Synthesis of Ten- and Eleven-vertex Hydridometallocarbaboranes by Oxidative Addition

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Summary The reaction of $NaC_2B_7H_{12}$ with $[MCl(PR_3)_3]$ (M = Rh, Ir; R = Ar) and $[RuHCl(PPh_3)_3]$ produced the *closo*-metallocarbaboranes 6,6-$(PR_3)_2$-6-H-6,2,3-$MC_2B_7H_9$ and 6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_9$ respectively; similar reaction of $[IrCl(PPh_3)_3]$ with $NaC_2B_8H_{11}$ produced the complex 1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$.

Recently we reported[1] the synthesis of catalytically active hydridometallocarboranes *via* formal oxidative addition of the *nido*-carbaborane anions 7,8- and 7,9-$C_2B_9H_{12}^-$ to $[MCl(PPh_3)_3]$ (M = Rh, Ir). We now describe the extension of this reaction to other *nido*- or *arachno*-carbaborane anions containing bridging hydrides.

Treatment of $[RhCl(PPh_3)_3]$ with an ethereal solution of $NaC_2B_7H_{12}$[2] produced a yellow compound (Ia). The i.r. spectrum of (Ia) in Nujol contained a medium intensity band at 2081 cm^{-1} assigned to Rh–H stretching. Its ^1H-decoupled, 80·5 MHz ^{11}B n.m.r. spectrum in CH_2Cl_2 consisted of broad singlets at τ −23·6, 5·9, 19·5, 22·1, and 33·6 p.p.m. (rel. to external ref. $BF_3 \cdot OEt_2$) of relative areas 1 : 2 : 2 : 1 : 1 respectively. The 100 MHz ^1H n.m.r. spectrum of (Ia) in CD_2Cl_2 contained broad singlets at τ 2·80 (Ph) and 6·35 (carbaborane (CH) of relative intensities 15 : 1. Due to extensive PPh_3 dissociation, no rhodium hydride resonance was observed in the high field region. However, a broad quartet centered at τ 23·45 was observed in a solution of (Ia) in 1·0 M PPh_3 in CH_2Cl_2; upon ^{31}P decoupling this resonance collapsed to a broad doublet with J(Rh–H) 16 Hz. The analogous complex (Ib) with the less labile P $(C_6H_4Me\text{-}p)_3$ ligand did show the expected hydride resonance at τ 22·24 in CH_2Cl_2 as a triplet of doublets. This pattern is consistent with the hydride ligand being coupled to ^{103}Rh [J(Rh–H) 16 Hz] and two equivalent ^{31}P nuclei [J(P–H) 25 Hz]; a similar pattern would be expected for (Ia) but was probably obscured by the broad signals observed. The ^{1}H-decoupled ^{11}B n.m.r. spectrum of (Ib) is similar to that of (Ia): broad singlets of relative area 1:2:3:1 at −22·9, 7·25, 20·5, and 34·0 p.p.m. These data suggest the formulation of compounds (Ia) and (Ib) as 6,6-$[PR_3]$-6-H-6,2,3-$RhC_2B_7H_9$ (Figure). The iridium analogue of (Ia) can be prepared by similar reaction of $NaC_2B_7H_{12}$ with $[IrCl(PPh_3)_3]$ [27% yield; ν Ir–H (Nujol): 2201 cm^{-1}; τ (CD_2Cl_2): 2·79 (30H, m, Ph), 6·72 (2H, s br, carbaborane CH), and 24·47 [1H, t, IrH, J(P–H) 24·5 Hz]. Compound (Ia) catalyses alkene hydrogenation and isomerization with activities comparable with those of the previously reported $[RhH(PPh_3)_2(C_2B_9H_{11})]$ complexes.

