Transition Metal–Boryl Compounds: Synthesis, Reactivity, and Structure

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I. Introduction

Transition metal−boryl compounds are classed as those in which a covalent two-center, two-electron bond exists between the metal center and a three-coordinate, sp^2-hybridized boron atom (M−BR$_2$). The majority of previously described metal−boryl compounds were reported by Nöth and Schmid,[1−21] most of which have been reviewed in the literature,[22,23] although there is some considerable doubt as to whether many of these compounds have been correctly formulated and many of the spectroscopic data (particularly ^{11}B NMR data) are inconsistent with more recent results. Nevertheless, much of this work is included here for the sake of completeness although an indication has been given where the data are clearly at odds with more recent studies.

More recently a number of research groups have examined a range of synthetic routes for the preparation of metal−boryls since these compounds have been proposed as intermediates in a number of catalytic systems including metal-catalyzed hydroboration of unsaturated substrates,[24] as well as the more recently studied metal-catalyzed diboration of alkynes, alkenes, 1,3-dienes, α,β-unsaturated ketones, and allenes.[25−37] In addition, related theoretical studies regarding M−B bond energies of metal−boryl compounds and the mapping of reaction coordinates for the proposed catalytic cycles have also been reported.[38−44]

Initially, Nöth and Schmid examined four general synthetic routes for the preparation of metal−boryl compounds, namely: (i) the nucleophilic reaction of anionic metal species with haloboranes (X−BR$_2$, X = Cl, Br, I), (ii) the reaction of metal hydride compounds with haloboranes, (iii) σ-bond metathesis reactions with cobalt bisboryl compounds, and (iv) oxidative addition of haloboranes by metal compounds. Recent investigations have generally involved similar synthetic approaches, although reactions involving oxidative addition of B−H bonds in alkoxy-stabilized boranes such as HBcat (cat = catecholato; 1,2-O$_2$C$_6$H$_4$) and HBpin (pin = pinacolato; OCMe$_2$CMe$_2$O), and B−B bonds in the related diborane(4) compounds[45] have also been utilized in preference to oxidative addition reactions utilizing the less stable halo, alkyl, or arylboranes.

The renewed interest in the synthesis, characterization, and reactivity of metal−boryl compounds in recent years has additionally provided the first structural data for these catalytically important species. In this work, particular attention will be given to more current studies involving metal−boryl

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Geoffrey J. Irvine completed his Ph.D. in 1996 at the University of Auckland, New Zealand. His thesis work, under the guidance of Professor Warren R. Roper and Dr. L. James Wright, concerned the synthesis and reactivity of ruthenium and osmium boryl complexes. In May 1996, he joined the research group of Associate Professor D. Scott Bohle at the University of Wyoming as a postdoctoral fellow where he developed the synthesis of new precursor molecules for the generation of the biologically relevant cytotoxin, hypothiocyanite. Currently he is working for Critical Angle LLC, developing innovative biosensors for medical, environmental, and security applications.

Gerry Lesley received his bachelor's and master's degrees from the University of Waterloo the latter under the supervision of Professor T. B. Marder. He then worked as a research associate with Professor S. Collins also at Waterloo and later with Dr. A. Hunter at the University of Edmonton. In 1993, he returned to Waterloo and received his Ph.D. with Professor T. B. Marder in 1996. After a few months of postdoctoral work with Professor S. Collins, he took up a second postdoctoral appointment at the University of Bristol working with Dr. N. C. Norman. Current interests are in the field of transition metal catalysis and conducting polymers.

Todd Marder received his B.Sc. in Chemistry from M.I.T. (1976) where he worked with Professor A. Davison, and his Ph.D. from the University of California at Los Angeles (1981) with Professor M. F. Hawthorne. He then carried out postdoctoral research with Professor F. G. A. Stone at the University of Bristol in England after which he spent two years as a Visiting Research Scientist at DuPont Central Research in Wilmington, DE. He joined the faculty at the University of Waterloo in Canada in 1985, and in 1995 was the recipient of the Rutherford Memorial Medal for Chemistry of the Royal Society of Canada. He moved to the University of Durham in England in 1997 where he holds the Chair in Inorganic Chemistry. His current research interests include synthesis, structure, bonding and reactivity of organometallic and metal–boron compounds, homogeneous catalysis, luminescence, nonlinear optics, liquid crystals, and crystal engineering.

Nick Norman received his B.Sc. in chemistry from the University of Bristol in 1979 and his Ph.D. from the same institution in 1982 under the supervision of Professor Michael Green. After two years of postdoctoral research with Professor Alan H. Cowley FRS at the University of Texas at Austin, he returned to the U.K. in 1985 to a one-year temporary lectureship at the University of Manchester. In 1986 he moved to the University of Newcastle upon Tyne and returned to Bristol in 1996 to take up a position as Reader in Inorganic Chemistry. Current interests center around the chemistry of boron and the heavier p-block elements.

compounds with an emphasis on synthesis, reactivity, structure, and spectroscopy.

II. Synthesis of Metal–Boryl Compounds

A. Reactions of Haloboranes with Transition Metal Salts

Nöth and Schmid were the first to report the synthesis of compounds containing two-center, two-electron metal–boron bonds although as discussed in section I, there is some doubt as to whether the compounds have been correctly formulated.[1] Their synthesis involved the reaction of anionic transition metal complexes with haloboranes (eq 1), affording metal–boryl compounds and 1 equiv of the halide salt.

$$\mathrm{Na[ML_n]} + \mathrm{ClBR_2} \longrightarrow \mathrm{[L_nMBR_2]} + \mathrm{NaCl} \qquad (1)$$

$$\begin{aligned}\mathrm{ML_n} &= \mathrm{Mn(CO)_5;\ BR_2 = B(NMe_2)_2,\ B(NMePh)_2} \\ &\qquad \mathrm{[BR_2 = BBu_2,\ BPh_2\ no\ reaction]} \\ &= \mathrm{Mn(CO)_4(PPh_3);\ BR_2 = B(NMe_2)_2,\ BBu_2,\ BPh_2} \\ &= \mathrm{CpFe(CO)_2;\ BR_2 = B(NMe_2)_2,\ B(NPh_2)_2,\ BCl_2}\end{aligned}$$

