Preparation and Crystallographic Characterization of a 2:1 Adduct of Ethynyldicarbadodecaborane(12) and *trans*-$IrCl(CO)(PPh_3)_2$

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Summary Ethynyldicarbadodecaborane(12) reacted with *trans*-$IrCl(CO)(PPh_3)_2$ to afford the 2:1 adduct $IrCl(CO)(PPh_3)_2(B_{10}C_4H_{11})(B_{10}C_4H_{13})$; *X*-ray crystallographic study showed the presence of σ-2-carboranylacetylide and σ-*trans*-2-carboranylvinyl substitutents.

MONOSUBSTITUTED acetylenes have been reported[1] to react with *trans*-$IrCl(CO)(PPh_3)_2$ (I) in a 1:1 molar ratio to form six-co-ordinate hydrido-acetylide complexes. In the course of an investigation ethynyldicarbadodecaborane(12),[2] we observed the formation of a 2:1 adduct and report its synthesis and crystal and molecular structure.

Treatment of a solution of complex (I) in dry benzene under N_2 with excess of $B_{10}C_2H_{11}C{:}CH$ at 80° for 18 h followed by chromatography on silica gel afforded the adduct $Ir(Cl)(CO)(PPh_3)_2(B_{20}C_8H_{24})$ (II);† ν_{max} (Nujol) 2080 (CO), 2140 (C≡C), and 2598 (BH) cm^{-1}; τ (100 MHz; CS_2) *ca.* 2·48 (30H, m, Ph), 3·20 (1H, dt, J_d 16, J_t 2·2 Hz) and 4·97 (1H, dt, J_d 16, J_t 1·7 Hz) (vinyl), and 6·46br (1H, s) and 8·26br (1H, s) (polyhedral CH). These assignments were confirmed by synthesis of deuteriated analogues of (II) from ethynyldicarbadodecaborane(12) deuteriated on the polyhedral carborane and the acetylenic carbon atoms. Reaction of equimolar amounts of the two components in attempts to produce a 1:1 adduct gave unchanged (I) (60·3% recovery) and (II) (75·3% based on consumed Ir). The structure of (II) as its CH_2Cl_2 solvate has been determined by a single-crystal *X*-ray diffraction study.

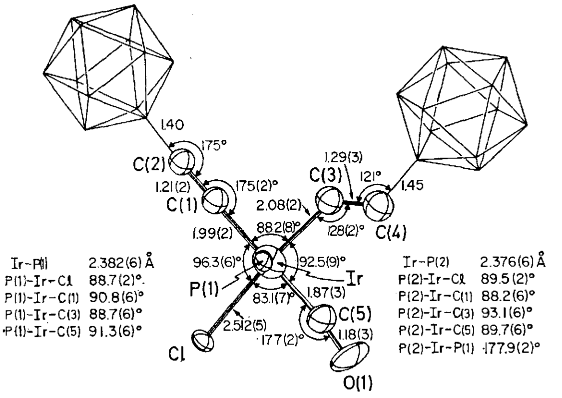

FIGURE. *Molecular structure of* $IrCl(CO)(PPh_3)_2(B_{10}C_4H_{11})$-$(B_{10}C_4H_{13})$. *Phenyl groups have been omitted for clarity.*

Crystal data: $C_{45}H_{54}B_{20}P_2OIrCl,2{\cdot}5CH_2Cl_2$; monoclinic, $P2_1/n$; $a = 12{\cdot}810(2)$, $b = 20{\cdot}033(4)$, $c = 25{\cdot}026(4)$ Å; $\beta = 105{\cdot}30(1)°$; $U = 6195$ Å^3; $D_c = 1{\cdot}42$; $D_m = 1{\cdot}41(2)$ g cm^{-3}, $Z = 4$.

X-Ray diffraction data were collected with a Syntex P$\bar{1}$ diffractometer ($2\theta_{max.}$ 40°) and the structure was solved by standard Fourier and Patterson methods. A correction was applied to compensate for a 16% decay in intensity of three standard reflections during the data collection. Trial absorption corrections gave a maximum deviation from the mean of 5% in F_{obs}. No correction for absorption has been applied at this stage.

In the full-matrix least-squares refinement, the Ph groups of the PPh_3 ligands were refined as rigid bodies (C–C 1·39 Å) as were the carborane cages. Perfect icosahedral symmetry was assumed for the carborane groups and no effort was made to identify the carbon atoms (B–B = B–C = 1·75 Å). Hydrogen atoms were not included in the refinement. The refinement included anisotropic temperature factors for Ir, Cl, P, and the C and O of the carbonyl group. Individual isotropic temperature factors were refined for all other non-hydrogen atoms. In the initial refinement cycles, two independent dichloromethane molecules were included. A difference electron density map indicated that a large hole around one of the crystallographic inversion centres is occupied by a disordered CH_2Cl_2 molecule. The presence of this molecule introduces some disorder into the positions of two neighbouring centrosymmetrically related CH_2Cl_2 molecules. This disordered molecule accounts for the Ir:Cl ratio (from elemental analysis) of 1:6·0. The one chlorine atom of this molecule which could be located in the electron density map was included (half-weighted) in the final refinement. A final discrepancy index of R_1 0·071 was obtained for a total of 3608 observed reflections.

The co-ordination of the iridium atom in this complex is roughly octahedral with the two PPh_3 ligands in *trans*-positions. The chloride, carbonyl, acetylide, and vinyl ligands lie in the same plane, with the acetylide *trans* to the carbonyl. This plane is nearly parallel to the plane of the vinyl ligand. Bond distances and angles obtained are summarized in the Figure.

Formation of this complex can be pictured as the result of oxidative-addition of the acetylene to give an intermediate hydrido-acetylide which reacts immediately with another acetylene molecule to form the vinyl acetylide. Recently, a similar iridium complex $[Ir[C(CN){=}CHCN](CO)(C_4N_2)$-$(PPh_3)_2]$, a product of the reaction of $Ir(PPh_3)_2(CO)_2H$ with dicyanoacetylene,[3] has been structurally characterized.[4] The complex, which contains a dicyanovinyl ligand and a π-bonded dicyanoacetylene, has been described as a model for the intermediate in the transition-metal-catalysed polymerization of acetylenes. Reaction of the ethylnylcarborane with $Ir(PPh_3)_2(CO)_2H$ gives a mixture of products which have not yet been fully characterized. It is interesting that no acetylene trimer was isolated in this reaction or in a similar reaction with Vaska's complex, although 1,2,4-tricarboranylbenzene was obtained from 1-ethynyl-1,2-carborane in the presence of bisacrylonitrilenickel(0).[2]

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† Satisfactory elemental analysis was obtained.

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