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METAL–BORON COMPOUNDS
XI*. COMPLEXES DERIVED FROM REACTIONS OF BIS(TRIPHENYLPHOSPHINE)(π-ETHYLENE)NICKEL WITH ALKYL AND BORON HALIDES

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SUMMARY

The reactions of bis(triphenylphosphine)(π-ethylene)nickel with boron halides have been examined. In benzene solution, both BBr_3 and $(C_6H_5)_2BBr$ give $[(C_6H_5)_3P]_2NiBr_2$. In diethyl ether, reaction with BBr_3 affords the monomeric nickel(I) complex $[(C_6H_5)_3P]_3NiBr$. The latter is derived from the ether cleavage product C_2H_5Br, and this type of reaction provides a new and convenient synthesis of such complexes. $[(C_6H_6)_3P]_2NiC_2H_4$ reacts with $(C_6H_5)_2BBr$ in ether to produce two crystalline complexes of formulae $\{[(C_6H_5)_3P]_2NiBr\}_n$ and $\{[(C_6H_5)_3P]_2NiB(C_6H_5)_2 \cdot \frac{1}{2}(C_2H_5OC_2H_5)\}_n$ where $n \geqslant 2$. The diamagnetic nickel boryl is thought to contain bridging $[B(C_6H_5)_2]$ groups.

The structures of the compounds and the mechanisms of the reactions involved are discussed in the light of NMR and far-infrared spectroscopic studies.

INTRODUCTION

There exist at present four principal methods for the synthesis of complexes containing metal–boron σ-bonds $M{-}BX_2$ (where X is a halogen or organic group):
(1). Reaction between a transition metal hydride derivative and a boron halide with the elimination of hydrogen halide[2].
(2). Reaction between a metal anion and a boron halide with the elimination of an alkali metal salt[3,4].
(3). Insertion of a transition metal into a boron–halogen bond by oxidative addition of a boron halide to a metal complex[5].
(4). A metathetical reaction between a particular type of cobalt–boron complex and a transition metal halide complex in which transfer of the boryl group takes place with the simultaneous formation of a cobalt-halogen bond[6].

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* For Part X see ref. 1.

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The interest of these compounds lies in the fact that boron is a metalloid having a stable trivalent state with a vacant p-type orbital. Thus, while the metal–boron bond has features in common with the metal–alkyl, the metal–carbene, and the metal–metal bond, it is possible for the boron atom to become four-co-ordinate by interaction with suitable electron-pair donors or to remain three-co-ordinate whilst achieving a degree of double-bonding to contiguous atoms by overlap of the vacant p-orbital on the boron atom with filled orbitals of compatible symmetry on its neighbours. The compounds $Cl_2B{-}M(CO)_3(\pi\text{-}C_6H_5)$, (where M=Mo, W), react with triethylamine to form 1/1 adducts formulated[7] $(C_2H_5)_3N\cdot Cl_2B{-}M(CO)_3(\pi\text{-}C_5H_5)$, while characteristics displayed by a number of the transition metal complexes may be taken[3,8] as evidence for a degree of back-bonding from the metal atom to boron. A review of metal–boron chemistry has very recently appeared[9].

Three compounds containing nickel–boron $M{-}BX_2$ bonds have so far been described in the literature. The nitrosyl complex $[(C_6H_5)_3P]_2Ni(NO)BCl_2$ was prepared[10] by a ligand exchange reaction between (dichloroboryl)bis[o-(diphenylboryl)dimethylglyoximato](triphenylphosphine)cobalt(III), $(C_6H_5)_3P[DMG{-}B(C_6H_5)_2]_2CoBCl_2$, and $[(C_6H_5)_3P]_2Ni(NO)Cl$ [synthetic method (4) above]. Similar metatheses gave[8] $(Diphos)Ni[B(C_6H_5)_2]_2$ and $(Diphos)_2Ni[B(C_6H_5)_2]_2$ from reactions between $(Diphos)_2Co[B(C_6H_5)_2]_2$ and the appropriate nickel halide complexes [where Diphos represents the chelating ditertiary phosphine 1,2-bis(diphenylphosphino)ethane]. The present report is principally concerned with the reactions between halogen compounds of boron and the formally zerovalent olefin complex[11] bis(triphenylphosphine)(π-ethylene)nickel.