Subsequently, the same authors used this general synthetic route to form several additional L_nM-BR_2 compounds, including some tin derivatives ($L_nM = Re(CO)_5$, $R = NMe_2$; $L_nM = Co(CO)_4$, $R = Cl$, Ph, NMe_2; $L_nM = Co(CO)_3L'$, $L' = PPh_3$, $R = Cl$, Ph, NMe_2, $L' = PBu_3$, $R = Ph$, $L' = AsPh_3$, $R = Cl$, Ph;[2] $L_nM = SnEt_3$, $R = NMe_2$;[3] $L_nM = Mn(CO)_4(PPh_3)$, $R = Ph$, Bu, Cl, OMe;[6] $L_nM = CpMo(CO)_3$, $CpW(CO)_3$ ($Cp = \eta\text{-}C_5H_5$), $R = Ph$, Cl;[7] $L_nM = Co(dmg)_2$ (dmg = dimethylglyoximato), $R = Ph$;[10] $L_nM = SnMe_3$, $R = NMe_2$, NEt_2,[19] and $L_nM = Co(PF_3)_4$, $R = Ph$, NMe_2[21]). Related bisboryl $[Co(dmg)_2(BR_2)_2]$ compounds were also prepared which appear to have $Co-BR_2$ ($R = Ph$, Cl, NMe_2) bonds.[10] However, although numerous metal–boryl compounds were prepared, characterization was generally limited (IR, ^{11}B NMR, melting

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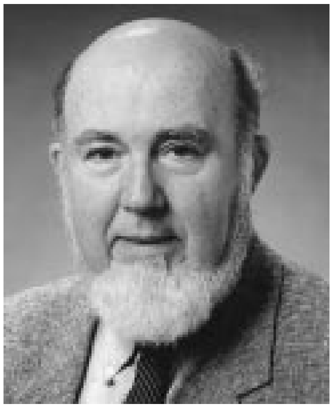
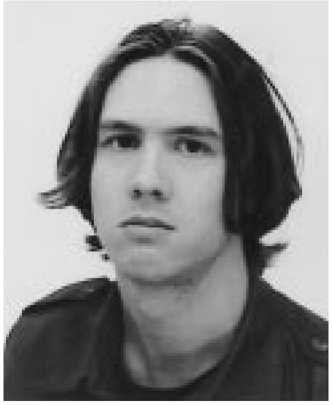
Edward Robins gained a B.Sc. in chemistry from the University of Newcastle upon Tyne in 1994 and his Ph.D. with Dr. N. C. Norman at the University of Bristol in 1997. He is currently a postdoctoral research associate at Durham University with Professor T. B. Marder but will shortly move to Purdue University to work with Jillian Buriak in the area of functionalization of porous silicon.



Warren R. Roper completed his Ph.D. in 1963 at the University of Canterbury, Christchurch, New Zealand, under the supervision of C. J. Wilkins. He then undertook postdoctoral research with J. P. Collman at the University of North Carolina, Chapel Hill, NC, and in 1966 returned to New Zealand as Lecturer in Chemistry at The University of Auckland where he is now Professor of Chemistry. His research interests are in synthetic and structural organometallic chemistry. He has lectured widely and been Visiting Professor at the Universities of Leeds and Rennes and Stanford University. His work was recognized by the Royal Society of Chemistry in 1983 by the Organometallic Chemistry award and in 1988 by the Centenary Lectureship. He was elected a Fellow of The Royal Society (London) in 1989. In 1992 he was a Fellow of the Japan Society for the Promotion of Science and the Burrows Lecturer for the Royal Australian Chemical Institute. In 1995, he was the Glenn T. Seaborg Lecturer in inorganic chemistry at the University of California, Berkeley.



George R. Whittell graduated with a B.Sc. in chemistry from the University of Bristol in 1996 and is currently working for his Ph.D. with Dr. N. C. Norman on transition metal BF_2 complexes.

L. James Wright completed his Ph.D. degree at the University of Auckland in 1980 under the supervision of Professor W. R. Roper. After working at the New Zealand Government Research Laboratory (DSIR) for two years, he joined the research group of Professor J. P. Collman at Stanford University as a postdoctoral research fellow. In 1984, he took up a lectureship at the University of Auckland where he is currently a Senior Lecturer in Chemistry. In 1990, he held a visiting Professorship at Carnegie Mellon University, Pittsburgh. He was awarded a University of Auckland Distinguished teaching Award in 1996 and was admitted as a Fellow of the New Zealand Institute of Chemistry in 1998. His current research interests include organometallic and inorgano-metallic chemistry, macrocyclic chemistry and the catalysis of wood pulping and bleaching.

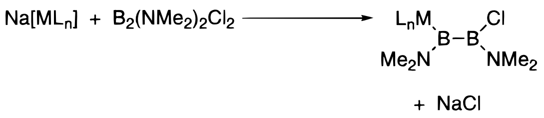
point, and elemental analysis) and discrepancies have arisen in comparisons with recent research. In particular, Hartwig et al.[44−52] have synthesized and structurally characterized several related metal−boryl derivatives using similar methods. The majority of these derivatives incorporate Bcat ligands, although BPh_2 ligands were also examined to afford a direct comparison with previous studies. For example, the reaction between $Na[CpFe(CO)_2]$ and ClBcat or $BrBPh_2$ resulted in the formation of $[CpFe(CO)_2(BR_2)]$ (BR_2 = Bcat, BPh_2),[46] the latter product being equivalent to that reported previously,[1] with the exception that the ^{11}B NMR chemical shift differed by about 100 ppm. Hartwig and Huber noted that the BPh_2 derivative was light-sensitive which may account for the discrepancy. The compound $[CpFe(CO)_2(Bcat)]$ was also prepared by the reaction of HBcat with $[CpFe(CO)_2(BPh_2)]$.

