

Synthesis of Ten- and Eleven-vertex Hydridometallo-carbaboranes by Oxidative Addition

By CHU W. JUNG and M. FREDERICK HAWTHORNE*

(Department of Chemistry, University of California, Los Angeles, California 90024)

Summary The reaction of $\text{NaC}_2\text{B}_7\text{H}_{12}$ with $[\text{MCl}(\text{PR}_3)_3]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{R} = \text{Ar}$) and $[\text{RuHCl}(\text{PPh}_3)_3]$ produced the *closo*-metallo-carbaboranes $6,6-(\text{PR}_3)_2-6\text{-H-}6,2,3\text{-MC}_2\text{B}_7\text{H}_9$ and $6,6-(\text{PPh}_3)_2-6,2,3\text{-RuC}_2\text{B}_7\text{H}_9$ respectively; similar reaction of $[\text{IrCl}(\text{PPh}_3)_3]$ with $\text{NaC}_2\text{B}_8\text{H}_{11}$ produced the complex $1,1-(\text{PPh}_3)_2\text{-I-H-}1,2,4\text{-IrC}_2\text{B}_8\text{H}_{10}$.

the extension of this reaction to other *nido*- or *arachno*-carbaborane anions containing bridging hydrides.

Treatment of $[\text{RhCl}(\text{PPh}_3)_3]$ with an ethereal solution of $\text{NaC}_2\text{B}_7\text{H}_{12}$ 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, $80.5\text{ MHz } ^{11}\text{B}$ n.m.r. spectrum in CH_2Cl_2 consisted of broad singlets at $\tau -23.6, 5.9, 19.5, 22.1$, and 33.6 p.p.m. (rel. to external ref. $\text{BF}_3\cdot\text{OEt}_2$) of relative areas $1:2:2:1:1$ respectively. The $100\text{ MHz } ^1\text{H}$ n.m.r. spectrum of (Ia) in CD_2Cl_2 contained broad singlets at $\tau 2.80$ (Ph) and 6.35 (carbaborane CH) of relative intensities $15:1$. Due to extensive PPh_3 dissociation, no rhodium hydride

RECENTLY we reported¹ the synthesis of catalytically active hydridometallo-carbaboranes *via* formal oxidative addition of the *nido*-carbaborane anions $7,8\text{-}$ and $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ to $[\text{MCl}(\text{PPh}_3)_3]$ ($\text{M} = \text{Rh}, \text{Ir}$). We now describe

resonance was observed in the high field region. However, a broad quartet centered at τ 23.45 was observed in a

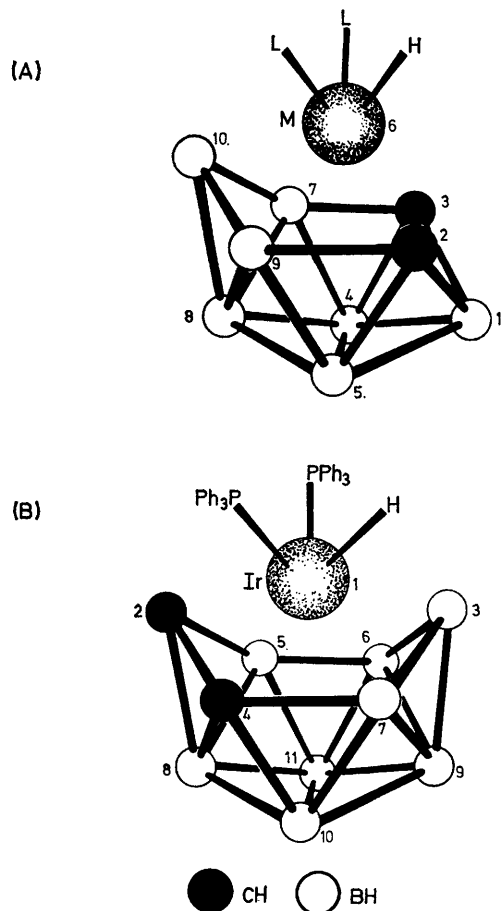


FIGURE. The proposed structures of (Ia) and (Ib) [$L = PPh_3$ or $C_6H_4Me-p)_3$] (A); and (V) (B).

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 $P(C_6H_4Me-p)_3$ 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 1H -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.

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); 1H -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 $NaC_2B_9H_{11}$ 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 $^{193}Ir^{11}B_9^{31}P_2^{12}C_{38}^{1}H_{41}$, 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 1H -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 $1,1-[PPh_3]_2-1-H-1,2,4-IrC_2B_9H_{10}$.

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