RESULTS AND DISCUSSION

Diphenylboron bromide reacts rapidly in benzene with an equimolar quantity of bis(triphenylphosphine)(π-ethylene)nickel. The orange-yellow solution rapidly becomes deep red, but soon begins to decompose so that after some hours at room temperature the reaction yields only bis(triphenylphosphine)nickel dibromide[12] and some elemental nickel. {The dehalogenated boron species which must form in the course of these reactions were not identified. Some boron NMR data on the $[(C_6H_5)_3P]_2NiC_2H_4/(C_6H_5)_2BBr$/ether system are given in the experimental section.} If diethyl ether is used as solvent the red colour persists and, in addition, a yellow crystalline precipitate (I) is formed. (I) may be separated by filtration, and from the filtrate red crystals (II) can be obtained. The reaction between bis(triphenylphosphine)(π-ethylene)nickel and boron tribromide exhibits a similar variation with solvent. In benzene, only a faint transient red colour is observed and $[(C_6H_5)_3P]_2NiBr_2$, together with metallic nickel, is formed. With ether as solvent, a yellow crystalline product (III) is obtained together with some elemental nickel. (In both cases, some unidentified white solids, presumably phosphine/boron halide adducts, are also formed.)

Elemental analysis showed that compound (III) is $[(C_6H_5)_3P]_3NiBr$, apparently identical with the paramagnetic (1.9 B.M.) nickel(I) bromide previously reported[13,14]. To elucidate its method of formation from boron tribromide in ether solution it is necessary to take account of the cleavage of ethers by boron trihalides[15]. Reac-

$$3\ C_2H_5OC_2H_5+BBr_3 \rightarrow 3\ C_2H_5Br+(C_2H_5O)_3B \qquad (1)$$

tion (1) is known to proceed in good yield, but its rate has not been determined. Therefore it is not possible to say whether, under the present conditions, the nickel olefin complex is attacked principally by the boron tribromide or by the cleavage product ethyl bromide. However, the running of a control experiment under identical conditions using ether, bis(triphenylphosphine)(π-ethylene)nickel and ethyl bromide itself showed that reaction (1) may be well advanced before appreciable interaction with the nickel complex occurs. In both cases, the reaction giving (III) appeared to be essentially complete after about 24 hours and the yields and appearance of products displayed great similarity. Inclusion of one molar equivalent of triphenylphosphine in the C_2H_5Br reaction mixture gave a correspondingly greater yield of (III) free from metallic nickel. Further confirmation of the identity of (III) was obtained from its synthesis in quantitative yield from equimolar quantities of bis(triphenylphosphine)(π-ethylene)nickel, triphenylphosphine and n-butyl bromide under the same conditions.

An additional example of the formation of a nickel(I) halide complex by reaction of a zerovalent nickel derivative with an alkyl halide is provided in a previous observation[16]. Tetrakis(triethylphosphine)nickel, in light petroleum solution, was found to react readily with one equivalent of methyl iodide below room temperature to afford a good (76%) yield of a bright yellow air-sensitive crystalline complex which was unstable at room temperature. The PMR spectrum of the product showed a very broad $(C_2H_5)_3P$ signal which could not be saturated, while the benzene (solvent) resonance was not greatly broadened. Elemental (I, Ni) analyses corresponded to the formulation $[(C_2H_5)_3P]_3NiI$. The compound reacted with tetrafluoroethylene to give quantitative yields of $[(C_2H_5)_3P]_2NiI_2$[17] and the heterocyclic complex $[(C_2H_5)_3P]_2Ni(CF_2)_4$[18]. On the basis of these results alone it was not possible to exclude completely the formulation $[(C_2H_5)_3P]_3Ni(CH_3)I$, but there now seems no doubt that the yellow product is the paramagnetic nickel(I) iodide.

