounds of the type *trans*-[(PR$_3$)$_2$NiR′$_2$] are bright or golden-yellow, whereas those containing a halogen atom, *trans*-[(PR$_3$)$_2$NiR′X], are brownish-yellow to deep brown, presumably owing to charge-transfer bands in their spectra.

TABLE 1. *Methods of preparation and physical properties of organonickel*(II) *complexes.*

Compound	Method *	Colour	M. p.‡	μ (D)
[(PEt$_3$)$_2$Ni(*o*-tolyl)Br]	1	Orange-brown	102—103°	
[(PEt$_3$)$_2$Ni(*o*-tolyl)Cl]	1	Orange-brown	75—77·5	2·35 †
[(PPhEt$_2$)$_2$Ni(*o*-tolyl)Br]	1	Orange-brown	114—117	
[(PPhEt$_2$)$_2$Ni(*o*-chlorophenyl)Br]	1	Yellowish-brown	137·5—138·5	
[(PPhEt$_2$)$_2$Ni(*o*-bromophenyl)Br]	1	Orange-brown	130—131	
[(PPhEt$_2$)$_2$Ni(*o*-methoxyphenyl)Br]	1	Yellowish-brown	125—128	
[(PPhEt$_2$)$_2$Ni($\omega\omega\omega$-trifluoro-*o*-tolyl)Cl]	3	Yellow	100—101	
[(PEt$_3$)$_2$Ni(mesityl)Br]	1,6	Brown	159—160	2·9
[(PEt$_3$)$_2$Ni(mesityl)Cl]	5	Yellowish-brown	166—167	2·4 †
[(PPhEt$_2$)$_2$Ni(mesityl)Br]	1	Brown	114—116 & 128—130	
[(PPhEt$_2$)$_2$Ni(mesityl)Cl]	5	Orange	106—107	
[(PPhEt$_2$)$_2$Ni(2-biphenylyl)Br]	1	Dark brown	126—128	
[(PEt$_3$)$_2$Ni(C$_6$Cl$_5$)Cl]	1	Brown	156—158	
[(PPhEt$_2$)$_2$Ni(C$_6$Cl$_5$)Cl]	1	Brown	133·5—135·5	
[(PEt$_3$)$_2$Ni(1-naphthyl)Br]	1	Brown	150—152·5 §	
[(PEt$_3$)$_2$Ni(1-naphthyl)SCN]	6	Orange	180—182 ‡	
[(PPhEt$_2$)$_2$Ni(1-naphthyl)Br]	1,3	Orange-brown	127—129	3·05 †
[(PPhEt$_2$)$_2$Ni(1-naphthyl)I]	6	Dark brown	129—132	
[(PPhEt$_2$)$_2$Ni(1-naphthyl)SCN]	6	Orange	160—163 ‡	
[(PPhEt$_2$)$_2$Ni(1-naphthyl)NO$_2$]	6	Pale yellow	144—153 ‡	
[(PEt$_3$)$_2$Ni(C$_6$Cl$_5$)I]	6	Dark brown	168—171	
[(PPh$_2$Et)$_2$Ni(1-naphthyl)Br]	1	Orange	132—139 ‡	
[(PPh$_3$)$_2$Ni(1-naphthyl)Br]	1	Orange	168·5—170 ‡	
[(PEt$_3$)$_2$Ni(9-phenanthryl)Br]	1	Brown	156—159 ‡	
[(PPhEt$_2$)$_2$Ni(9-phenanthryl)Br]	1	Brown	148—152	
[(PPhEt$_2$)$_2$Ni(9-anthryl)Br]	1	Brown	166—169 ‡	
[(PEt$_3$)$_2$Ni(phenyl)$_2$]	1	Pale yellow	125—130 ‡	
[(PPr$^n{}_3$)$_2$Ni(phenyl)$_2$]	1	Pale yellow	129—135 ‡	
[(PPhEt$_2$)$_2$Ni(*o*-tolyl)$_2$]	2,3	Pale yellow	146—148 ‡	0
[(PEt$_3$)$_2$Ni(mesityl)$_2$]	2	Pale yellow	148—150 §	
[(PPhEt$_2$)$_2$Ni(mesityl)$_2$]	2	Pale yellow	154—157 §	0 †
[(PPhEt$_2$)$_2$Ni(2-biphenylyl)$_2$]	3	Pale yellow	119—121 ‡	
[(PEt$_3$)$_2$Ni(C$\equiv$CH)$_2$]	4	Pale yellow	36—36·5	
[(PEt$_3$)$_2$Ni(C$\equiv$CMe)$_2$]	4	Bright yellow	74—75	
[(PEt$_3$)$_2$Ni(C$\equiv$CPh)$_2$]	4	Yellowish-orange	149—151	0·45
[(PPr$^n{}_3$)$_2$Ni(C$\equiv$CPh)$_2$]	4	Yellowish-orange	65—67	
[(PPhEt$_2$)$_2$Ni(C$\equiv$CPh)$_2$]	4,6	Yellowish-orange	106—108	
[(PPh$_2$Et)$_2$Ni(C$\equiv$CPh)$_2$]	4	Orange	155—158 ‡	
[(PPh$_3$)$_2$Ni(C$\equiv$CPh)$_2$]	4	Orange	170—172 ‡	1·4 †
[(PPhEt$_2$)$_3$Ni(C$\equiv$CPh)$_2$]	4,7	Dark red	65—68 ‡	
[(PPhEt$_2$)$_2$Ni(C$\equiv$CPh)Cl]	5	Brown	87—89	2·0 †
[(PPhEt$_2$)$_2$Ni(1-naphthyl)Br$_3$]	7	Deep blue	186—188	
[(PPhEt$_2$)$_2$Ni(1-naphthyl)Cl$_2$Br]	7	Bright blue	178—180	

* See Experimental Section.
† Calculated by using estimated values of the density and the refractivity (see Part I of this series).
‡ With decomposition. § With slight decomposition.

The complex halides, *e.g.*, *trans*-[(PEt$_3$)$_2$NiBr$_2$], and their solutions have a strong odour of the free phosphine. Since the organonickel complexes and their solutions smell only

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[7] Venanzi, *J.*, 1958, 719.

weakly or not at all of free phosphine, it is apparent that replacement of even one of the halogen atoms by an organic radical stabilises the P–Ni linkage.

