We wish to report a very simple preparation of the diiodide by electrolysis of a solution of aluminium triiodide in iodomethane using aluminium electrodes.

The solution of the triiodide was prepared *in situ* by warming a solution of iodine in iodomethane with aluminium wire. The resulting solution was electrolysed, using concentric coils of aluminium wire as the electrodes (applied potential: 12 volts). The current slowly rose until the diiodide began to crystallize from solution. The crystals which were obtained as colourless hexagonal plates formed on both electrodes, m.p. 67–68° (lit.[1] 68–71°). (Found: Al, 9.17; I, 84.71; CH_3, 5.22. CH_3AlI_2 calcd.: Al, 9.12; I, 85.80; CH_3, 5.07 %.) The aluminium and iodide were determined by conventional gravimetric methods and the methyl group was determined by reaction with water to produce a measured volume of methane

$$CH_3AlI_2 + 3H_2O \longrightarrow Al(OH)_3 + 2HI + CH_4$$

The filtered electrolyte reacted violently with water to yield methane together with a small amount of hydrogen (0.7 %)*.

The formation of hydrogen would seem to indicate the presence of monovalent aluminium which has been postulated as an intermediate in aqueous electrolysis using aluminium electrodes[2].

It is suggested that monovalent aluminium may be formed initially at the anode [while Al(III) discharges as metal on the cathode], but that this unstable species rapidly reacts with iodomethane to form the diiodide:

$$AlI + CH_3I \longrightarrow CH_3AlI_2$$

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* Identified by mass-spectrometric analysis performed by Messrs. G. GOUGH and B. H. STRINGER of Distillers Company Ltd. (Epsom).

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Zero-valent nickel complexes of bis(phosphino)-o-carboranes

The recent synthesis[1] of *o*-carborane [1,2-dicarbaclovododecaborane(12)][2] provides a new basic molecular framework which, when appropriately substituted at the two carbon atoms, can act as a bi-functional ligand toward metals. Unsub-

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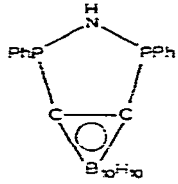
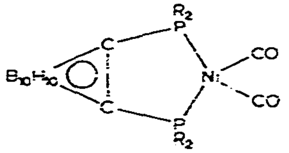
stituted *o*-carborane possesses a nearly regular icosohedral structure as inferred from the structural determinations of the derivatives $B_{10}Cl_8H_2C_2H_2$[3] and $B_{10}H_{10}(CCH_2Br)_2$[4]. Despite the long carbon–carbon distance in the cage [1.67 (ref. 3), 1.64 (ref. 4) Å] and the C–C–C(H_2Br) average external angle of 121° (ref. 4) the carbons of *o*-carborane can be implicated in five-membered exocyclic rings, as demonstrated by the isolation of a number of compounds possessing this ring structure[5,6], including (I)[6]. Inasmuch as the steric and electronic properties of the carborane cage when present in a ligand system were completely uninvestigated at the outset of our studies, we have undertaken the synthesis of complexes in which the donor atoms are directly bound to the cage carbon atoms. Our present report is prompted by the work of Smith[7], who has isolated one mono- and several bis-complexes of nickel(II) with bis(diphenylphosphino)-*o*-carborane and certain brominated derivatives.

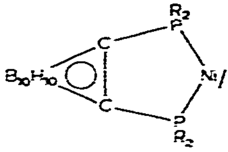
The only functionally di-substituted carborane with ligand potentiality which has been previously isolated is $Ph_2PCB_{10}H_{10}CPPh_2$[6]. We have prepared the bis(diethylphosphino) variant and examined the reactions of both of these phosphinocarboranes with nickel carbonyl. Mono- and di-substituted complexes (II) and (III) (R = Et, Ph) have been isolated. These complexes are diamagnetic, monomeric in benzene solution, and appear entirely analogous to those prepared by the reaction of chelating di-tertiary phosphines with nickel carbonyl[8] or by reduction of the bis-diphosphino nickel(II) cations[9]. The complexes (III) may then be considered as the terminal reduced members of an electron transfer series of complexes with total charge 0, +1, and +2 (ref. 7). The extremely low solubility of (III) in suitable solvents has prevented the study of polarographic oxidation potentials which for complexes with more conventional ligand systems have been used to demonstrate the existence of extensive electron transfer series of complexes[10]. The complexes (II) show two strong carbonyl absorptions at 2021 and 1966 cm^{-1} (R = Ph) and 2013 and 1955 cm^{-1} (R = Et) in dichloromethane solution. These frequencies are ~ 30–40 cm^{-1} higher than those for other bis(ditertiaryphosphino) nickel dicarbonyl complexes such as $\{Ni(CO)_2[o\text{-}C_6H_4(PEt_2)_2]_2\}$ and may be reflective of a greater tendency of the diphosphino-*o*-carborane group to back accept electron density than that of conventional di-phosphine ligands in related tetrahedral complexes. Studies of other functionally di-substituted *o*-carboranes are continuing.



(I)



(II)



(III)

Experimental

All preparations were performed under dry oxygen-free nitrogen. Dilithio-*o*-carborane and bis(diphenylphosphino)-*o*-carborane were prepared as previously described[6]. All analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Systematically low phosphorus analyses were obtained on extensively purified samples which analyzed satisfactorily for other elements. Molecular weights were determined osmometrically in benzene at 37°. All melting points were determined in a sealed tube under nitrogen and are uncorrected.