In similar studies, Hartwig et al. have used this methodology to prepare $[Mn(CO)_5(Bcat)]$,[44] $[Re(CO)_5(Bcat)]$,[48] and the related bisboryl derivatives [Fe-

$(CO)_4(BR_2)_2$], where R_2 = cat, 4-Bu^tcat, or 3,5-Bu^t_2-cat.[49] Previously,[1] reactions involving $Na_2[Fe(CO)_4]$ and haloboranes were reported to yield $Fe_3(CO)_{12}$. The reactivity of salts of metal–hydride compounds has also been studied by Hartwig and De Gala.[47,52] The reaction of ClBcat with $[LiCp_2WH]_4$ in toluene resulted in the formation of $[Cp_2WH(Bcat)]$. In the absence of anionic metal fragments, the reactions involve a combination of oxidative addition and reductive elimination of hydrogen. These reactions are discussed in more detail in section II.B. Recently, Hartwig and Waltz[53] have used this same synthetic approach in the synthesis of $[Cp^*M(CO)_n(B\text{-}1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_3)]$ ($Cp^* = \eta\text{-}C_5Me_5$; M = Fe, Ru, $n = 2$; M = W, $n = 3$).

The preparation of the isomeric compounds, *endo*- and *exo*-$[Cp_2TaH_2(Bcat)]$, was also accomplished by utilizing this synthetic route. The isomers were separated by fractional crystallization in moderate yields.[54]

Recently, Braunschweig et al.[55] have prepared the first examples of diboran(4)yl complexes of transition metals. The compounds $Na[CpFe(CO)_2]$ and $Na[CpW(CO)_3]$ were found to react in benzene solution with 1 equiv of $B_2Cl_2(NMe_2)_2$ to yield the metal–boryl compounds shown in eq 2.



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B. Reactions Involving Oxidative Addition to Metal Compounds

The oxidative addition of various boranes and diborane(4) compounds to transition metal compounds has been extensively studied largely because, with only a few noted exceptions,[47,50,54,56–61] metal–boryl compounds are likely intermediates in the metal-catalyzed hydroboration and diboration of unsaturated organic substrates. A common theme in these reactions is the use of low-valent metal precursors containing ligands which readily dissociate in solution. This creates vacant sites in the metal coordination sphere which allows for the oxidative addition of the boron reagents to the electron-rich metal center. Numerous examples of mono-, bis-, and trisboryl compounds have been reported via the oxidative addition of H–B, Cl–B, and B–B bonds to such metal complexes. Alternatively, a combination of oxidative addition and reductive elimination may be employed wherein the evolution of HCl or H_2 occurs concomitantly with the formation of metal–boryl compounds.

1. Reactions with Haloboranes (X–BR_2)

Nöth and Schmid examined the reactions of several metal hydride compounds with haloboranes,[4,9,11] the reactions reportedly proceeding with the generation of metal–boryl compounds and 1 equiv of HX (eq 3).

$$[MHL_n] + XBR_2 \longrightarrow L_nM(BR_2) + HX \qquad (3)$$

Initially, the reactions of $[CoH(dppe)_2]$ and $[PtHCl(PEt_3)_2]$ with $ClBPh_2$ were reported to yield the novel bisboryl compound $[Co(dppe)_2(BPh_2)_2]$ (a 19-electron compound), and the monoboryl compound $[PtCl(PEt_3)_2(BPh_2)]$, respectively. Several additional bisboryl derivatives of the same proposed general formula, $[Co(dppe)_2(BR_2)_2]$ were subsequently synthesized by this route (R_2 = 9-borafluorenyl = C_8H_{12};[9] R_2 = Cl(Ph), Br_2, I_2[11]). Compounds given by the formula, $[Co\{1,2\text{-}(PMe_2)_2C_6H_4\}_2(BR_2)_2]$ (R = Ph; $R_2 = C_8H_{12}$[9]) were also reportedly prepared by similar routes. The interest in these Co(II)–bisboryl derivatives resulted from the unique reactivity displayed in σ-bond metathesis reactions which were used to prepare several metal–boryl derivatives involving different metal centers (section II.C). The cobalt bisboryls were believed to have *trans*-boryl ligands but in light of more recent studies (vide infra) this seems unlikely.

Additionally, Nöth et al.[8] reported that $[Cp_2Ti]_2$ (misformulated, although not known at the time of the report) and $[Co(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) underwent an oxidative addition reaction with the boron–halogen bonds in $ClBPh_2$, BCl_3, BBr_3, and BI_3, yielding compounds formulated as *cis*-$[MXL_2(BR_2)]$ (X = halide). The compound, $[Pt(PPh_3)_4]$, was reported to react with $ClBPh_2$ in boiling cyclohexane to produce $[PtCl(PPh_3)_2(BPh_2)]$ with loss of 2 equiv of phosphine; the bromo analogue, $[PtBr(PPh_3)_2(BPh_2)]$, was also reportedly prepared using $BrBPh_2$. In this case, no reactions were observed with $ClBBu_2$, $ClB(NMe_2)_2$, $B(NMe_2)_3$, or $Ph_2B(NEt_2)$. Reactions involving $[Pt(dppe)_2]$ were also unsuccessful, yielding products involving adduct formation such as $[Pt(dppe)_2(Ph_2BX)_2]$. Similar adduct formation was observed in reactions between $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ with BF_3 or BCl_3.[18] Reaction of $[Ni(PPh_3)_2(\eta\text{-}C_2H_4)]$ with $BrBPh_2$, however, was reported to yield diamagnetic products with the formulas, $[Ni(PPh_3)_2(BPh_2)\cdot{}^1/_2Et_2O]_n$ for $n \geq 2$. These compounds were proposed to contain bridging BPh_2 groups.[16] Interestingly, no oxidative addition products were obtained from reactions using $Fe_2(CO)_9$, and reactions involving R_2NBBr_2 (R = Me, Et) were reported to give borylene compounds (i.e., Fe=B–NR_2) although it is unlikely that such terminal borylene complexes were in fact prepared.[13] The reaction between $Fe_2(CO)_9$ and $MeB(NMe_2)_2$ resulted in the formation of products containing N–B–N π-ligands.[14] This mode of bonding was also apparent in the products derived from the reactions between $[Ni(\pi\text{-}C_3H_5)_2]$[14] and $[PdCl_2(NCPh)_2]$[15] with X–$B(NMe_2)_2$ where X = Me or Cl. Similar behavior has been noted in reactions between BBu_3 and Nb_2Cl_{10}; however, the initial metal–boryl formed from addition of the Bu–B bond was reported to react further to give niobium–boron-containing polymers.[62]

The general reaction described in this section was also thought to occur with some rhodium[4] and iridium[22] hydrides (eqs 4 and 5).