Fission Reactions.—Dry hydrogen chloride in ether–benzene or tetrahydrofuran–benzene cleaves the organic groups from the nickel atom. *trans*-[(PEt$_3$)$_2$Ni(mesityl)$_2$] was cleaved rather slowly by dry hydrogen chloride (1 mol.) to give *trans*-[(PEt$_3$)$_2$Ni(mesityl)Cl] in good yield. *trans*-[(PPhEt$_2$)$_2$Ni(mesityl)$_2$] was even more resistant to fission by hydrogen chloride and the product, *trans*-[(PPhEt$_2$)$_2$Ni(mesityl)Cl], was recovered in good yield even after the passage of dry hydrogen chloride through its solution for $\frac{1}{2}$ hr. The phenylethynyl group could also be cleaved in this manner, but the resultant complex, *trans*-[(PEt$_3$)$_2$Ni(C≡CPh)Cl], was rather labile and difficult to purify. As in the case of the platinous organometallic compounds, the organic groups were removed according to equation (3).

$$trans\text{-}[(PR'_3)_2NiR_2] + HCl \longrightarrow trans\text{-}[(PR'_3)_2NiRCl] + RH \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Attempts to effect fission of aryl groups by using magnesium iodide in ether were not successful. Thus the complex *trans*-[(PPhEt$_2$)$_2$Ni(mesityl)$_2$] on treatment with magnesium iodide in ether for 2 days gave a good recovery of starting material and no mesitylmagnesium iodide appeared to have been formed since carbonation failed to yield any mesitoic acid [see equation (4)]. Similarly the complex *trans*-[(PEt$_2$Ph)$_2$Ni(1-naphthyl)Br] on treatment with magnesium iodide and subsequent carbonation failed to yield any α-naphthoic acid.

$$trans\text{-}[(PPhEt_2)_2Ni(mesityl)_2] + MgI_2 \longrightarrow trans\text{-}[(PPhEt_2)_2(mesityl)I] + mesitylMgI \quad . \; . \; . \; . \quad (4)$$

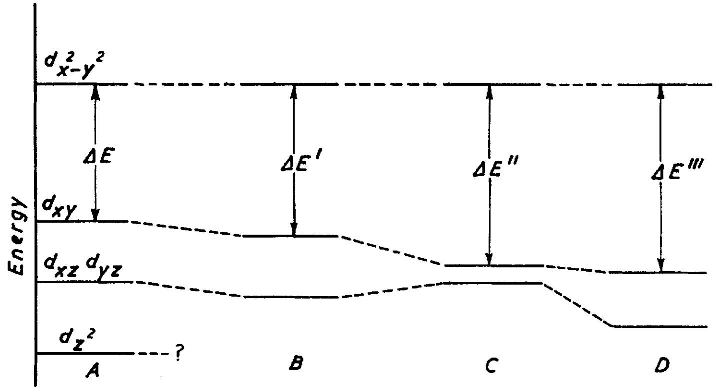
Metathetical Replacement Reactions.—The halogen atom (X) in organonickel complexes of the type [(PR$_3$)$_2$Ni(aryl)X] could readily be replaced by other radicals. Thus, by treatment with the appropriate alkali-metal salt in acetone, chloride could be replaced by bromide, and bromide by iodide or nitro- or thiocyanato-groups. Treatment of the monohalide complex *trans*-[(PEt$_2$Ph)$_2$Ni(1-naphthyl)Br] with NaC≡CPh in liquid ammonia, however, yielded *trans*-[(PEt$_2$Ph)$_2$Ni(C≡CPh)$_2$] and not the expected *trans*-[(PEt$_2$Ph)$_2$Ni(1-naphthyl)(C≡CPh)].

A 5-Co-ordinate Nickel(II) *Complex*, [(PPhEt$_2$)$_3$Ni(C≡CPh)$_2$].—It was found that by treatment of *trans*-[(PPhEt$_2$)$_2$NiBr$_2$] with NaC≡CPh in liquid ammonia, besides the expected *trans*-[(PPhEt$_2$)$_2$Ni(C≡CPh)$_2$] which is yellow, a large quantity of the deep red, very soluble complex [(PPhEt$_2$)$_3$Ni(C≡CPh)$_2$] was obtained. This unusual complex, readily prepared according to equation (5), dissociates reversibly in solution. It was thus too unstable to permit measurements, such as of dipole moment or molecular weight in solution. However, the solid was diamagnetic, showed a strong absorption band in the infrared at 2088 cm.$^{-1}$, characteristic of a polar acetylenic linkage, and had a low m. p. (62—68°) and a high solubility in organic solvents. It thus seems likely that the new complex is monomeric and 5-co-ordinate. Attempts to prepare similar complexes by using other phosphines were not successful; thus, addition of triethylphosphine to *trans*-[(PEt$_3$)$_2$Ni(C≡CPh)$_2$] gave no darkening in colour and no evidence of complex formation. A similar negative result was obtained for the action of triphenylphosphine on *trans*-[(PPhEt$_2$)$_2$Ni(C≡CPh)$_2$].

$$\underset{\text{Yellow}}{trans\text{-}[(PPhEt_2)_2Ni(C{\equiv}CPh)_2]} + PPhEt_2 \rightleftharpoons \underset{\text{Dark red}}{[(PPhEt_2)_3Ni(C{\equiv}CPh)_2]} \quad . \; . \; . \; . \; . \quad (5)$$

Factors affecting the Stability of Organo-nickel Complexes.—Qualitatively it is evident that the stabilities of the nickel complexes [(PR'$_3$)$_2$NiR$_2$] and [(PR'$_3$)$_2$NiRX] increase in the order of R groups: alkyl < phenyl ~ *m*- and *p*-substituted aryl < ethynyl or substituted ethynyl ~ *o*-substituted aryl. Two properties of the group R appear to be important for stability: (*a*) it should allow the possibility of conjugation to the nickel atom and (*b*) it should have at least one *ortho*-substituent when it is an aryl group. The crucial factor about the substituent appears to be its size rather than its electronic character. The fact that the presence of bulky *ortho*-substituents in the phenyl groups of $[(PR_3)_2NiPh_2]$ can cause an increase in stability, although they also introduce steric strain within the molecule, indicates a kinetic rather than a thermodynamic explanation of their stabilising action. These facts can be accommodated in terms of the ideas put forward in Part I on the stabilisation of the organic derivatives of transition metals,[5] and of what we know of the mechanism of substitution reaction in square planar complexes.[8]

(a) *Instability of alkyl derivatives.* In Part I we suggested that the energy difference between the highest occupied electronic level and the lowest unoccupied level had to exceed some crucial value, before organo-transition metal complexes became sufficiently stable to be isolated. The Fig. shows the splitting of *d*-energy levels (according to crystal-field theory) which probably occurs in complexes of d^8 type [9] such as the organometallic compounds $[(PR_3)_2MR_2]$ (M = Pt, Pd, and Ni), and according to our hypothesis the energy difference ΔE between the d_{xy}- and the $d_{x^2-y^2}$-orbitals is the crucial factor (the x, y plane is the plane of the complex). These are non-bonding and antibonding orbitals respectively in molecular orbital theory. The phosphine ligands give a sufficiently large ΔE to stabilise the alkyl derivatives of platinum and palladium, but the ligand-field splitting decreases on passing from the heavier to lighter elements in any Group of the Periodic Table.[10] Evidently, the splitting in the nickel complexes is not sufficient to stabilise the alkyl derivatives.