1) Bis(diethylphosphino)-o-carborane. Dilithio-*o*-carborane prepared from 5.0 g (35 mmole) of the carborane was isolated as a solid and then suspended in 40 ml of dry ether. With stirring and ice-cooling a solution of 9.8 g (79 mmole) of diethylphosphine in 30 ml of dry ether was added over the course of 30 minutes. The reaction mixture was stirred overnight at room temperature and then refluxed for one hour. Ether and excess diethylchlorophosphine were distilled off under 0.1 mm Hg at room temperature leaving a yellowish oil. To the oil was added 10 ml of ether and then, under ice-cooling, 30 ml of water. The ether layer was separated. Addition of 15 ml of methanol to this solution precipitated the product as white micro-crystals. The product was transferred to a short path distillation apparatus and distilled at 0.01 mm Hg using a bath temperature of 150°. The distillate on cooling solidified to a white crystalline mass; yield 4.2 g (38 %), m.p. 56–57.5°. (Found: C, 38.09; H, 9.49; B, 33.85; P, 17.90. $C_{10}H_{30}B_{10}P_2$ calcd.: C, 37.46; H, 9.49; B, 33.77; P, 19.34 %.)

2) [Bis(diphenylphosphino)-o-carborane]nickel dicarbonyl. To a solution of 1.54 g (3.0 mmole) of bis(diphenylphosphino)-*o*-carborane in 30 ml of chloroform was added a solution of 2.4 g (14 mmole) of nickel carbonyl in 15 ml of chloroform. The reaction temperature was maintained at 15–20°. After one hour the evolution of carbon monoxide ceased. The solvent was evaporated under reduced pressure and the solid residue recrystallized from *n*-heptane giving shining yellowish plates; yield 1.4 g (75 %), m.p. 205–208° with decomposition. (Found: C, 53.55; H, 5.01; B, 17.43; P, 8.75; mol. wt., 628. $C_{28}H_{20}B_{10}NiO_2P_2$ calcd.: C, 53.60; H, 4.82; B, 17.25; P, 9.87 %; mol. wt., 627.)

3) Bis[bis(diphenylphosphino)-o-carborane]nickel. Bis(diphenylphosphino)-*o*-carborane (0.40 g, 0.78 mmole) and 0.48 g (0.77 mmole) of bis(diphenylphosphino)-*o*-carboranenickel dicarbonyl were suspended in 15 ml of the hydrocarbon Soltrol 130 (b.p. 180°, Phillips Petroleum Company). The slurry was heated to 180° during which the solid completely dissolved. The solution was refluxed for 25 min with evolution of carbon monoxide. On cooling orange plate-like crystals formed which were filtered off and washed with *n*-pentane (2 × 5 ml); yield 0.75 g. (88 %), m.p. 267–270° with decomposition. (Found: C, 57.46; H, 5.65; B, 19.13; P, 11.26. $C_{52}H_{60}B_{20}NiP_4$ calcd.: C, 57.61; H, 5.58; B, 19.96; P, 11.43 %.)

4) [Bis(diethylphosphino)-o-carborane]nickel dicarbonyl. Bis(diethylphosphino)-*o*-carborane (2.0 g, 6.3 mmole) was dissolved in 50 ml of dichloromethane. The solution was cooled in ice and 1.4 g (8.2 mmole) of nickel carbonyl was added. The reaction mixture was stirred for two hours and allowed to warm to room temperature during that time. The solvent was distilled off under reduced pressure until crystallization began. At this point 5 ml of *n*-heptane was added and the removal of solvent continued until the volume was reduced to ~ 5 ml. Cooling to 5° afforded a crystalline product which was collected and washed with *n*-heptane (2 × 2 ml). Recrystallization from *n*-heptane gave 1.9 g (70 %) of slightly yellowish crystals; m.p. 119–120°. (Found: C, 33.17; H, 6.98; B, 24.74; P, 13.64; mol. wt., 430. $C_{12}H_{30}B_{10}NiO_2P_2$ calcd.: C, 33.12; H, 6.95; B, 24.86; P, 14.23 %; mol. wt., 435.)

5) Bis[bis(diethylphosphino)-o-carborane]nickel. [Bis(diethylphosphino)-*o*-carborane]nickel dicarbonyl (0.96 g, 2.2 mmole) and 0.71 g (2.2 mmole) of bis(diethylphosphino)-*o*-carborane were dissolved in 10 ml of Soltrol (*vide supra*) and refluxed for 40 min. Carbon monoxide was evolved and an orange-red solution was produced.

Cooling to room temperature produced yellow crystals which were collected and washed with *n*-heptane (2 × 4 ml). The product was recrystallized from methylcyclohexane; yield 1.3 g (84 %), m.p. 287–290° with decomposition. (Found: C, 33.68; H, 8.47; B, 29.96; P, 17.51. $C_{20}H_{60}B_{20}NiP_4$ calcd.: C, 34.33; H, 8.64; B, 30.93; P, 17.71 %.)

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PRELIMINARY NOTE

Concerning the amine-catalyzed addition of trichlorosilane to phenylacetylene. The structure of the diadduct

While the hydrosilation of unsaturated hydrocarbons catalyzed by peroxides, platinum or chloroplatinic acid has been investigated intensively, relatively little attention has been given to additions catalyzed by organic bases[1–4]. Accordingly, we undertook a study of base-catalyzed silane additions to alkynes with the object of elucidating the general mechanisms of such reactions.

In agreement with earlier workers[3], we have found that the addition of trichlorosilane to phenylacetylene, catalyzed by tri-*n*-butylamine, gives a considerable amount