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Boryliridium and Boraethyliridium Complexes *fac*-$[IrH_2(PMe_3)_3(BRR')]$ and *fac*-$[IrH(PMe_3)_3(\eta^2\text{-}CH_2BHRR')]$[†]

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The bonding and reactivity of unsaturated boron-containing fragments coordinated to mononuclear transition-metal centers is currently an active area of research[1] with significant implications for transition-metal-catalyzed hydroboration[2] of unsaturated organic substrates and dehydrocoupling of boranes.[3] Although transition-metal boryl ($M-BR_2$) complexes were prepared over 25 years ago,[4] little is known regarding their structure and reactivity, and few contributions have appeared[5] since the area was reviewed[6] in 1970. The present work was undertaken as part of a program to define more completely the role of the transition metal in metal-catalyzed hydroboration reactions. We now report two new boryliridium complexes derived from B-H bond activation of alkylboranes, the first structural characterization of the $M-BR_2$ linkage,[7] and the conversion of $IrCH_3$ and BR_2H into boraethyl ($M-CH_2BHR_2$) complexes.

Reactions of $[IrH(PMe_3)_4]$[8] with thexylborane or 9-BBN dimer give the phosphine-boranes $Me_3P-BHRR'$ (R = H, R' = CMe_2CHMe_2, **1a**; BRR' = borabicyclo[3.3.1]nonyl, **1b**) and colorless crystals of the new boryliridium complexes *fac*-$[IrH_2(PMe_3)_3(BRR')]$ **2a**,**b**. The boryl complexes are characterized by a low-field (>100 ppm) ^{11}B NMR chemical shift.[9] For **2a**, the terminal B-H is observed as a broad ^1H NMR resonance at δ 11.5 which becomes a triplet of doublets ($^3J_{HP}$ = 14, 12 Hz) upon ^{11}B decoupling. Coupling constants ($^2J_{HP}$ = 100, 18 Hz for **2a**) for the typical AA′ Ir-H ^1H NMR resonances were obtained by selective ^{31}P decoupling. The molecular structure[10] of **2b** (Figure 1A) consists of a distorted octahedral geometry about the Ir(III) center containing a facial arrangement of PMe_3 ligands, two cis hydrides, and a trigonal-planar boryl ligand (sum of angles about B = 359°). The plane of the boryl ligand is nearly aligned with the P3-Ir-H1′ axis. The Ir-B bond distance, 2.093 (7) Å, is similar to Ir-B (2.071 (14) Å[11]) in *cis,trans*-$[IrBr_2(PMe_3)_2(CO)(\sigma\text{-}2\text{-}B_5H_8)]$ and to Ir-C (2.127 (6) Å) in $[IrH(I)(Me)[NH(SiMe_2CH_2PPr^i{}_2)_2]$,[12] suggesting that $d\pi-p\pi$ backbonding from Ir to B is weak.

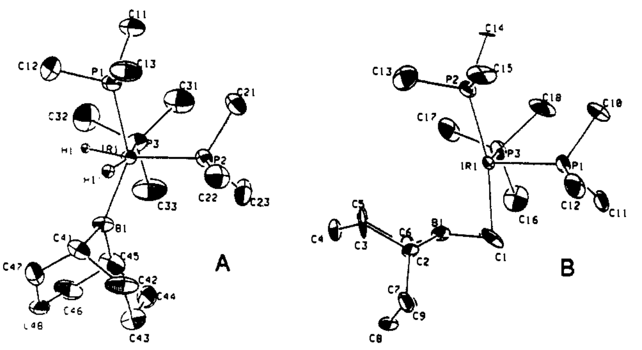

Figure 1. Molecular structures of (A) *fac*-$[IrH_2(PMe_3)_3(BC_8H_{14})]$ (**2b**) and (B) *fac*-$[IrH(PMe_3)_3(\eta^2\text{-}CH_2BHC_8H_{14})]$ (**3b**). Hydrogen atoms (except H1 and H1′) are omitted for clarity.