A, Alkyl complexes; B, pheny and meta- *and* para-*substituted aryl complexes; C,* ortho-*substituted aryl complexes; D, acetylide complexes.*

(b) *Stability of aryl derivatives.* In Part II [5] we provided evidence that in the platinum compounds *cis*- and *trans*-$[(PR'_3)_2PtPh_2]$, there is a significant mesomeric drift of electrons from the metal into the anti-bonding π-orbitals of the aromatic systems. The phenyl groups will certainly rotate about the metal to carbon bonds, consequently their π-orbitals must overlap with d_{xz}- and/or d_{yz}-orbitals of the metal, as well as with the crucial d_{xy}-orbital, so causing some lowering of all of these energy levels, *i.e.*, a small increase in ΔE. At the same time a certain amount of π-bonding is introduced into the metal–phenyl bond. Thus the stabilisation of the phenyl relative to the methyl derivatives could be due both to an increase in ΔE and to an increase in Pt–C bond strength, both increases caused by the addition of some π-bonding, accompanied by mesomeric electron drift from the metal to the phenyl groups.

The *meta*- and *para*-substituted aryl complexes should be similar electronically to the

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[8] Basolo and Pearson, " Mechanisms of Inorganic Reactions," John Wiley & Sons, New York, 1958, 172.

[9] Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

[10] Jörgensen, " Quelques Problèmes de Chimie Minérale " (a report of the tenth Solvay Conference of Chemistry), R. Stoops, Brussels, 1956, 355.

unsubstituted phenyl complexes, except in so far as the substituents withdraw or release electrons, so slightly increasing or decreasing ΔE and the double-bond character of the $Ni-C_{ar.}$ bond. The electronic effects of *para*-substituents should be the more marked; nevertheless the few *para*-substituted phenyl complexes which we have prepared had similar stabilities to those of their phenyl analogues.

In the *ortho*-substituted aryl derivatives a new situation arises, and additional stabilisation is found owing, we think, to a combination of electronic and steric factors. Models show that the interference of the *ortho*-substituents with the bulky tertiary phosphine ligands on each side of the nickel atom would prevent the rotation of the aryl group about the Ni–C bond, and the *ortho*-substituted aryl group would thus be held with its plane perpendicular to that of the complex. In these circumstances its π-orbitals must interact specifically with the crucial d_{xy}-orbital of the metal. Thus ΔE will be greater than it would have been had the aryl group rotated and so have interacted with the d_{xz}- or d_{yz}-orbital as well. This increase in ΔE probably prevents thermal dissociation of the organometallic complex leading to free radicals, a common mode of thermal decomposition of organometallic compounds, but the *ortho*-substituted aryl complexes are also relatively inert to attack by chemical reagents and this we believe to be caused mainly by the shielding of the nickel atom by the *ortho*-substituent.

In solution "square planar" complexes may react to give ligand replacement by either an S_N1 or an S_N2 mechanism. In most solvents they are solvated so that weakly held solvent molecules occupy the octahedral positions along the z axis. There is considerable evidence that these solvent molecules assist the initial dissociation of the complex during reaction by an S_N1 mechanism by moving in towards the metal atoms as the dissociating ligand breaks away.[8] The *ortho*-substituents in our *ortho*-substituted aryl complexes of nickel would prevent this action of the solvent and so stabilise the complex to attack by an S_N1 mechanism. Similarly, they would also hinder the approach of reagent molecules for attack by an S_N2 mechanism, but in the case of the monosubstituted aryl complexes of the type *trans*-$[(PR_3)_2Ni(aryl)X]$ one side of the molecule would still be available for attack by a bimolecular mechanism, and perhaps it is significant that the most inert complexes have an aryl group with two *ortho*-substituents, *e.g.*, *trans*-$[(PR_3)_2Ni(mesityl)X]$ and *trans*-$[(PR_3)_2Ni(C_6Cl_5)X]$. Thus the stabilising action of the *ortho*-substituents may be due to the electronic effect of the increased ΔE together with the steric effect of the *ortho*-group hindering or preventing suitably directed attack by reagents or solvents, at the nickel atom.

(c) *Stability of the acetylides.* In the compounds *trans*-$[(PR'_3)_2Ni(C{\equiv}CR)_2]$ there are two sets of antibonding π-orbitals associated with each acetylide group. These are in planes at right angles and together have cylindrical symmetry so will always interact with the d_{xy}-orbital, independently of any rotation about the Ni–C bond. Also, since the acetylide group is strongly electron-withdrawing, ΔE will be appreciably increased and the Ni–C bond should have considerable double-bond character. This appears to be sufficient to stabilise the acetylides completely, and stability increases, as would be expected on this basis, in the order: $R' = H <$ alkyl $<$ aryl. Even the ethynyls are stable and have no tendency to detonate or inflame after the manner of the complex acetylides, *e.g.*, $K_2[Ni(C{\equiv}CH)_4]$ described by Nast and his co-workers.

The way in which we consider ΔE to increase throughout the above types of nickel complexes is summarised qualitatively in the Fig., where $\Delta E < \Delta E' < \Delta E'' \sim \Delta E'''$. The level of the $d_{x^2-y^2}$-orbital has been arbitrarily chosen as a final energy level. The relative energy of the d_{z^2}-orbital is uncertain and the d_{xz},d_{yz}-orbitals may have slightly different energies but these do not affect our arguments.

The order of increasing ΔE is not that of increasing stability, because the steric blocking effects of the *ortho*-substituents are an important additional factor, rendering many *ortho*-substituted aryl complexes even more stable than phenylethynyl complexes.