Recently, the reactions of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ with ClBcat and BrBcat have been reported to give the *trans*-$[PtX(PPh_3)_2(Bcat)]$ compounds via oxidative addition and isomerization.[30,63] The trans configuration of the phosphine ligands was confirmed by X-ray crystallography.

$$\mathrm{Ph_2BCl + [IrHCl_2L_3] \longrightarrow [IrCl_2L_3(BPh_2)] + HCl} \qquad (4)$$

$$(\mathrm{L = PEt_3,\ PPh_3})$$

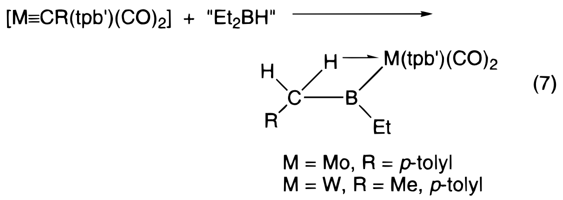
$$\mathrm{Ph_2BCl + [RhHCl_2(AsMePh_2)_3] \longrightarrow [RhCl_2(AsMePh_2)_3(BPh_2)] + HCl} \qquad (5)$$

2. Reactions with Hydridoboranes (H–BR$_2$)

Oxidative addition of boranes to transition metals has been studied extensively due to its importance with respect to transition metal-catalyzed hydroboration of unsaturated organic substrates. In general, oxidative addition occurs with transition metals in low oxidation states and a source of B−H bonds, e.g., R_2BH, RBH_2 and $(RO)_2BH$ (eq 6).

$$\mathrm{R_2BH + ML_n \longrightarrow [ML_nH(BR_2)]} \qquad (6)$$

A novel example has recently been reported by Wadepohl and co-workers. In this case, the first synthesis of a metal−boryl compound from the reaction between a borane and metal carbynes was described (eq 7).[64] The compounds [M≡CR(tpb′)(CO)$_2$], (tpb′ = tris(3,5-dimethylpyrazol-1-yl)hydroborate) reacted readily at room temperature (R = Me) or at 60 °C (R = *p*-tolyl) with Et_2BH to yield the tungsten and molybdenum boryl compounds. The structural studies of the tungsten derivative were consistent with the presence of a β-agostic hydride interaction. Although this reaction is included in this section, it probably does not involve an oxidative addition of the B−H bond to the metal center.



$$\mathrm{[M{\equiv}CR(tpb')(CO)_2] + "Et_2BH" \longrightarrow} \qquad (7)$$

M = Mo, R = *p*-tolyl
M = W, R = Me, *p*-tolyl

In 1975, Kono et al.[65] reported the oxidative addition of the B−H bonds in HBcat and 4,4,6-trimethyl-1,3,2-dioxaborane to the Rh(I) center in Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$] although in unspecified yield. This result, in conjunction with the subsequent discovery by Männig and Nöth[20] that the same rhodium compound was a highly selective catalyst for the hydroboration of alkenes and 1-hexyne with HBcat, sparked a renewed interest in late transition metal−boryl compounds. Subsequent work showed that the reaction of HBcat with 1 equiv of [RhCl(PPh$_3$)$_3$] afforded the metal−hydridoboryl compound [RhHCl(PPh$_3$)$_2$(Bcat)] but a number of other products were also formed (see eq 43 later) as a result of reactions between this compound and the free PPh$_3$ generated. The related Rh(I) dimer [{Rh(PPh$_3$)$_2$(μ-Cl)}$_2$], however, afforded this compound cleanly since there was no accompanying loss of PPh$_3$ (eq 8). In addition, upon further reaction with catecholborane, the formation of a metal bisboryl was observed (eq 9).[66,67]

Other analogous rhodium− and iridium−boryl compounds have been synthesized by similar means (eqs 10−17).[68−74] These metal−boryl compounds have been characterized by ^{1}H, ^{31}P, ^{11}B, and ^{13}C NMR spectroscopy and, in some cases, by X-ray crystallography. For example, the dissociation of the labile N$_2$ ligand in [RhCl(N$_2$)(PPr$^i_3$)$_2$] followed by oxidative addition of HBcat results in the formation of a five-coordinate Rh(III) complex (eq 10).[68] The compound [RhCl(PMe$_3$)$_3$] exhibits similar reactivity resulting in the formation of a six-coordinate Rh(III) species (eq 11).[69]

$$\mathrm{[\{Rh(PPh_3)_2(\mu\text{-}Cl)\}_2] + HBcat \longrightarrow [RhHCl\,(PPh_3)_2(Bcat)]} \qquad (8)$$

$$\mathrm{[RhHCl(PPh_3)_2(Bcat)] + HBcat \longrightarrow [RhCl(PPh_3)_2(Bcat)_2] + H_2} \qquad (9)$$

$$\mathrm{[RhCl(N_2)(PPr^i_3)_2] + HBcat \longrightarrow \mathit{trans}\text{-}[RhHCl(PPr^i_3)_2(Bcat)] + N_2} \qquad (10)$$

$$\mathrm{[RhCl(PMe_3)_3] + HBcat \longrightarrow \mathit{mer}\text{-}[RhHCl(PMe_3)_3(Bcat)]} \qquad (11)$$

Similar products were obtained with the analogous iridium complexes [IrCl(PMe$_3$)$_3$] and [IrCl(PEt$_3$)$_3$]. Reactions involving [IrH(PMe$_3$)$_4$] were shown to give the expected metal−boryl complex as well as 1 equiv of a phosphine−borane adduct (eq 12) where BBN = 9-borabicyclo[3.3.1]nonane.[70] A number of bisphosphine−iridium(I) complexes were also examined for reactivity with H−B bonds (eq 13). Iridium−boryl compounds were prepared from a variety of mono[71] and bidentate[72] phosphine derivatives (chiraphos = Ph$_2$PCH(Me)CH(Me)PPh$_2$).

$$\mathrm{[IrH(PMe_3)_4] + 2\ HBR_2 \longrightarrow [IrH_2(PMe_3)_3(BR_2)] + Me_3P\text{-}BR_2H} \qquad (12)$$

$$\mathrm{HBR_2 = 9\text{-}BBN,\ H_2B(CMe_2CHMe_2)}$$

$$\mathrm{[IrX(CO)P_2] + HBcat \longrightarrow \mathit{trans}\text{-}[IrHX(CO)P_2(Bcat)]} \qquad (13)$$