Similar reactions of $[IrMe(PMe_3)_4]$[13] with thexylborane or 9-BBN give colorless crystals of the boraethyl complexes *fac*-$[IrH(PMe_3)_3(\eta^2\text{-}CH_2BHRR')]$, **3a**,**b**. The ^{11}B NMR chemical shifts are indicative of four-coordinate boron, and the CH_2 moiety was identified by ^1H and low-temperature ^{13}C NMR spectroscopy.[14] The ^{31}P and ^1H NMR spectra of **3a** indicate three inequivalent PMe_3 ligands and distinct Ir-H and Ir-H-B resonances at 25 °C. While the latter resonances broaden only slightly at 80 °C, complex **3b** has equivalent equatorial cis hydride and PMe_3 ligands even at -80 °C. The molecular structure of **3b** (Figure 1B), however, features an unsymmetrically bound (CH_2BHR_2) moiety (Ir-B = 2.50 (2) Å, Ir-C = 2.19 (2) Å, Ir-C1-B = 82 (1)°). While the hydrogen atoms bonded to iridium were not located in the crystal structure, the boron atom is 0.30 Å out of the C1-C2-C6 plane toward the Ir-H that is presumably trans to P1, suggestive of an M-H-B interaction. Indeed, the IR spectra of **3a** (**3b**) in hexane contain absorptions at 2049 (2039) cm^{-1} and broad absorptions at 1995 (1980) cm^{-1} which are assigned to Ir-H and Ir-H-B vibrations, respectively. Two alternative structures, A and B, illustrate the nature of the 3c-2e$^-$ Ir-H-B interactions in **3a**,**b**. The spectroscopic data suggest a larger contribution from A for **3a** than for **3b**.

[†] Dupont contribution No. 5531.

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(9) Selected NMR spectral data in toluene-d_8 are as follows. **2a**: $^{31}P\{^1H\}$ -53.0 (d, $^2J_{PP}$ = 20 Hz, 2 P), -63.0 ppm (br, 1 P); $^{11}B\{^1H\}$ NMR 107.8 ppm (br); ^1H δ 11.5 (br, BH), -11.20 (d tr, AA′, $^2J_{HP}$ = 100, 18 Hz, IrH); $^1H\{^{11}B\}$ δ 11.5 (tr d, $^3J_{HP}$ = 14, 12 Hz). **2b**: $^{31}P\{^1H\}$ -52.0 (d, $^2J_{PP}$ = 20 Hz, 2 P), -64.1 ppm (br, 1 P) [at -80 °C: -50.1 (d, $^2J_{PP}$ = 21 Hz, 2 P), -62.7 ppm (tr, 1 P)]; $^{11}B\{^1H\}$ 106.2 (br); ^1H δ -11.23 (d tr, AA′, $^2J_{HP}$ = 133, 14 Hz).

(10) Crystal data for **2b** (from hexane/toluene): $C_{17}H_{43}BP_3Ir$: FW = 543.46, monoclinic, space group $P2_1$ (No. 4), a = 10.092 (4) Å, b = 11.154 (1) Å, c = 10.692 (4) Å, β = 116.21 (2)°, V = 1176.6 Å^3, Z = 2, ρ(calcd) = 1.534 g cm^{-3}; T = 203 K. Anisotropic refinement of all non-hydrogen atoms (H1, H1′ isotropic, remaining H's fixed; 215 variables) using 2599 reflections with $I > 3\sigma(I)$, from 2731 unique data collected, gave R = 0.024 and R_w = 0.023. One wing of the BBN ligand was disordered between chair and boat conformations (with only one shown for clarity) and was refined as two half-weighted atoms. Crystal data for **3b** (from hexane): $C_{18}H_{45}BP_3Ir$; FW = 557.55, orthorhombic, space group $P22_12_1$ (No. 18), a = 9.879 (2) Å, b = 12.353 (3) Å, c = 20.047 (6) Å, V = 2446 (1) Å^3, Z = 4, ρ(calcd) = 1.51 g cm^{-3}; T = 150 K. Anisotropic refinement of all non-hydrogen atoms (209 variables) using 2333 reflections with $I > 3\sigma(I)$, from 2464 unique data collected, gave R = 0.051 and R_w = 0.060. The empirical absorption correction (ψ-scan) was incomplete due to an equipment malfunction resulting in loss of the crystal. This inadequacy is responsible for the corruption of some of the light-atom thermal parameters, particularly U_{33}. Full details will be published separately (see also supplementary material).