Halogenation of Arylnickel Complexes.—In general, treatment of arylnickel complexes with bromine or chlorine yielded intractable dark green or blue products, but *trans*-$[(PPhEt_2)_2Ni(1\text{-naphthyl})Br]$ gave crystalline products. Bromination of this complex gave a deep blue, crystalline product, which was stable in air but decomposed in most organic solvents. Analyses were in agreement with a molecular formula $C_{30}H_{37}Br_3NiP_2$. A similar product was formed on chlorination, *viz.*, $C_{30}H_{37}BrCl_2NiP_2$; the magnetic moments (μ) of the two solid compounds, measured at 20°, were 3·4 and 3·8 Bohr magnetons and the molar conductivities, in nitrobenzene solution at 25°, were 18·7 and 16·8 mho, respectively. These two products could be complexes of nickel(IV), *e.g.* $(PPhEt_2)_2Ni(1\text{-naphthyl})Br_3$, but their exact nature has not been established.

EXPERIMENTAL

Microanalyses are by Messrs. W. A. Brown and A. G. Olney and by Miss S. Lathwell of these laboratories. M. p.s were determined on a Kofler hot-stage and are corrected. Spence grade " H " alumina was used for chromatography.

The nickel halide complexes of tertiary organic phosphines were prepared by adding the phosphine (2 mol.) to a solution of the appropriate nickel halide, in ethyl alcohol containing a little water, as described by Jensen.[11] Only the following two are new: trans-*Bis(diethylphenylphosphine)dibromonickel*, obtained as dark red prisms, m. p. 114—116°, from ethyl alcohol (Found: C, 43·3; H, 5·5. $C_{20}H_{30}Br_2P_2Ni$ requires C, 43·6; H, 5·5%), and *bis(ethyldiphenylphosphine)dibromonickel*, obtained as dark green prisms, m. p. 173—175°, from methylene chloride–ether (Found: C, 51·95; H, 4·75. $C_{28}H_{30}Br_2P_2Ni$ requires C, 51·95; H, 4·65%).

The nickel halide complexes were converted into organometallic complexes as follows:

Method (1): *Arylnickel Complexes prepared from Grignard Reagents at Low Temperatures.*—Organonickel complexes of the type *trans*-$[(PR_3)_2Ni(\text{aryl})X]$ were prepared by adding the appropriate nickel complex $[(PR_3)_2NiX_2]$ to the Grignard reagent at *ca.* −10°, followed by hydrolysis after a few minutes, and isolation of the product. The preparation of *trans*-bis(triethylphosphine)bromo(*o*-tolyl)nickel is typical.

trans-*Bis(triethylphosphine)bromo*-(o-*tolyl)nickel*, trans-$[(PEt_3)_2Ni(o\text{-tolyl})Br]$. *trans*-$[(PEt_3)_2NiBr_2]$ (3·0 g.), as a slurry in benzene (20 c.c.), was added at *ca.* −10° to the Grignard reagent prepared from magnesium (0·24 g.), *o*-bromotoluene (1·71 g.), ether (50 c.c.), and benzene (30 c.c.). After 2 min. the mixture was cooled to *ca.* −40° and hydrolysed with dilute hydrobromic acid. Isolation of the product from the organic layer and crystallisation from ethanol–methanol afforded trans-*bis(triethylphosphine)bromo*-(o-*tolyl)nickel* (2·58 g., 84%) as prisms (Found: C, 48·8; H, 8·0. $C_{19}H_{37}BrNiP_2$ requires C, 48·95; H, 8·0%).

trans-*Bis(diethylphenylphosphine)bromo*-(o-*tolyl)nickel* was similarly prepared and formed needles (75%) from ethyl alcohol (Found: C, 57·95; H, 6·75. $C_{27}H_{37}BrNiP_2$ requires C, 57·7; H, 6·65%).

trans-*Bis(triethylphosphine)chloro*-(o-*tolyl)nickel* was prepared by treating *trans*-$[(PEt_3)_2NiCl_2]$ in tetrahydrofuran–benzene at −10° for 5 min. with *o*-tolylmagnesium chloride (*ca.* 2 mol.). Hydrolysis at *ca.* −40° with dilute hydrochloric acid and isolation then gave the required product as prisms (54%) from methyl alcohol (Found: C, 53·7; H, 8·75. $C_{19}H_{37}ClNiP_2$ requires C, 54·15; H, 8·85%).

trans-*Bis(diethylphenylphosphine)bromo*-(o-*chlorophenyl)nickel* was prepared by method (1) and formed prisms (84%) from ethyl alcohol (Found: C, 53·65; H, 5·9. $C_{26}H_{34}BrClNiP_2$ requires C, 53·6; H, 5·9%).

trans-*Bis(diethylphenylphosphine)bromo*-(o-*bromophenyl)nickel* was similarly prepared and formed prisms (60%) from ethyl alcohol (Found: C, 49·65; H, 5·6. $C_{26}H_{34}Br_2NiP_2$ requires C, 49·8; H, 5·45%).

trans-*Bis(diethylphenylphosphine)bromo*-(o-*methoxyphenyl)nickel* was prepared by the general method and formed needles (32%) from ethyl alcohol or light petroleum (b. p. 60—80°) (Found: C, 56·15; H, 6·55. $C_{27}H_{37}OBrNiP_2$ requires C, 56·1; H, 6·45%).

trans-*Bis(triethylphosphine)bromo(mesityl)nickel* formed needles (69%) from ethyl alcohol (Found: C, 50·85; H, 8·35. $C_{21}H_{41}BrNiP_2$ requires C, 51·05; H, 8·4%).

[11] Jensen, *Acta Chem. Scand.*, 1949, **3**, 474; *Z. anorg. Chem.*, 1936, **229**, 265.

trans-*Bis(diethylphenylphosphine)bromo(mesityl)nickel* was obtained as prisms, m. p. 114—116°, from methyl alcohol or as needles, m. p. 129—130° after resolidification of the melt. The needles on recrystallisation from methyl alcohol formed the prisms (72%), m. p. 114—116° (Found: C, 58·9; H, 7·4%; *M*, ebullioscopically in 1·5% benzene solution, 639. $C_{29}H_{41}BrNiP_2$ requires C, 58·9; H, 7·15%; *M*, 590).

trans-*Bis(diethylphenylphosphine)bromo-*(2-*biphenylyl*)*nickel* formed prisms (78%) from light petroleum (b. p. 80—100°) (Found: C, 61·55; H, 6·3. $C_{32}H_{39}BrNiP_2$ requires C, 61·55; H, 6·3%).