$P_2 = (PPh_3)_2$; X = Cl
P_2 = dppe; X = Br, I
P_2 = Chiraphos; X = Br

The dissociation of coe (coe = *cis*-cyclooctene) from dimeric (eq 14)[71] or monomeric (eq 15)[73] iridium compounds also results in the formation of iridium−boryl compounds and a similar type of reaction is observed with an iridium trihydride.

$$\mathrm{[\{Ir(coe)_2(\mu\text{-}Cl)\}_2] + 4PPr^i_3 + 2\ HBcat \longrightarrow 2\mathit{trans}\text{-}[IrHCl(PPr^i_3)_2(Bcat)] + 2\ coe} \qquad (14)$$

$$\mathrm{[IrCl(PMe_3)_3(coe)] + HBcat \longrightarrow \mathit{mer}\text{-}[IrHCl(PMe_3)_3(Bcat)] + 2\ coe} \qquad (15)$$

Four novel iridium−trisboryl compounds have been synthesized, in high yield, by Nguyen et al. (eq 16),[74] although the exact mechanism for the formation of these compounds is not certain. In this case, the

$$\mathrm{[Ir(\eta^5\text{-}Ind)(\eta^4\text{-}cod)] + 5\ HBcat + Arene \longrightarrow [Ir(\eta^6\text{-}Arene)(Bcat)_3]} \qquad (16)$$

$$\mathrm{Arene = C_6H_6,\ C_6D_6,\ C_6H_5Me,\ 1,3,5\text{-}C_6H_3Me_3}$$

compound [Ir(η^5-indenyl)(cod)] (cod = cycloocta-1,5-diene) reacts with excess (5 equiv) HBcat in arene solvents to yield complexes of the form [Ir(η^6-arene)(Bcat)$_3$]. It is assumed that oxidative addition occurs, in competition with hydroboration and hydrogenation of the ligands initially bound to the iridium center. The iridium−trisboryl compounds were the only iridium-containing products observed from these reactions. Similar reactivity was observed in reactions involving [IrH$_3$(CO)(dppe)] and 2 equiv of HBcat (eq 17), yielding an Ir(III) bisboryl compound.[72]

$$[IrH_3(CO)(dppe)] + 2HBcat \longrightarrow [IrH(CO)(dppe)(Bcat)_2] + 2H_2 \quad (17)$$

Certain ruthenium− and osmium−hydrido complexes react with HBcat to form a metal−boryl with elimination of H$_2$. A number of ruthenium− and osmium−boryl species have also been prepared from the reaction between the respective HBR$_2$ and either a ruthenium−hydride (eq 18) or phenyl−osmium complex (eq 19).[75,76] Several derivatives incorporating a variety of heteroatoms in the boryl ligands were also prepared. The products derived from reactions involving [RuHCl(PPh$_3$)$_3$(CE)] (E = O, S) (although not all ruthenium−hydride compounds react with HBcat; see section III.B.1.ix) could also be prepared from the ruthenium−phenyl complex although in reactions involving osmium, the more reactive osmium−phenyl complex was necessary to facilitate the reaction. The formation of [RuCl(CO)(PPh$_3$)$_2$(Bcat)] was also accomplished from the reaction between HBcat and [RuCl(CO)(PPh$_3$)$_2${C(H)=C(H)Ph}].

$$[RuHCl(CE)(PPh_3)_3] + HBR_2 \longrightarrow [RuCl(CE)(PPh_3)_2(BR_2)] + H_2 \quad (18)$$

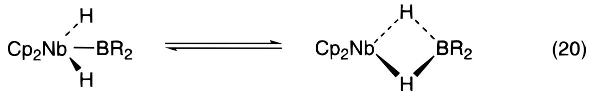
E = O;
BR$_2$ = Bcat, B(1,2-(NH)$_2$C$_6$H$_4$), B(1-S-2-NHC$_6$H$_4$), B(2,3-O$_2$-naphthyl)
E = S;
BR$_2$ = Bcat, B(1-S-2-NHC$_6$H$_4$),
E = N-*p*-tolyl;
BR$_2$ = Bcat

$$[OsClPh(CE)(PPh_3)_2] + HBR_2 \longrightarrow [OsCl(CE)(PPh_3)_2(BR_2)] + PhH \quad (19)$$

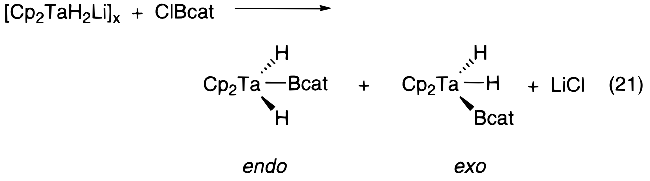
E = O;
BR$_2$ = Bcat, B(1,2-(NH)$_2$C$_6$H$_4$), B(1-S-2-NHC$_6$H$_4$), B(1,2-O$_2$-4-MeC$_6$H$_3$)
E = S;
BR$_2$ = Bcat, B(1-S-2-NHC$_6$H$_4$)

Metal−boryl formation was observed for other osmium complexes through simple oxidative addition reactions. For example, the reaction of HBcat or HB-1,2-(NMe)$_2$C$_6$H$_4$ with [Os(CO)$_2$(PPh$_3$)$_3$] or [OsCl(NO)(PPh$_3$)$_3$] resulted in the formation of [OsH(CO)$_2$(PPh$_3$)$_2$(BR$_2$)] and [OsHCl(NO)(PPh$_3$)$_2$(BR$_2$)] (two isomers), respectively. The complex [OsHCl(PPh$_3$)$_3$(CN-*p*-tolyl)] was shown to react with HBCl$_2$·OEt$_2$ with loss of PPh$_3$ and H$_2$ to yield the compound [OsCl(PPh$_3$)$_2$(CN-*p*-tolyl)(BCl$_2$)].