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(14) Selected NMR spectral data in toluene-d_8 are as follows. **3a**: $^{31}P\{^1H\}$ -48.8 (br, 1 P), -56.5 ppm (br ov, 2 P); $^{11}B\{^1H\}$ 4.8 ppm (br); ^1H δ 0.94 (m, CH_2), -12.06 (br d, $^2J_{HP}$ = 105 Hz, IrHB), -14.70 (d d d, $^2J_{HP}$ = 151, 22, 22 Hz, IrH); ^{13}C (-80 °C) 4.3 ppm (br tr d, J_{CH} = 130 Hz, $^2J_{CP}$ = 23 Hz). **3b**: $^{31}P\{^1H\}$ -55.1 (d, $^2J_{PP}$ = 11 Hz, 2 P), -57.2 ppm (tr, 1 P); $^{11}B\{^1H\}$ 20.6 ppm (br); ^1H δ 0.96 (d tr, $^3J_{HP}$ = 9, 6 Hz, CH_2), -13.25 (d tr, AA′, 113, 18 Hz, IrH/IrHB); ^{13}C (-80 °C) 2.7 ppm (br tr d, J_{CH} = 132 Hz, $^2J_{CP}$ = 25 Hz).

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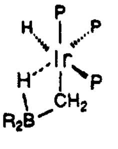
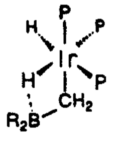


A



B

The formation of **3a**,**b** likely results from oxidative addition of the organoborane B–H bond to the unsaturated Ir center, followed by B–C bond reductive elimination and β-H abstraction from the resulting B–Me group.[15] While an analogous reductive elimination process has been proposed[2] as the B–C-bond-forming step in rhodium-catalyzed alkene hydroboration, the additional β-H abstraction process observed here likely results from the increased basicity of the iridium center, which retains the BR_2Me Lewis acid in the metal coordination sphere. The reactivity of complexes **2** and **3** with unsaturated organic substrates is under investigation.

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Supplementary Material Available: Typical preparation of **2** and **3**, X-ray experimental details, and tables of bond distances and angles, atomic coordinates, and temperature factors for complexes **2b** and **3b** (10 pages); complete listings of observed and calculated structure factors for complexes **2b** and **3b** (16 pages). Ordering information is given on any current masthead page.

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Iridium(III) Hydride Complexes for the Catalytic Enantioselective Hydrogenation of Imines

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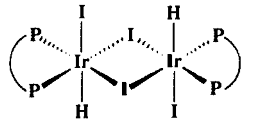
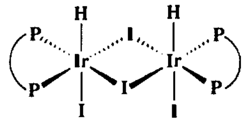
Considerable research during the past 20 years has produced remarkable catalysts based on Rh and Ru for enantioselective homogeneous hydrogenation of olefins and ketones where in many cases optical yields >95% have been observed.[1] On the other hand, few publications have appeared that deal with asymmetric hydrogenation of the C=N bond of imines to form chiral amines,[2] the greatest success having been obtained by using in situ mixtures of M/chiral diphosphine/X (M = Rh^I or Ir^I, X = NEt_3 or halide) but the nature and the mechanism of action of the catalyst is not well-defined.

We report herein the discovery of a new class of iridium(III)–diphosphine–monohydrido complexes, $[Ir(P\text{-}P)HI_2]_2$, **1a–d** (e.g., P–P = DIOP, BDPP, NORPHOS, BINAP),[3] that are effective for asymmetric reduction of prochiral imines to the corresponding amine with high turnover numbers and moderate to good enantioselectivity.

We have previously reported[4] that when $[Ir(P\text{-}P)(COD)]BF_4$ (P–P = dppe, dpe, R-prophos) is refluxed with excess LiI (>30 equiv) in acetone, the complexes $Li[Ir(P\text{-}P)I_4]$ were isolated and found to be chemoselective catalysts for the hydrogenation of imines. Under similar conditions,[5] complexes **1** are prepared and isolated as air-stable pale yellow powders that can be recrystallized from CH_2Cl_2/Et_2O or CH_2Cl_2/hexane in 50–60% yield. In solution the ^1H and ^{31}P NMR spectra show that **1** exists as a mixture of two geometrical isomeric dimers,[5b] where the hydride ligands are either transoid or cisoid to each other. The structure of the transoid isomer has been confirmed by an X-ray determination.[6]