trans-*Bis(triethylphosphine)chloro(pentachlorophenyl)nickel.* Pentachlorophenylmagnesium chloride was prepared by first activating magnesium (0·48 g.) in tetrahydrofuran (20 c.c.) with benzyl chloride (0·3 g.) and then adding hexachlorobenzene (5·7 g.). After the initial exothermic reaction had subsided the mixture was stirred for 1 hr. at 20° and benzene (20 c.c.) was added. The whole was cooled to −20°, *trans*-$[(PEt_3)_2NiCl_2]$ (3·0 g.) was added, and the mixture stirred for 2 mins. at 0°; a mixture of brown prisms and colourless needles was collected; when this was heated at 130°/0·01 mm. the colourless, wholly organic, portion sublimed and the residue on recrystallisation from ethyl alcohol yielded trans-*bis(triethylphosphine)chloro(pentachlorophenyl)nickel* (3·8 g.) as prisms (Found: C, 37·5; H, 5·3; Cl, 36·45. $C_{18}H_{30}Cl_6NiP_2$ requires C, 37·3; H, 5·2; Cl, 36·7%).

trans-*Bis(diethylphenylphosphine)chloro(pentachlorophenyl)nickel* was similarly prepared and formed prisms from light petroleum (b. p. 80—100°) (Found: C, 46·5; H, 4·55; Cl, 31·2. $C_{26}H_{30}Cl_6NiP_2$ requires C, 46·2; H, 4·5; Cl, 31·45%). trans-*Bis(triethylphosphine)bromo-*(1-*naphthyl*)*nickel* formed prisms (67%) from light petroleum (b. p. 60—80°) or ethyl alcohol (Found: C, 52·65; H, 7·5. $C_{22}H_{37}BrNiP_2$ requires C, 52·65; H, 7·45%), and the *diethylphenylphosphine* analogue, similarly prepared, formed rhombs (89%) from ethyl alcohol (Found: C, 60·3; H, 6·35%; *M*, ebullioscopically in 1·64% benzene solution, 526; in 4·22% benzene solution, 566. $C_{30}H_{37}BrNiP_2$ requires C, 60·15; H, 6·4%; *M*, 598). The *ethyldiphenylphosphine compound*, prepared from $[(PPh_2Et)_2NiBr_2]$, formed prisms from light petroleum (b. p. 80—100°) (analyses were erratic. Found: C, 64·55, 66·6; H, 5·4, 5·45. $C_{38}H_{37}BrNiP_2$ requires C, 65·75; H, 5·35%); and the *triphenylphosphine analogue*, prepared from $[(PPh_3)_2NiBr_2]$ in 60% yield, formed prisms from methylene chloride–ethyl alcohol (Found: C, 69·6; H, 4·8. $C_{46}H_{37}BrNiP_2$ requires C, 69·9; H, 4·7%).

trans-*Bis(triethylphosphine)bromo-*(9-*phenanthryl*)*nickel* was prepared in 54% yield as elongated prisms from ethyl alcohol (Found: C, 56·4; H, 7·2. $C_{26}H_{39}BrNiP_2$ requires C, 56·55; H, 7·1%). The analogous *diethylphenylphosphine compound*, after one recrystallisation from ethyl alcohol and one from light petroleum (b. p. 80—100°), was obtained as prisms (Found: C, 63·05; H, 6·1. $C_{34}H_{39}BrNiP_2$ requires C, 63·0; H, 6·05%); yield 65%.

trans-*Bis(diethylphenylphosphine)bromo-*(9-*anthryl*)*nickel* as obtained by the general method was mixed with anthracene, a difficult impurity to remove. However, removal was effected by heating this mixture at 140°/10^{-3} mm., and the residue on crystallisation from n-propyl alcohol yielded the desired complex as prisms (Found: C, 63·0; H, 6·15. $C_{34}H_{39}BrNiP_2$ requires C, 63·0; H, 6·05%).

Bis(triethylphosphine)diphenylnickel $[(PEt_3)_2Ni(C_6H_5)_2]$.—A solution of *trans*-$[(PEt_3)_2NiBr_2]$ (1·14 g.) in benzene (20 c.c.) was added at −20° during 20 min. to a solution of phenylmagnesium bromide, prepared from magnesium (0·48 g.), bromobenzene (3·45 g.), ether (40 c.c.), and benzene (30 c.c.). The yellow solution which formed was cooled to −30° and hydrolysed by cautious addition of dilute hydrochloric acid. The organic layer was separated, dried ($MgSO_4$), and evaporated down under reduced pressure. Very pale yellow needles of impure *bis(triethylphosphine)diphenylnickel* separated. These were filtered off, washed with a little cold benzene, and dried under high vacuum (Found: C, 59·7; H, 8·3. $C_{24}H_{40}NiP_2$ requires C, 64·15; H, 9·0%). The product decomposed very rapidly in ethyl alcohol solution and in air decomposed with the formation of biphenyl (from evidence of smell).

Bis(tripropylphosphine)diphenylnickel. Similarly, treatment of *trans*-$[(PPr^n_3)_2NiBr_2]$ with phenylmagnesium bromide yielded needles of impure *bis(tri-n-propylphosphine)diphenylnickel* (Found: C, 63·4; H, 9·4. $C_{30}H_{52}NiP_2$ requires C, 67·55; H, 9·85%).

Method (2): *Diarylnickel and Nickel Acetylide Complexes formed by the Grignard Method at High Temperatures.*—trans-*Bis(diethylphenylphosphine)di-*(o-*tolyl*)*nickel. trans*-$[(PPhEt_2)_2NiBr_2]$ (2·0 g.) was added to a solution of *o*-tolylmagnesium bromide, prepared from magnesium (0·48 g.), *o*-bromotoluene (3·42 g.), tetrahydrofuran (25 c.c.), and benzene (30 c.c.). After being heated under reflux for 10 min. the mixture was cooled to −30° and hydrolysed by cautious addition of dilute hydrobromic acid. The organic layer was separated, washed with water, dried ($MgSO_4$), filtered, and evaporated to dryness. Addition of ethyl alcohol to the residue gave yellow needles which were filtered off and recrystallised by dissolving them in cold benzene and adding cold methyl alcohol. trans-*Bis*(*diethylphenylphosphine*)*di*-(o-*tolyl*)*nickel* was obtained as needles (Found: C, 71·2; H, 7·8. $C_{38}H_{44}NiP_2$ requires C, 71·2; H, 7·75%); yield 0·21 g.

trans-*Bis*(*triethylphosphine*)*di*(*mesityl*)*nickel,* prepared in 65% yield by a similar method to the above, formed glistening needles from benzene–ethyl alcohol (Found: C, 67·3; H, 9·8. $C_{30}H_{52}NiP_2$ requires C, 67·55; H, 9·85%); and the *diethylphenylphosphine analogue*, prepared by using a slightly longer reaction time (17 min. under reflux), was obtained as needles (58%) from benzene–methyl alcohol (Found: C, 72·95; H, 8·45. $C_{38}H_{52}P_2Ni$ requires C, 72·5; H, 8·35%).