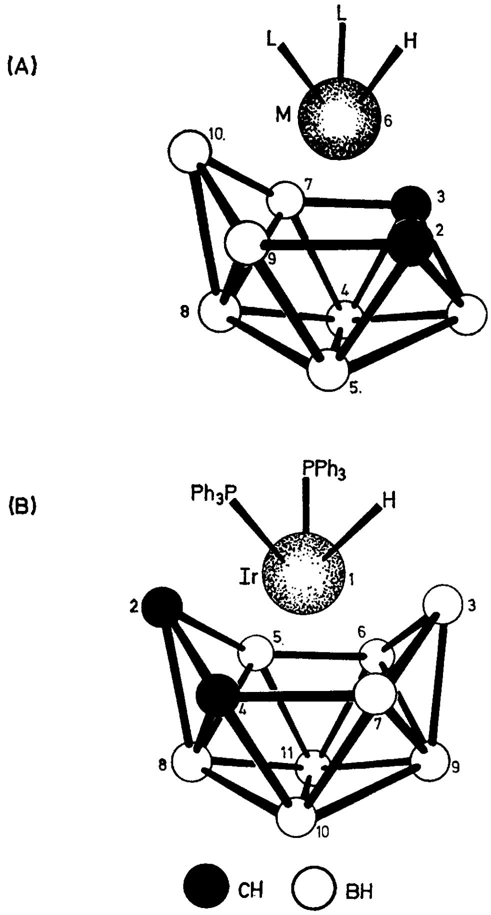

FIGURE. The proposed structures of (Ia) and (Ib) [L = PPh_3 or $C_6H_4Me\text{-}p)_3$] (A); and (V) (B).

The reaction of $[RuHCl(PPh_3)_3]$ with $NaC_2B_7H_{12}$ furnished deep blue needles of 6,6-$[PPh_3]_2$-6,2,3-$RuC_2B_7H_9$ (III) in 89% yield; τ CD_2Cl_2: 2·78 (30H, m, Ph) and 6·19 (2H, s br carbaborane CH); ^{1}H-decoupled ^{11}B n.m.r. spectrum (CH_2Cl_2): τ −108 (1B), −16·4 (1B), 4·17 and 5·86 p.p.m. (5B, overlapping resonances). Complex (III) was probably formed by the ready reductive elimination of H_2 from an intermediate complex $[RuH_2(PPh_3)_2(C_2B_7H_9)]$. This dihydrido complex was not detected, but the analogous compound 2,2-$[PPh_3]$-2,2-H_2-2,1,7-$RuC_2B_9H_{11}$ reversibly eliminates H_2 to form 2,2-$[PPh_3]_2$-2,1,7-$RuC_2B_9H_{11}$ (IV) upon pyrolysis under reduced pressure.[3] Unlike (IV), compound (III) does not oxidatively add H_2 at atmospheric pressure to form a dihydrido Ru^{IV} complex and show virtually no catalytic activity in alkene hydrogenation. Compound (III) reacts instantly with CO in toluene solution to give 6,6-$[CO]_2$-6-PPh_3-6,2,3-$RuC_2B_7H_9$. The derivative chemistry of (III) is extensive and will be reported elsewhere.

Similar treatment of $[IrCl(PPh_3)_3]$ with $NaC_2B_8H_{11}$[4] yielded yellow crystals of (V). The mass spectrum of (V) contained an envelope of parent peaks at m/e 836 with a cut-off at m/e 840 consistent with $^{193}Ir^{11}B_8{}^{31}P_2{}^{12}C_{38}{}^{1}H_{41}$, μ Ir–H) (Nujol) 2133 cm^{-1} (medium intensity); τ (CD_2Cl_2) 2·90 (30H, m, Ph), 6·88 and 7·60 (each 1H, s br, carbaborane CH), and 16·30 [1H, equal intensity q, J(P–H) 14 and 32 Hz, hydride H); the ^{1}H-decoupled ^{11}B n.m.r. spectrum (CH_2Cl_2): τ −55·2, −10·1, −2·7, 6·0, 11·2, 24·8, and 45·0 p.p.m. (all s br of relative area 1:1:1:1:1:2:1 respectively). The n.m.r. spectra are consistent with the absence of symmetry in (V),[5] and with the formulation of (V) as the *closo*-complex 1,1-$[PPh_3]_2$-1-H-1,2,4-$IrC_2B_8H_{10}$.

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[1] T. E. Paxson and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1974, **96**, 4674.

[2] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1968, **90**, 869.

[3] H. S. Wong and M. F. Hawthorne, *J.C.S. Chem. Comm.*, 1976, 257.

[4] B. Štíbr, J. Plešek, and S. Heřmánek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 338.

[5] T. E. Paxson and M. F. Hawthorne, unpublished results; W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 3063; C. J. Jones, J. N. Francis, and M. F. Hawthorne, *ibid.*, 1972, **94**, 8391.