Synthesis of $(PPh_3)_2RhH(SB_{10}H_{10})$ and $2\text{-}(L_2IrHCl)\text{-}1\text{-}SB_nH_{n-1}$ ($L = PPh_3$ or $AsPh_3$) by Oxidative Addition of $7\text{-}SB_{10}H_{11}^-$ and *closo*-SB_nH_n ($n = 9$ or 11) to Rhodium and Iridium Phosphines

By David A. Thompson and Ralph W. Rudolph*

(*Department of Chemistry, The University of Michigan, Ann Arbor, MI* 48109)

Summary Oxidative addition of $7\text{-}SB_{10}H_{11}^-$ to $(PPh_3)_3$-RhCl in alcohol results in formation of a stable hydride complex formulated as $(PPh_3)_2RhH(SB_{10}H_{10})$ which functions as a hydrogenation catalyst; the reaction of L_2IrCl ($L = PPh_3$ or $AsPh_3$) with *closo*-$1\text{-}SB_9H_9$ or *closo*-$1\text{-}SB_{11}H_{11}$ results in $2\text{-}(L_2IrHCl)\text{-}1\text{-}SB_nH_{n-1}$ ($n =$ 9 or 11) which contains a B–Ir exodeltahedral bond.

The oxidative addition of exopolyhedral B–H and B–Br bonds in carbaboranes and boranes to Ir, Rh, Pt, and Fe complexes forms borane[1,2] and carbaborane[2,3] complexes containing a metal-boron, two-centre, two-electron bond. Similar oxidative addition reactions provide novel π-bonded rhodium carbaborane complexes capable of the catalytic hydrogenation of olefins.[4] We also have recently demonstrated the oxidative addition of several *closo-* and *nido*-thiaboranes to transition metals and report three new Ir-thiaboranes and a Rh-thiaborane which is a hydrogenation catalyst.

The reaction of L_2IrCl[5] ($L = PPh_3$ or $AsPh_3$) in cyclohexane with *closo*-$1\text{-}SB_nH_n$ ($n = 9$ or 11)[6] under nitrogen results in high yields (>70%) of yellow crystalline compounds formulated by elemental analysis† and spectral data as $2\text{-}(L_2IrHCl)\text{-}1\text{-}SB_9H_8$ (I), and $2\text{-}[(PPh_3)_2IrHCl]\text{-}1\text{-}SB_{11}H_{10}$ (II). This new class of metallothiaboranes is proposed to contain an exodeltahedral[7] metal bonded to a single boron atom of the *closo* framework (Figure). The ^1H n.m.r. spectra of (I) and (II) in $CDCl_3$ show a 1:2:1 hydride triplet at τ 28·3 (J_{P-Ir-H} 14·7 Hz) and 27·3 (J_{P-Ir-H} 14·5 Hz), respectively. ν(Ir–H) occurs at 2199 and 2191 cm^{-1}, respectively, for (I) and (II). These data, consistent with other iridium phosphine complexes, favour formulation of (I) and (II) as trigonal bipyramidal compounds with *trans* H–Ir–Cl bonding.[8] The triphenylarsine derivative of (I) shows a hydride singlet at τ 30·4 and ν(Ir–H) at 2196 cm^{-1}.

On the basis of the broad 32·1 MHz ^{11}B n.m.r. spectra of (I) and (II) the site of the Ir–B bond remains equivocal.

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† Satisfactory elemental analyses were obtained for (I), (II), and (III). Mass spectra of (I) show thiaborane resulting from cleavage of the Ir–B bond.

However, the site of addition was ascertained by reaction with 6,7,8,9,10-D_5-1-SB_9H_4 which gave only a ν(Ir–H) i.r. absorption and no evidence of ν(Ir–D). This observation is indicative of oxidative addition at the undeuteriated belt of 4 boron atoms adjacent to the sulphur heteroatom (sites 2,3,4,5 Figure A).

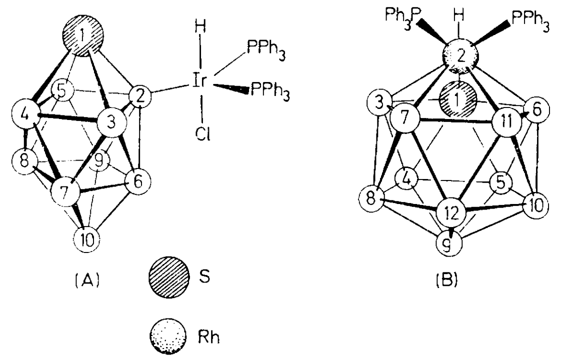

FIGURE. Proposed structures for compounds (I) and (III). (A) 2-[$(PPh_3)_2IrHCl$]-1-SB_9H_8; (B) 2,2-$(PPh_3)_2$-2-H-2,1-Rh-$SB_{10}H_{10}$.

Similar reactions of 6-Br-1-SB_9H_8 and the linked thiaborane 2,2′-$(SB_9H_8)_2$ both appear to result in addition to the B–H bond, but the products are less stable in solution than (I) or (II) and they readily regenerate 6-Br-1-SB_9H_8 or 2,2′-$(SB_9H_8)_2$ respectively.[9] Only after several weeks in $CDCl_3$ do (I) and (II) slowly form SB_9H_9 or $SB_{11}H_{11}$. Attempted inhibition by 10 mole % of galvinoxyl results in no significant decrease in the yield of (I) suggesting no involvement of a radical-chain mechanism.

The new rhodium thiaborane complex, isolated from the reaction of $(PPh_3)_3RhCl$ and $SB_{10}H_{11}^-$ in > 90% yield from refluxing ethanol and formulated as $(PPh_3)_2RhHSB_{10}H_{10}$ (III), has been shown to function as a homogeneous isomerization and hydrogenation catalyst.

The air-stable yellow crystals of (III) obtained by recrystallization from CH_2Cl_2–EtOH under nitrogen show no evidence of decomposition in air as a solid but do slowly darken to a red solution in methylene chloride or benzene when exposed to air. The ν(Rh–H) absorption at 2080 cm^{-1} and 100 MHz ^1H n.m.r. signal at τ 17·2 (J_{P-Rh-H} 26 Hz, J_{Rh-H} 18 Hz) support the proposed hydride structure (Figure). As is observed for other transition-metal boranes containing phosphines, the ^{11}B n.m.r. spectrum is very broad at 32·1 MHz; however, the peaks centred at (relative intensity in parentheses) −10·6(6), +12·2(2), and +15·6(2) p.p.m. in $CDCl_3$ relative to BF_3–OEt_2 are consistent with known transition-metal derivatives of $SB_{10}H_{10}^{2-}$.[10]

10^{-3}M-Solutions of (III) in benzene isomerize and hydrogenate 0·2M solutions of oct-1-ene at 100 atm of H_2 and 25 °C. 50% conversion into octane in < 1 h has been observed with concurrent isomerization of the oct-1-ene. The catalyst is recovered unchanged. Under similar conditions < 1% of the cyclohexene is hydrogenated during the same period. The reduction of (−)-carvone (*p*-mentha-6,8-dien-2-one), proceeding slower than reduction of oct-1-ene, is only 50% complete after 60 h at 100 atm H_2. Selective hydrogenation of the terminal olefinic group is indicated by ^{13}C n.m.r. and mass spectral data. Both isomerization and hydrogenation are inhibited by addition of triphenylphosphine implying loss of a ligand as a prerequisite to catalysis. The addition of $SB_{10}H_{11}^-$ does not inhibit the catalysis.

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