transoid-**1**



cisoid-**1**

Some preliminary results on the enantioselective hydrogenation of selected imines (≥1000 equiv) catalyzed by complexes **1a–d** are compiled in Table I. Reactions were carried out at ambient temperature and >10 bar of H_2 pressure and proceeded smoothly to completion. The reduction of imine I by catalysts **1a** and **1b** (entries 1 and 2) occurred rapidly but with modest ee (11–40%). However, II (entries 3–5) could be hydrogenated conveniently, and an ee of 80% was obtained by using $[Ir((-)\text{-}BDPP)HI_2]_2$ as catalyst. The asymmetric reduction of a model herbicide precursor, III (entries 6–10), shows **1a**, $[Ir((-)\text{-}DIOP)HI_2]_2$, to yield the highest ee (63%), but extensive screening of other chiral diphosphine ligands for this substrate reduction has not been carried out. Interestingly, the BINAP complex **1d** is ineffective

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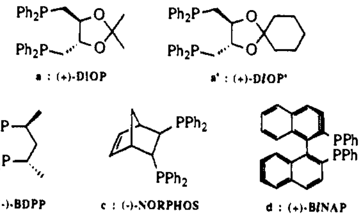
[1] For reviews, see: (a) Kagan, H. B. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, p 463. (b) Morisson, J. D., Ed. *Asymmetric Synthesis*; Vol. 5, Chiral Catalysis; Academic Press: Orlando, FL, 1985. (c) Nogradi, M. *Stereoselective Synthesis*; VCH Verlagsgesellschaft: Weinheim, 1987. (d) Kagan, H. B. *Bull. Soc. Chim. Fr.* **1988**, *5*, 846. (e) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129. (f) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (g) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187.

[2] (a) Spindler, F.; Pugin, B.; Blaser, H.-U. *Angew. Chem. Int. Ed. Eng.* **1990**, *29*, 558. (b) Bakos, J.; Toth, I.; Heil, B.; Szalontai, G.; Parkanyi, L.; Fulop, V. *J. Organomet. Chem.* **1989**, *370*, 263. (c) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466. (d) Vastag, S.; Bakos, J.; Toros, S.; Takach, N. E.; King, R. B.; Heil, B.; Marko, L. *J. Mol. Catal.* **1984**, *22*, 283.

[3] Abbreviations defined:



[4] Ng Cheong Chan, Y.; Meyer, D.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 869.

[5] (a) For example, the $[Ir(DIOP)HI_2]_2$ complex is synthesized as follows: $[Ir(DIOP)(COD)]BF_4$ (600 mg; 0.68 mmol) was refluxed with LiI (900 mg; 6.7 mmol) in acetone (10 mL) for 20 h, whereby a yellow precipitate was slowly formed. After cooling to room temperature, the yellow solid was separated by centrifuge, then washed two times with acetone (5 mL), and dried. The crude product thus obtained was extracted with dichloromethane (10 mL) to remove insoluble LiI. Ether (10 mL) was then added to the solution, and after 1 day at room temperature, pale yellow crystals had formed (375 mg; 58%). All new complexes have been characterized by elemental analyses, ^1H and ^{31}P NMR, and FAB mass spectroscopy. (b) Ratio of isomers and corresponding hydride shifts (200 MHz, CD_2Cl_2, δ in ppm and $^2J_{PH}$ in Hz): P–P = DIOP (same with DIOP'), major/minor = 9/1 ($\delta = -16.2$ (t), $J = 11$, and -16.7 (t), $J = 11$); P–P = BDPP, major/minor = 7/3 ($\delta = -16.2$ (dd), $\sum J = 21.5$, and -16.9 (dd), $\sum J = 21.4$); P–P = NORPHOS, major/minor = 7/3 ($\delta = -11.9$ (dd), $J = 17.0$, and -12.3 (dd) $\sum J = 18.0$); P–P = BINAP, major/miinor = 10/0 ($\delta = -19.5$ (dd), $\sum J = 21.5$). In all cases, the major isomer is probably transoid. (c) GC–MS analysis of the solution after reaction shows the presence of free COD and an excess of $CH_3COCH{=}C(CH_3)_2$, the product of an aldol condensation of acetone catalyzed by Li^+. The hydride source is thus probably H_2O. Further synthesis using wet acetone (0.2% H_2O) gave similar results. Synthesis using acetone-d_6 yielded the corresponding dideuteride complex.

[6] Ng Cheong Chan, Y.; Meyer, D.; Osborn, J. A., unpublished results.

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