The compound (I) formed in the reaction between bis(triphenylphosphine)(π-ethylene)nickel and diphenylboron bromide was shown by elemental analysis to have the formula $\{[(C_6H_5)_3P]_2NiBr\}_n$. It is sensitive to oxygen and moisture, only sparingly soluble in organic solvents, and disproportionates readily into $[(C_6H_5)_3P]_2NiBr_2$ and nickel. A complex of the same stoichiometry is reported[13] to be monomeric in benzene. By reaction with triphenylphosphine in benzene solution (I) undergoes an essentially quantitative conversion into tris(triphenylphosphine)nickel(I) bromide. The latter is obtained as a solvate identical with that produced by recrystallising complex (III) from benzene. Comparison of the far-infrared spectra* of (I) and (III) suggests that (I) is not three-co-ordinate in the solid state. Complex (III) is known[14] to have a tetrahedral structure in the crystal, and accordingly only a single Ni–Br stretch is observed (252 cm^{-1}). The far-infrared spectrum of (I) exhibits three bands assignable[19,20] to such vibrations (276, 270, 245 cm^{-1}). Only a single Ni–P stretch was resolved in each case [196 (III) and 190 (I) cm^{-1}]. Ligand vibrations correspond to those found elsewhere[19]. The Ni–Br and Ni–P frequencies are very close to those observed[19] for the tetrahedral complexes $(R_3P)_2NiBr_2$. The compounds $(1,5\text{-}C_8H_{12})NiX$, ($X = Br, I$)[21], and $[R_2P(CH_2)_2PR_2]NiI$, (R = cyclohexyl)[22], have been previously reported, but their molecular complexity is unknown.

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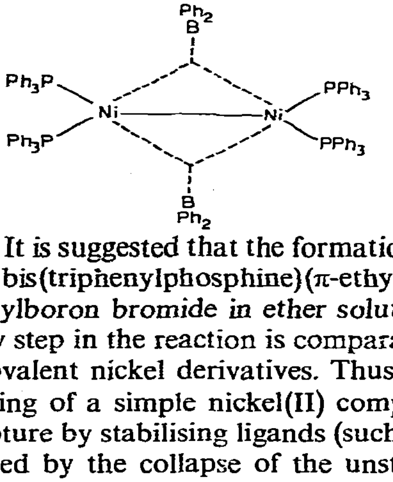
* We thank Herr J. Hönigschmid for recording these spectra.

The second nickel complex obtained in the reaction between bis(triphenylphosphine)(π-ethylene)nickel and diphenylboron bromide is the red, crystalline, very air-sensitive complex (II). The crystals obtained directly from the reaction mixture show a boron resonance at −45.4 ppm [with respect to external $(C_2H_5)_2O\cdot BF_3$], and contain diethyl ether. The latter was clearly seen as the only absorption in the 4.5–16.5 τ region of the NMR spectrum, although melting points and analytical values varied between different crystalline samples. The PMR spectrum was superimposable upon that obtained from a similar concentration of ether in the same solvent (benzene). Since no change in internal chemical shifts was observed, it follows that the ether is not co-ordinated in any way and is therefore most probably present in the crystal itself as lattice solvent only. Recrystallisation of this material gave, in low yield, crystals of similar appearance and infrared spectrum, but of constant melting point and composition, corresponding to $\{[(C_6H_5)_3P]_2NiB(C_6H_5)_2\cdot \frac{1}{2}(C_2H_5OC_2H_5)\}_n$. Owing to the very high sensitivity of solutions of (II) to oxygen and moisture, no direct measurement of n could be made, but a value of $n=2$ is reasonable since the compound, as examined in benzene solution by Evans' NMR method[23], is diamagnetic. Higher values for n cannot be excluded. However, even with this limited information, it appears that complex (II) is likely to contain a boron-bridge system (Ni_2B three-centre bond) with nickel–nickel bonding as illustrated below for $n=2$. This is similar to the hydrogen-bridged structure thought to exist in the compounds[22] $\{[R_2P(CH_2)_xPR_2]NiH\}_2$, (R = cyclohexyl, $x=2$–4).