trans-*Bis*(*triethylphosphine*)*di*(*phenylethynyl*)*nickel.* Ethylmagnesium bromide was prepared from magnesium (0·24 g.), ethyl bromide (1·09 g.), and ether (15 c.c.). A solution of phenylacetylene (1·02 g.) in benzene (10 c.c.) was added, and after 15 minutes' heating under reflux the mixture was cooled to 20° and a solution of *trans*-$[(PEt_3)_2NiBr_2]$ (1·14 g.) in benzene (20 c.c.) was added with stirring. After 50 min. the dark brown solution was cooled to 0° and hydrolysed with dilute hydrochloric acid, and the product isolated from the organic layer. Three recrystallisations from ethyl alcohol then gave trans-*bis*(*triethylphosphine*)*di*(*phenylethynyl*)*nickel* as needles (0·23 g.) (Found: C, 67·65; H, 8·1%; *M*, ebullioscopically in 1·53% benzene solution 500; in 3·72% benzene solution, 470. $C_{28}H_{40}P_2Ni$ requires C, 67·65; H, 8·1%; *M*, 496). The magnetic susceptibility of the solid at 20° (χ) was $-[0{\cdot}51 \pm 0{\cdot}40] \times 10^{-6}$.

trans-*Bis*(*tripropylphosphine*)*di*(*phenylethynyl*)*nickel.* A solution of phenylethynylmagnesium bromide was prepared as above, and to it *trans*-$[(PPr^n_3)_2NiCl_2]$ (1·1 g.) in benzene (30 c.c.) was added at 20°. After being stirred for 6 min. at 20° the mixture was cooled to 0° and hydrolysed with dilute hydrochloric acid. The crude product, isolated from the organic layer, was chromatographed on alumina, and elution with light petroleum (b. p. 40—60°)–ether (20 : 1) then gave the required *product*, which formed needles (0·75 g.) from methyl alcohol (Found: C, 70·45; H, 9·13. $C_{34}H_{52}NiP_2$ requires C, 70·25; H, 9·02%).

Method (3). *Preparation of Arylnickel Complexes by using an Aryl-lithium.—Preparation of* trans-*bis*(*diethylphenylphosphine*)*di*-(o-*tolyl*)*nickel by use of* o-*tolyl-lithium. trans*-$[(PPhEt_2)_2NiBr_2]$ (0·8 g.) in benzene (10 c.c.) was treated with a solution of *o*-tolyl-lithium in ether (2·0 c.c.; 1·75N). After 15 min. water was added and the organic layer was separated, dried ($MgSO_4$), and evaporated to dryness. The residue gave the desired product as bright yellow prisms (0·203 g.) from benzene–methyl alcohol.

trans-*Bis*(*diethylphenylphosphine*)*bromo*-(1-*naphthyl*)*nickel.* A 1·1N-solution of n-butyllithium (4·0 c.c.) was added to a solution of 1-bromonaphthalene (0·55 c.c.) in benzene (5 c.c.) and after 1 min. the resultant solution was added to *trans*-$[(PPhEt_2)_2NiBr_2]$ (2·00 g.), dissolved in benzene (25 c.c.). After 2 min. the precipitated lithium bromide was filtered off, and *trans*-bis(diethylphenylphosphine)bromo-(1-naphthyl)nickel (0·36 g.) isolated from the filtrate by evaporation and crystallisation from ethyl alcohol.

trans-*Bis*(*diethylphenylphosphine*)*di*-(2-*biphenylyl*)*nickel.* Butyl-lithium (20 c.c.; 0·43N) was added to a solution of 2-bromobiphenyl (2·4 g.) in ether (50 c.c.), and the mixture set aside for 10 min. *trans*-$[(PPhEt_2)_2NiBr_2]$ (1·8 g.) was added, and after 1 hr. at 15° the mixture was cooled to −30° and hydrolysed with dilute hydrobromic acid. The organic layer was separated, dried ($MgSO_4$), and evaporated to dryness. Digestion of the residue with warm ethyl alcohol followed by repeated crystallisation from benzene–methyl alcohol afforded trans-*bis*(*diethylphenylphosphine*)*di*-(2-*biphenylyl*)*nickel* as needles (0·030 g.) (Found: C, 75·8; H, 7·0. $C_{44}H_{48}NiP_2$ requires C, 75·8; H, 6·95%).

trans-*Bis*(*diethylphenylphosphine*)*chloro*-(*ωωω-trifluoro*-o-*tolyl*)*nickel.* A solution of ωωω-trifluoro-*o*-tolyl-lithium was prepared by heating a mixture of ωωω-trifluorotoluene (2·00 g.) and propyl-lithium in ether (25 c.c.; 0·563N) under reflux for 3 hr. This solution was then added to a solution of *trans*-$[(PPhEt_2)_2NiCl_2]$ (4·1 g.) in benzene (15 c.c.) and after 10 min. at 15° water was added, and the product isolated. trans-*Bis*(*diethylphenylphosphine*)*chloro*-(*ωωω-trifluoro*-o-*tolyl*)*nickel* formed prisms (1·12 g., 22%) from ethyl alcohol or light petroleum (b. p. 60—80°) (Found: C, 56·85; H, 6·1. $C_{27}H_{34}ClF_3NiP_2$ requires C, 56·75; H, 6·0%).

Method (4): *Preparation of Nickel Acetylide Complexes in Liquid Ammonia.*—To a suspension of the sodium acetylide ($NaC{\equiv}CR'$) (10 mol.) in liquid ammonia–ether (*ca.* 4 : 1 v/v) was added the appropriate nickel halide complex (*trans*-[$(PR_3)_2NiX_2$]; R = Et, Pr^n, and/or Ph; X = Cl, Br) (1 mol.) either as the solid or in a slurry with a small quantity of ether. After intermittent agitation for 20 min. ammonium chloride was added (to destroy excess of sodium acetylide), and the ammonia allowed to evaporate; addition of water and isolation by chromatography and/or crystallisation then gave the required product. The following were prepared by this method: trans-*Bis(triethylphosphine)diethynylnickel,* purified by chromatography and elution with light petroleum (b. p. 40—60°) containing ether (2%), formed needles (39%) from aqueous methyl alcohol (Found: C, 55·3; H, 9·3. $C_{16}H_{32}NiP_2$ requires C, 55·7; H, 9·35%), $\nu_{max.}$ (in Nujol) 3229s ($\equiv$C–H stretching) and 1923s cm.$^{-1}$ (C$\equiv$C stretching). trans-*Bis(triethylphosphine)dipropynylnickel* as prisms (66%) from methyl alcohol (charcoal) (Found: C, 58·1; H, 9·75. $C_{18}H_{36}NiP_2$ requires C, 57·95; H, 9·75%), infrared light absorption $\nu_{max.}$ (in Nujol) 2100s cm.$^{-1}$ (C$\equiv$C stretching); trans-*Bis(triethylphosphine)di(phenylethynyl)-nickel* formed needles (94%) from ethyl alcohol.