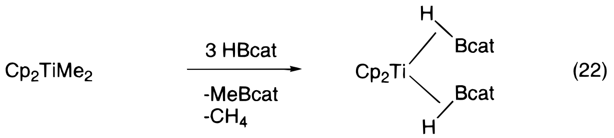
Studies involving early transition metal complexes with boranes have been reported to be independent of metal−boryl formation in catalytic processes and sometimes result in the formation of hydridoborate compounds.[47,50,54,56−61] Hartwig and De Gala[47] reported that the reaction of [Cp$_2$NbH$_3$] with catecholborane or 9-borabicyclononane (9-BBN) yielded 1 equiv of hydrogen gas as well as the metal−boryl compound, [Cp$_2$NbH$_2$(Bcat)], or the hydridoborate compound, [Cp$_2$Nb{BH$_2$(C$_8$H$_{14}$)}$_2$], respectively; the latter compound may not necessarily be formed via an oxidative addition mechanism. The metal−boryl and the hydridoborate species were not detectable individually in solution by NMR with only an average chemical shift for the two species being seen, but studies involving deuterium labeling provided evidence for the equilibrium shown (eq 20).



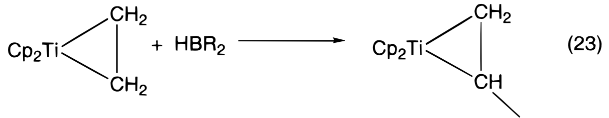
As mentioned previously, Smith et al. have prepared similar tantalum derivatives from reactions involving ClBcat.[54] The products in this case were consistent with the formation of tantalum−boron bonds in both the endo and exo isomers (eq 21).



The preparation of titanium−boryl compounds has yet to be reported. Instead, adduct formation or activation of ligands bound to the metal was observed. For example, Hartwig et al. reported the formation of a bis-HBcat adduct from the reaction between Cp$_2$TiMe$_2$ and HBcat (eq 22).[56] The titanium adduct thus formed was highly reactive undergoing insertion reactions with unsaturated substrates and substitution reactions with CO and different borane derivatives.

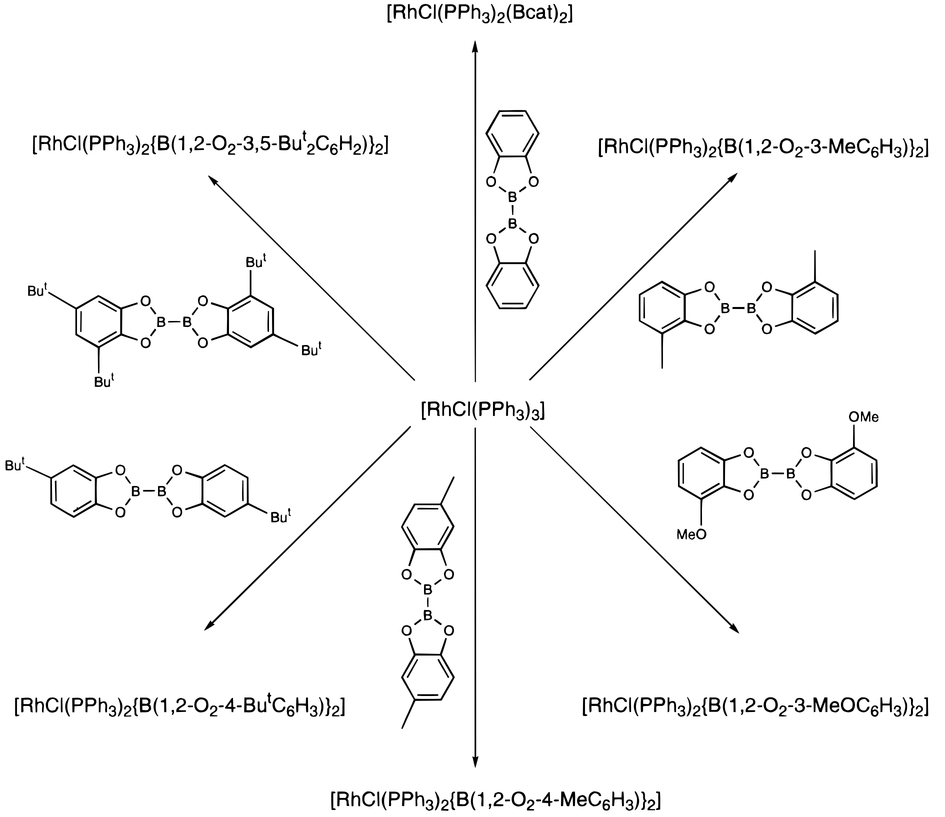


Motry et al. have reported reactions between [Cp$_2$Ti(η-C$_2$H$_4$)] and a variety of boranes (eq 23).[57] In



BR$_2$ = Bcat, B(1,2-O$_2$C$_{10}$H$_6$), B(1,2-(NH)$_2$C$_6$H$_4$)

Scheme 1. Synthesis of $[RhCl(PPh_3)_2(BR_2)_2]$ Compounds



these cases, the borylation of the olefin moiety proceeds without bond reduction presumably via σ-bond metathesis that forms the B–C bond. Subsequent studies indicated that this process may be fine-tuned by variation of the boryl moiety to give rapid conversion to the coordinated boronate ester product.[58] Similar reactivity in the catalytic processes involving addition of boranes to unsaturated substrates using organolanthanides and zirconocene complexes has been reported. Thus, hydroboration of olefins[59,60] and alkynes[61] may involve reactions at the unsaturated substrate without formation of a distinct metal–boryl complex, i.e., in the case of the titanium reactions, the alkene coordinates to the metal center whereas in the zirconium and lanthanide systems, the alkene probably inserts directly into the M–H bond.

3. Reactions with Diborane(4) Compounds

The use of diborane(4) compounds to form metal bisboryl compounds has received considerable attention in recent years, since such compounds can be added catalytically to certain organic functional groups resulting in the formation of two carbon–boron bonds. As mentioned previously, the reaction of $[RhCl(PPh_3)_3]$ with 2 equiv of HBcat affords a rhodium bisboryl (eq 9). However, reaction of $[RhCl(PPh_3)_3]$ with 1 equiv of B_2cat_2 gives the Rh(III)–bisboryl compound directly. This method of preparation has proven useful for the synthesis of a wide range of Rh–bisboryl compounds (Scheme 1).[77–80]