It is suggested that the formation of the halide complexes (III) and (I) by reaction of bis(triphenylphosphine)(π-ethylene)nickel with ethyl (or n-butyl) bromide and diphenylboron bromide in ether solution may be mechanistically similar, and that the key step in the reaction is comparable to that involved in the classical synthesis of zerovalent nickel derivatives. Thus, the latter process can be pictured[24] as the alkylating of a simple nickel(II) compound by an organoaluminium reagent and the capture by stabilising ligands (such as olefins or phosphines) of the nickel entity produced by the collapse of the unstable nickel alkyl intermediate. Consistently with this representation, it is found that when certain combinations of ligands are present in the intermediates themselves are captured and stabilised so that nickel alkyl complexes, for example bipyridinediethylnickel[24–26] are formed. In the present instance, the following sequence is thought to occur for the alkyl bromides R–Br:

$$\underset{\text{(A)}}{L_2NiC_2H_4} \xrightarrow[-C_2H_4]{R-Br} \underset{\substack{\text{(B)}\\ \text{(IV)}}}{L_2Ni(R)Br} \xrightarrow{-[R^{\cdot}]} \underset{\substack{\text{(C)}\\ \text{(V)}}}{[L_2NiBr]_x} \xrightarrow{L} L_3NiBr$$

$L=(C_6H_5)_3P$; $R=C_2H_5$ or n-C_4H_9

The detailed mechanism by which the alkyl group (R) is lost is not known but a concerted multicentre process, possibly involving hydride formation with expulsion of olefin, is likely. The triphenylphosphine in (C) arises (together with metallic nickel) from one of the triphenylphosphine–nickel species in solution by a disproportionation process. It has previously been observed[16] that oxidative addition of perfluoromethyl iodide to bis(tri-n-butylphosphine)(1,5-cyclooctadiene)nickel in an exactly comparable reaction gives one analogue of (IV) {$[(n\text{-}C_4H_9)_3P]_2Ni(CF_3)I$}* as an isolable compound {albeit together with some $[(n\text{-}C_4H_9)_3P]_2NiI_2$}. In a more recent report[20], oxidative addition reactions to $(R_3P)_2Ni(C_2H_4)$, ($R=C_6H_5$, C_2H_5), gave stable complexes of a similar type from those organic halides which yielded *o*-substituted aryl or perhalovinyl nickel compounds. [The zerovalent nickel precursors were prepared *in situ* and isolated (for $R=C_6H_5$) in one case only.] Thus, evidence for the participation of an intermediate nickel alkyl exists in this case also. It is interesting to note that addition of excess perfluoroalkyl iodide, R_fI ($R_f=CF_3$, C_3F_7), to bis(triphenylphosphine)(π-ethylene)nickel results[27] in the formation of the nickel(III) compounds $[(C_6H_5)_3P]_2Ni(R_f)I_2$, possibly by a similar process involving the collapse of a nickel(IV) intermediate.

The reaction of bis(triphenylphosphine)(π-ethylene)nickel with diphenylboron bromide is comparable with that of the alkyl bromides, the intermediate alkyl being replaced by a boryl. However, owing to the very much greater reactivity of the $(C_6H_5)_2B$–Br bond as compared to that in R–Br, reaction is faster, so that it is the product resulting from a rapid build up of (V) which, in the absence of readily available triphenylphosphine, crystallises from the reaction mixture as the sparingly soluble $\{[(C_6H_5)_3P]_2NiBr\}_n$, (I). The reactions in benzene solution between bis(triphenylphosphine)(π-ethylene)nickel and the boron halides are thought also to involve transient boryls. The product $[(C_6H_5)_3P]_2NiBr_2$ could arise from disproportionation of intermediate (V), since complex (I), while almost insoluble in ether, dissolves in benzene: the solution decomposes at room temperature over a period of hours to give bis(triphenylphosphine)nickel dibromide and nickel.