trans-*Bis(diethylphenylphosphine)di(phenylethynyl)nickel.* As described below, the general method gave an anomalous result in that much tris(diethylphenylphosphine)di(phenylethynyl)-nickel was also formed in the reaction. Sodamide was prepared from sodium (1·95 g.), liquid ammonia (300 c.c.), and a small crystal of ferric nitrate. Phenylacetylene (4·27 g.) in ether (40 c.c.) was added, followed by *trans*-[$(PPhEt_2)_2NiBr_2$] (16·5 g.) portionwise with stirring. After ½ hr. ammonium chloride (3 g.) and ether (100 c.c.) were added and the ammonia was allowed to evaporate. After addition of sufficient water to dissolve the inorganic salts, the ether layer was separated, dried ($MgSO_4$), and evaporated to dryness. Recrystallisation of the residue from methyl alcohol gave dark red prisms of slightly impure tris(diethylphenylphosphine)di(phenylethynyl)nickel, m. p. 64—68° (decomp.). These on recrystallisation from light petroleum (b. p. 80—100°) afforded trans-*bis(diethylphenylphosphine)di(phenylethynyl)-nickel* (4·6 g.) as prisms (Found: C, 72·9; H, 6·8%; *M*, ebullioscopically in 1·8% benzene solution, 560. $C_{36}H_{40}NiP_2$ requires C, 72·85; H, 6·8%; *M*, 593). The mother-liquors from this recrystallisation were dark red and when kept at 15° for several days deposited *tris(diethylphenylphosphine)di(phenylethynyl)nickel* (1·2 g.) as prisms (Found: C, 72·55; H, 7·2. $C_{46}H_{55}NiP_3$ requires C, 72·75; H, 7·3%). $\nu_{max.}$ (in Nujol) 2088 cm.$^{-1}$ (C$\equiv$C stretching).

A similar preparation from *trans*-[$(PPhEt_2)_2NiCl_2$) afforded the former nickel compound in 62% yield, which was isolated from the crude product either by chromatography (elution with ether) and crystallisation from ethyl alcohol, or by careful crystallisation from ethyl alcohol.

trans-*Bis(ethyldiphenylphosphine)di(phenylethynyl)nickel.* This was prepared by the general method and purified by chromatography [elution with benzene–light petroleum (b. p. 60—80°) (1 : 1 v/v)] and formed rhombs from acetone (Found: C, 76·65; H, 5·9. $C_{44}H_{40}NiP_2$ requires C, 76·65; H, 5·85%).

trans-*Bis(triphenylphosphine)di(phenylethynyl)nickel* was prepared in 27% yield and formed prisms from chloroform–methyl alcohol (Found: C, 79·35; H, 5·2. $C_{52}H_{40}NiP_2$ requires C, 79·5; H, 5·15%).

Method (5): *Fission with Hydrogen Chloride.*—trans-*Bis(triethylphosphine)chloro(mesityl)-nickel.* *trans*-[$(PEt_3)_2$Ni(mesityl)$_2$] (1·20 g.) in benzene (15 c.c.) was treated with a 0·248N-solution of hydrogen chloride in ether (10 c.c.), and the mixture stored for 1 hr. The solution was filtered and evaporated to dryness, and the residue recrystallised from methyl alcohol, giving *trans*-bis(triethylphosphine)chloro(mesityl)nickel (0·82 g.) as prisms, which sublimed slowly at 155°/1 atm. with very little decomposition.

trans-*Bis(diethylphenylphosphine)chloro(mesityl)nickel.* *trans*-[$(PPhEt_2)_2$Ni(mesityl)$_2$] (1·00 g.) in benzene (10 c.c.) and tetrahydrofuran (5 c.c.) was treated with a slow stream of dry hydrogen chloride for ½ hr. The solvent was evaporated under reduced pressure, and the residue recrystallised from methyl alcohol, to give trans-*bis(diethylphenylphosphine)chloro(mesityl)nickel* as prisms (Found: C, 63·8; H, 7·6. $C_{29}H_{41}ClNiP_2$ requires C, 63·8; H, 7·55%).

trans - *Bis(diethylphenylphosphine)chloro(phenylethynyl)nickel.* *trans* - Bis(diethylphenylphosphine)di(phenylethynyl)nickel (0·93 g.) in tetrahydrofuran (8 c.c.) was treated with a 0·514N-solution of dry hydrogen chloride in ether (3·00 c.c., 1 mol.). After 30 min. evaporation of the solvent and recrystallisation of the residue, first from light petroleum (b. p. 40—80°) and then from methyl alcohol, afforded trans-*bis(diethylphenylphosphine)chloro(phenylethynyl)-nickel* (0·66 g.) as prisms (Found: C, 63·55; H, 6·8. $C_{28}H_{35}ClNiP_2$ requires C, 63·75; H, 6·7%), $\nu_{max.}$ (in hexane) 2098 cm.$^{-1}$ (C$\equiv$C stretching).

Method (6): *Metathetical Replacement Reaction of Organonickel Complexes.*—The arylnickel halide complex (chloride or bromide), in acetone solution, was heated under reflux for 10 min. with an excess of the appropriate alkali-metal salt, lithium bromide for bromides from chlorides, sodium iodide for iodides, sodium nitrite for nitro-complexes, and potassium thiocyanate for thiocyanates. After evaporation of the acetone under reduced pressure water was added to the residue, and the insoluble portion collected, dried, and purified by crystallisation. The following first five complexes were prepared by this method in yields of 70—97%.