While the addition reactions of aryloxy diborane(4) compounds are numerous, the addition of alkyloxy based diborane(4) compounds to rhodium centers is much more limited, the only one example known shown in eq 24.[79]

$$[RhCl(PPh_3)_3] + B_2tart_2 \longrightarrow [RhCl(PPh_3)_2(Btart)_2] + PPh_3 \qquad (24)$$

$$\text{tart} = R,R\text{-}OCH(CO_2Me)CH(CO_2Me)O$$

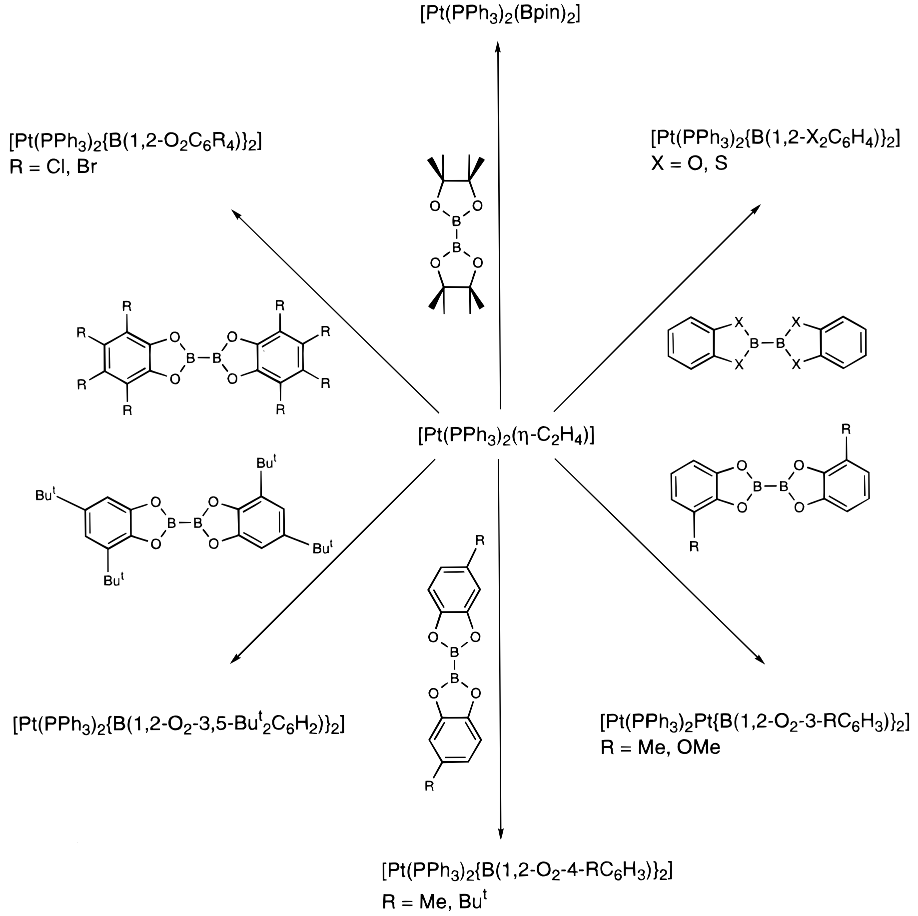
Mono- and trisboryl derivatives of rhodium have also been prepared from reactions involving diborane(4) compounds.[80] For example, the reaction between $[RhMe(PMe_3)_4]$ and 1 equiv of B_2cat_2 gave the rhodium–monoboryl compound $[Rh(PMe_3)_4(Bcat)]$ presumably via a bisboryl intermediate which subsequently lost MeBcat (eqs 25 and 26). The monoboryl compound $[Rh(PMe_3)_4(Bcat)]$ then reacted with a further equivalent of B_2cat_2, yielding the novel Rh–trisboryl complex (eq 27). Both the mono- and trisboryl compounds of rhodium have been structurally characterized. Additional examples involving L_3MCl complexes as the starting point in synthetic applications have also been described for the PEt_3 derivatives of rhodium[79] and iridium,[81] and the structures of the resultant $[MCl(PEt_3)_2(Bcat)_2]$ (M = Rh, Ir) have been reported.

$$[RhMe(PMe_3)_4] + B_2cat_2 \longrightarrow \text{"}[RhMe(PMe_3)_3(Bcat)_2]\text{"} + PMe_3 \qquad (25)$$

$$\text{"}[RhMe(PMe_3)_3(Bcat)_2]\text{"} + PMe_3 \longrightarrow [Rh(PMe_3)_4(Bcat)] + MeBcat \qquad (26)$$

$$[Rh(PMe_3)_4(Bcat)] + B_2cat_2 \longrightarrow [Rh(PMe_3)_3(Bcat)_3] + PMe_3 \qquad (27)$$

Scheme 2. Synthesis of *cis*-$[Pt(PPh_3)_2(BR_2)_2]$ Compounds



The platinum compound $[Pt(PPh_3)_2(BPh_2)_2]$ has been reported,[23] although the synthetic details were not described, but as the diborane(4) compound, B_2Ph_4, has not been prepared, it is unlikely that this compound was formed by oxidative addition of a B−B bond. Recently, the structures of several platinum−bisboryl compounds have been presented. Miyaura et al.[25] initially reported NMR evidence for the formation of *cis*-$[Pt(PPh_3)_2(Bpin)_2]$ presumably formed by dissociation of 2 equiv of PPh_3 from $[Pt(PPh_3)_4]$ followed by oxidative addition of B_2pin_2 although the precise mechanism has not been established. Recently, the same authors have described the structure of this compound.[26] In addition, Iverson and Smith[28] also reported that $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ reacted with B_2cat_2 via the dissociation of ethylene (see also section III.B.1.ix). As mentioned previously, dissociation of ethylene from $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ gives rise to highly reactive intermediates for oxidative addition. In fact, $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ reacts with a wide range of diborane(4) compounds, which include both aryl- and alkyloxy−diborane(4) compounds as well as $B_2(1,2\text{-}S_2C_6H_4)_2$ $[B_2thiocat_2]$, as shown in Scheme 2.[30,63]

Recently, Nöth[82] has also reported the synthesis of *cis*-$[Pt(PPh_3)_2\{B(OMe)_2\}_2]$ resulting from the oxidative addition of $B_2(OMe)_4$ which is the sole example of a nonchelating tetraalkoxy−diborane(4) derivative involving a $[Pt(PPh_3)_2]$ center. Replacement of the phosphine ligands in $[Pt(PPh_3)_2(Bcat)_2]$ with dppe and dppb (1,2-bis(diphenylphosphino)butane) in toluene gave the corresponding *cis*-$[Pt(dppe)(Bcat)_2]$ and $[Pt(dppb)(Bcat)_2]$ compounds. While these compounds may also be prepared from the respective ethylene complexes, $[Pt(dppe)(\eta\text{-}C_2H_4)]$ or $[Pt(dppb)(\eta\text{-}C_2H_4)]$, phosphine exchange gave enhanced yields and higher purity isolated products.[30]