In view of the ether cleavage reaction mentioned earlier for boron tribromide, it was of interest to establish the extent of the reaction between diethyl ether and diphenylboron bromide. Accordingly, a solution of diphenylboron bromide in ether (5% v/v) was examined by boron NMR spectroscopy. Pure diphenylboron bromide showed a single very broad resonance at -66 ± 1 ppm (lit.[28] -66.7 ppm). Addition of ether instantly produced a white crystalline precipitate which dissolved on shaking. The solution gave a single NMR signal at -33.4 ppm. After a few hours, a second resonance could be detected at -45.1 ppm, and the relative intensities gradually changed until after one week at room temperature only a single signal at -45.1 ppm was observed. The absorptions are assigned as follows and show that, excluding any catalytic effects, the active boron species in the reaction between $[(C_6H_5)_3P]_2NiC_2H_4$ and $(C_6H_5)_2BBr$ is the etherate, $(C_2H_5)_2O\cdot BBr(C_6H_5)_2$, which may be regarded as equivalent to the halide itself in the above consideration of mechanism.

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* $\delta(CF_3)$ 8.4 ppm ($CFCl_3$ internal reference). J(P–F) 42.0 Hz (between outer lines of triplet).

$$\begin{array}{ccccc} (C_6H_5)_2BBr & \xrightarrow{(C_2H_5)_2O} & (C_2H_5)_2O\cdot BBr(C_6H_5)_2 & \rightarrow & (C_6H_5)_2BOC_2H_5+C_2H_5Br \\ -66\text{ ppm} & & -33.4\text{ ppm} & & -45.1\text{ ppm}^{*} \end{array}$$

Time (h)	Relative intensities
0	1/0
10	1/0.25
48	1/0.6
168	0/1

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls on Perkin–Elmer 157 and Beckmann I.R.10 and I.R.11 instruments, using CsBr and polyethylene discs. Proton magnetic resonance (PMR) spectra were measured on a Varian Associates A60A instrument (60 mHz); boron spectra were recorded at 32.1 mHz with a Varian Associates model HA 100 using $(C_2H_5)_2O\cdot BF_3$ as external reference. Melting points were determined in sealed, evacuated tubes and are uncorrected. Benzene, light petroleum (b.p. 50–70°) and diethyl ether were distilled from $LiAlH_4$ under nitrogen. Operations involving solutions of (II) were performed in an evacuated apparatus; otherwise a nitrogen atmosphere was employed. Identification of known compounds was achieved by comparison with authentic samples of their infrared spectra and melting/decomposition behaviour.

(1). *Preparation of bis(triphenylphosphine)(π-ethylene)nickel*

Bis(triphenylphosphine)(π-ethylene)nickel[11] was prepared as described[27] by Ashley-Smith, Green and Stone. Yield 92%. (Found: C, 74.2; H, 5.6; Ni, 9.6. $C_{38}H_{34}NiP_2$ calcd.: C, 74.4; H, 5.6; Ni, 9.6%.)

(2). *Preparation of diphenylboron bromide*

Diphenylboron bromide was prepared as described by Nöth and Vahrenkamp[28]. Yield 79%; b.p. 153–156°/10 mm (lit. 153–159°/10 mm); authentic boron NMR spectrum.

(3). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel with diphenylboron bromide in benzene*

Bis(triphenylphosphine)(π-ethylene)nickel (0.500 g, 0.819 mmole), diphenylboron bromide (0.201 g, 0.819 mmole) and benzene (20 ml) were sealed (liquid air) in a Carius tube (60 ml) *in vacuo*. On warming to room temperature, a red solution formed which rapidly began to decompose. After 60 h the green solution was filtered from some metallic nickel. Concentration of the filtrate and addition of ether gave green crystals of $[(C_6H_5)_3P]_2NiBr_2$ (0.260 g, 86%).

(4). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel with boron tribromide in benzene*

Substitution of boron tribromide (0.206 g, 0.819 mmole) for diphenylboron bromide in (3) gave geen crystals (0.300 g) of $[(C_6H_5)_3P]_2NiBr_2$ contaminated with a small amount of white solid.

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* *cf.*[29]: $(C_6H_5)_3B$ −60.0, $(C_6H_5)(OC_2H_5)_2B$ −28.6, $(C_2H_5O)_3B$ −18.3 ppm.