TABLE 2. *Dipole moments of some organonickel*(II) *complexes in benzene at* 25°.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_{\mathrm{T}}P$	$_{\mathrm{E}}P$	$_{\mathrm{O}}P$	μ (D)
[(PEt$_3$)$_2$Ni(*o*-tolyl)Cl]							
5·607	1·894						
7·229	1·915	—	(0·30)	257 *	(127)	112 *	2·35 *
[(PEt$_3$)$_2$Ni(mesityl)Br]							
7·674	2·291						
9·087	2·291						
5·923			0·304				
7·037			0·327				
20·02		7·099					
29·96		7·330		336	140	175	2·9
[(PEt$_3$)$_2$Ni(mesityl)Cl]							
4·531	1·912						
6·114	1·922		(0·30)	276 *	(137)	118 *	2·4 *
[(PEt$_2$Ph)$_2$Ni-(1-naphthyl)Br]							
8·143	2·318	—	(0·37)	400 *	(182)	191 *	3·05 *
[(PEt$_2$Ph)$_2$Ni-(*o*-tolyl)$_2$]							
7·367	0·506						
5·116	0·524						
11·69		11·92					
16·30		11·33					
5·650			0·372				
5·984			0·368	188	164	0	0
[(PEt$_2$Ph)$_2$Ni(mesityl)$_2$]							
5·631	0·534						
6·140	0·524	—	(0·37)	208 *	(184)	−3 *	0 *
[(PEt$_3$)$_2$Ni(C≡CPh)$_2$]							
4·914	0·623						
6·660	0·621						
6·645	0·640						
21·42			0·247				
16·94			0·256				
56·85		11·73					
36·08		12·03		191	162	4·5	0·45
[(PPh$_3$)$_2$Ni(C≡CPh)$_2$]							
4·567	0·896						
4·839	0·895		(0·30)	331 *	(251)	41 *	1·4 *
[(PEt$_2$Ph)$_2$Ni(C≡CPh)Cl]							
5·934	1·453						
6·221	1·482		(0·30)	279 *	(171)	83 *	2·0 *

* Calculated by using estimated values of densities and refractivities (see Part I of this series [5]).

trans-*Bis*(*triethylphosphine*)-(1-*naphthyl*)*thiocyanonickel* formed needles from benzene–light petroleum (b. p. 80—100°) (Found: C, 57·25; H, 7·85; N, 2·9. $\mathrm{C_{23}H_{37}NSNiP_2}$ requires C, 57·5; H, 7·75; N, 2·9%). trans-*Bis*(*diethylphenylphosphine*)*iodo*-(1-*naphthyl*)*nickel* formed needles from ethyl alcohol–isopropyl alcohol (Found: C, 56·0; H, 5·85. $C_{30}H_{37}INiP_2$ requires C, 55·85; H, 5·8%). trans-*Bis(diethylphenylphosphine)nitro-(1-naphthyl)nickel* formed prisms from ethyl alcohol (Found: C, 63·75; H, 6·75; N, 2·2. $C_{30}H_{37}O_2NNiP_2$ requires C, 63·9; H, 6·6; N, 2·5%). trans-*Bis(diethylphenylphosphine)-(1-naphthyl)thiocyanatonickel* formed prisms from ethyl alcohol (Found: C, 64·75; H, 6·65; N, 2·3. $C_{31}H_{37}NSNiP_2$ requires C, 63·9; H, 6·6; N, 2·5%). *trans*-Bis(triethylphosphine)bromo(mesityl)nickel formed prisms, m. p. 158—160°, from methyl alcohol (Found: C, 51·05; H, 8·5. Calc. for $C_{21}H_{41}BrNiP_2$ C, 51·05; H, 8·35%). trans-*Bis(triethylphosphine)iodo(pentachlorophenyl)nickel* was obtained as prisms from ethyl alcohol (Found: C, 32·2; H, 4·5. $C_{18}H_{30}Cl_5INiP_2$ requires C, 32·45; H, 4·65%).

trans-*Bis(diethylphenylphosphine)di(phenylethynyl)nickel.* A solution of sodium phenylacetylide was prepared from sodium (0·46 g.), phenylacetylene (2·2 c.c.), liquid ammonia (60 c.c.), and ether (25 c.c.). A solution of *trans*-[$(PPhEt_2)_2$Ni(α-naphthyl)Br] (0·80 g.) in ether (25 c.c.) was added and then after 5 min. ammonium chloride (2·0 g.). The ammonia was then allowed to evaporate, water added, and the crude product isolated from the organic layer and chromatographed. Elution with light petroleum (b. p. 40—60°)–ether (10 : 1) followed by recrystallisation from methyl alcohol afforded *trans*-[$(PPhEt_2)_2Ni(C{\equiv}CPh)_2$] (0·27 g.), identical with an authentic sample (Found: C, 72·6; H, 6·8. Calc. for $C_{36}H_{40}NiP_2$: C, 72·85; H, 6·8%).

Miscellaneous.—Action of diethylphenylphosphine on trans-*bis(diethylphenylphosphine)di(phenylethynyl)nickel.* The phosphine (1 c.c.) was added under nitrogen to a suspension of the nickel complex (0·4 g.) in light petroleum (b. p. 60—80°), and the mixture heated; a deep red solution formed which, on cooling, deposited deep red prisms (0·22 g.), m. p. 64—68°, of tris(diethylphenylphosphine)di(phenylethynyl)nickel.

Halogenation of trans-*bis(diethylphenylphosphine)bromo-(1-naphthyl)nickel.* Bromination. A 0·587N-solution of bromine in benzene (11 c.c.) was added to a solution of the 1-naphthyl complex (1·8 g.) in benzene (20 c.c.). The precipitated oil was collected by decantation, and washed with benzene and then ethyl alcohol; it became crystalline, and recrystallisation from ethyl methyl ketone gave prisms (0·22 g.) (Found: C, 47·3; H, 5·05; Br, 32·2. $C_{30}H_{37}Br_3NiP_2$ requires C, 47·55; H, 4·9; Br, 31·65%); μ (solid at 20°) = 3·4 B.M.

Chlorination. A 1·9N-solution of chlorine in carbon tetrachloride (1·1 c.c.) was added to a solution of the 1-naphthyl complex (0·60 g.) in benzene (10 c.c.). The blue oily precipitate was collected by decantation, washed with light petroleum (b. p. 60—80°), and treated with ethyl alcohol. The *product* slowly crystallised as prisms (0·075 g.) (Found: C, 53·25; H, 5·55. $C_{30}H_{37}BrCl_2NiP_2$ requires C, 53·85; H, 5·5%); μ (solid at 20°) = 3·8 B.M.

Determination of Dipole Moments.—These were determined as described in Parts I and II of this series; the measurements and estimated values (shown in parentheses) are recorded in Table 2. The margin of error is less than ±0·2 D for dipole moments between 4 and 2·5 D. For dipole moments <2·5 D the margin of error will be greater than this but is difficult to estimate. The errors in determining small dipole moments are largely due to the uncertainty in the magnitude of the atom polarisation which has been assumed to be 15% of the electron polarisation in the following Table but may be higher than this in complex compounds.

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