(5). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel with boron tribromide in ether*

Bis(triphenylphosphine)(π-ethylene)nickel (0.500 g, 0.819 mmole), boron tribromide (0.206 g, 0.819 mmole) and diethyl ether (20 ml) were sealed in a Carius tube as in (3). After 48 h undisturbed at room temperature the tube was shaken periodically to break up the crystalline mass of product. After one week, decantation and washing freed the precipitated product of excess metallic nickel and there remained tris(triphenylphosphine)nickel(I) bromide, (III), as blackened yellow crystals (0.350 g, 93%) separated by crystal picking and identical in substance with the material from (7) (below), together with some white solid (0.040 g).

(6). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel with ethyl bromide in ether*

Substitution of ethyl bromide (0.089 g, 0.819 mmole) for boron tribromide in (5) gave (III) as blackened yellow crystals (0.370 g, 98%) under similar conditions.

(7). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel and triphenylphosphine with alkyl bromides in ether*

Diethyl ether (15 ml) was condensed (liquid air) on to bis(triphenylphosphine)(π-ethylene)nickel (0.500 g, 0.819 mmole) and triphenylphosphine (0.213 g, 0.819 mmole) in a Carius tube (60 ml). The mixture was warmed to room temperature, shaken, and refrozen. Ethyl bromide (0.089 g, 0.819 mmole) in ether (5 ml) was distilled in and the tube sealed. The procedure as in (5) gave yellow crystals of pure tris(triphenylphosphine)nickel(I) bromide, (III), (0.680 g, 90%), m.p. 162–3° (dec.). (Found: C, 70.3; H, 5.0; Br, 8.7; Ni, 6.4. $C_{54}H_{45}BrNiP_3$ calcd.: C, 70.1; H, 4.9; Br, 8.6; Ni, 6.3%.) Infrared spectrum (cm^{-1}): 1583 w, 1570 w, 1473 vs, 1429 vs, 1328 vw, 1309 w, 1277 w, 1186 m, 1159 w (sh), 1151 m, 1117 vw, 1087 s, 1082 s (sh), 1067 m, 1026 m, 996 m, 980 vw, 977 vw, 971 vw, 964 vw, 919 w, 853 vw, 845 vw, 840 w, 752 s, 744 vs, 740 vs, 733 vs, 722 w(sh), 706 s, 693 vs, 682 s, 621 w, 543 w, 508 vs, 481 s, 443 w, 424 w(sh), 412 m, 402 w(sh), 252 s, 218 w, 196 m, 132 w.

A similar experiment using n-butyl bromide (0.112 g, 0.819 mmole) gave 0.720 g (95%) of identical material.

(8). *Reaction of bis(triphenylphosphine)(π-ethylene)nickel with diphenylboron bromide in ether*

Diethyl ether (20 ml) was condensed (liquid air) on to coarsely powdered bis(triphenylphosphine)(π-ethylene)nickel (0.500 g, 0.819 mmole). Diphenylboron bromide (0.201 g, 0.819 mmole) was added under nitrogen and, after re-evacuation of the apparatus, the stirred mixture was allowed to reach room temperature over 30 min. After a further 30 min, filtration gave impure $\{[(C_6H_5)_3P]_2NiBr\}_n$, (I), as a grey-green precipitate (0.410 g). The red filtrate was kept at 0° for 15 h to afford red crystals (IIa), (0.138 g). Recrystallisation of the latter from ether/light petroleum at 0° gave the red crystalline product $\{[(C_6H_5)_3P]_2NiB(C_6H_5)_2\cdot\frac{1}{2}(C_2H_5OC_2H_5)\}_n$, (II), (0.044 g, 7%), m.p. 153–5° (dec.). [Found: C, 76.26; H, 5.65; B, 1.46; Ni, 7.52; O (by difference), 1.24; O (by analysis), 0; P, 7.87. $(C_{50}H_{45}BNiO_{\frac{1}{2}}P_2)_n$ calcd.: C, 76.47; H, 5.78; B, 1.38; Ni, 7.48; O, 1.02; P, 7.89%.] Unsolvated $(C_{48}H_{40}BP_2Ni)_n$ requires: C, 77.04; H, 5.39; B, 1.44; Ni, 7.85; P, 8.28%. Infrared spectrum (cm^{-1}): 1584 w, 1572 w (sh), 1473 s, 1429 vs, 1304 w, 1266 vw, 1238 vw, 1221 m, 1205 m, 1185 w (sh), 1176 m, 1156 vw, 1152 vw, 1115 vw, 1088 s, 1080 m, 1068 w (sh), 1062 w (sh), 1049 vw, 1071 m, 997 m (sh), 994 m, 983 w, 979 w, 969 vw, 955 vw, 935 w, 929 vw, 915 w, 905 vw (sh), 867 vw, 855 m, 838 vw, 832 vw, 763 w, 750 s, 742 vs, 735 s, 725 vs, 706 vs, 692 vs, 628 w, 619 vw, 610 w, 600 m, 589 s, 544 m (sh), 528 vs, 515 vs, 495 s, 487 s, 470 w, 454 m, 441 m, 428 m, 415 m, 402 m (sh), 335 w, 292 w.

The presence of the ether of crystallisation is inferred from the above analysis since it is unlikely that any direct oxygen determination for a compound of 1% oxygen content containing both boron and phosphorus will be reliable.

The mother liquor which afforded (IIa) showed boron NMR signals at −43.8 and −10.9 ppm (1/0.8), while distillation at 100°/10^{-2} mm gave a colourless solution having a single boron resonance at −44.9 ppm. Solutions of (IIa) in benzene or toluene displayed a resonance at −45.4 ppm. Heating the toluene solution in a sealed NMR tube at 100° for 5 h produced a nickel mirror, and a clear, colourless solution showing a boron resonance at −4.0 ppm. The benzene resonance from a solution of (IIa) (76 mg/ml) showed an average shift of 2.7 Hz to higher field than that of the pure solvent contained in a second NMR tube. For a paramagnetism corresponding to the presence of one unpaired electron, the expected[23] shift is a power of ten greater.

Both (IIa) and (II) deteriorate slowly in the solid state.

To obtain complex (I) in a pure state, it is necessary to separate the compound as soon as it is precipitated from the reaction when it is obtained, after washing with ether, as dull yellow microcrystals, $\{[(C_6H_5)_3P]_2NiBr\}_n$ (0.420 g, 78%); m.p. 172–7° (dec.). [Found: C, 63.2; H, 4.5; Br, 12.0; Ni, 8.8%. $(C_{36}H_{30}BrP_2Ni)_n$ calcd.: C, 65.2; H, 4.6; Br, 12.0; Ni, 8.9%.] Infrared spectrum (cm^{-1}): 1584 w, 1570 vw, 1475 s, 1427 vs, 1299 w, 1181 w, 1149 w, 1117 m, 1091 s, 1068 m, 1024 m, 995 m, 968 vw, 927 vw, 916 vw, 854 vw, 844 vw, 759 m, 746 vs, 741 vs, 724 w, 706 s (sh), 693 vs, 618 vw, 540 m (sh), 532 s, 508 vs, 492 s, 484 s, 435 w, 429 w, 415 m, 276 m, 270 s, 245 w, 221 w, 190 w, 151 w.

(9). *Conversion of* $\{[(C_6H_5)_3P]_2NiBr\}_n$ *to tris(triphenylphosphine)nickel(I) bromide*

Benzene (15 ml) was added to a mixture of (I) (0.164 g) and one equivalent of triphenylphosphine (0.065 g) at 0°. After degassing, the frozen (liquid air) mixture was allowed to warm to room temperature and was stirred for 2 h. Filtration and concentration gave tris(triphenylphosphine)nickel(I) bromide as a solvate identical to that obtained from benzene recrystallisation of unsolvated (III). Yield 0.219 g {85% assuming $[(C_6H_5)_3P]_3NiBr \cdot 3\ C_6H_6$[14]}.

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