Diborane(4) compounds also undergo oxidative addition to other metal centers. Hartwig et al. reported the oxidative addition of B−B bonds under photolytic conditions with $Fe(CO)_5$[49] and Cp_2WH_2.[51] In these examples, photolysis was used to generate the active metal intermediates, $Fe(CO)_4$ and Cp_2W, which then readily add the diborane(4) compounds. For example, Cp_2W generated in situ by photolysis of Cp_2WH_2, reacts with substituted $B_2cat'_2$ compounds (eq 28). Photolysis of $Fe(CO)_5$ in the presence of a substituted $B_2cat'_2$ species also gave the iron−bisboryl compounds (eq 29).

$$Cp_2WH_2 + B_2cat'_2 \longrightarrow [Cp_2W(Bcat')_2] \quad (28)$$

$$[cat' = 1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3 \text{ or } 1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2]$$

$$Fe(CO)_5 + B_2cat'_2 \longrightarrow [Fe(CO)_4(Bcat')_2] + CO \quad (29)$$

$$[cat' = 1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3 \text{ or } 1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2]$$

As mentioned above, the formation of cobalt−boryl compounds has been reported via the reaction of a transition metal salt with haloboranes. Reaction of

[$Co(PMe_3)_4$] with B_2cat_2 led to the first structurally characterized cobalt−bisboryl complex as shown in eq 30.[83] Iridium−bisboryl compounds may be synthesized directly from [$IrCl(PMe_3)_3(coe)$] and B_2cat_2 (eq 31).[81]

$$[Co(PMe_3)_4] + B_2cat_2 \longrightarrow [Co(PMe_3)_3(Bcat)_2] + PMe_3 \quad (30)$$

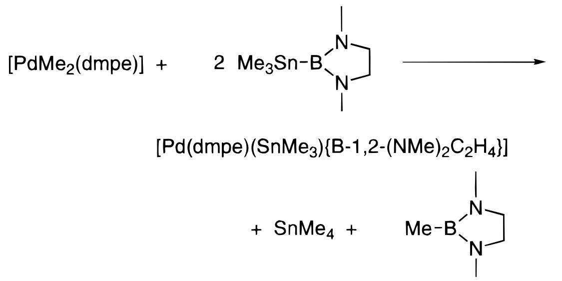
$$[IrCl(PMe_3)_3(coe)] + B_2cat_2 \longrightarrow [IrCl(PMe_3)_3(Bcat)_2] + coe \quad (31)$$

Although these reactions appear to be, for the most part, straightforward, the reactivity does not always proceed as expected. For example, Braunschweig and Wagner recently reported the synthesis and the first structural characterization of dinuclear complexes containing bridging borylene ligands.[84] This synthesis was achieved by the reaction of 2 equiv of $K[CpMn(CO)_2(SiMePh_2)]$ with the diborane(4) compound, $B_2Cl_2(NMe_2)_2$, the product, [$\{CpMn(CO)_2\}_2\{\mu\text{-}B(NMe_2)\}$] containing a Mn−Mn bond although this may not involve any oxidative addition of the B−B bond.

4. Reactions with Other Boron Reagents

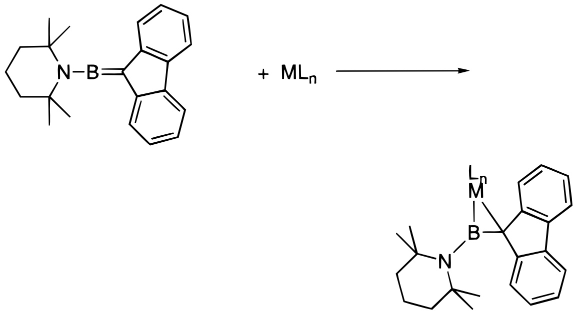
Reactions involving heteroatom borane reagents are limited. Reaction of $MeB(NMe_2)_2$ with a source of palladium(II) was reported to give the corresponding metal−boryl compound (eq 32) although no spectroscopic data were given to support this conclusion.[15] Recently, reports concerning the oxidative addition of B−Si[85,86] and B−Sn[87] bonds and related catalytic processes have been described. For example, Tanaka et al. have reported the oxidative addition of B−Sn bonds to palladium centers (eq 33) while examining the catalyzed borylstannation of alkynes.[87] The compound *cis*-[$Pd(dmpe)(SnMe_3)\{B\text{-}1,2\text{-}(NMe)_2C_2H_4\}$] was structurally characterized.

$$[PdCl_2(PhCN)_2] + MeB(NMe_2)_2 \longrightarrow [PdCl_2Me\{B(NMe_2)_2\}] + 2\,PhCN \quad (32)$$



(33)

Recently, Nöth and co-workers have reported the reactions of B=C double bonds in the preparation of a series of amino-9-fluorenylideneborane complexes with the isolobal fragments $Fe(CO)_4$, $CpCo(CO)$, $Cp'Mn(CO)_2$ ($Cp' = \eta\text{-}C_5H_4Me$), and $(\eta\text{-}C_6H_6)Cr(CO)_2$ (eq 34).[88−90] The reactions were carried out in toluene solutions under photolytic conditions to achieve optimal yields. In reactions involving $Fe_2(CO)_9$, the initial product was described as an η^4-complex of $Fe(CO)_3$ which underwent further photolysis in the presence of ligands to give a series of [$Fe(CO)_3(L)(L')$] complexes where $L' = \eta^2$-amino-9-fluorenylideneborane and $L = PPh_3$, $P(C_6H_{11})_3$, $P(OCH_3)_3$, $SbPh_3$ or CO.[89] The η^4 bonding mode of the B=C−C=C unit, occurring at the expense of the aromaticity of the ligand, was determined on the basis of structural studies. In the absence of photolytic conditions, reactions involving $Fe_2(CO)_9$ were reported to give the $Fe(CO)_4$ complex directly, albeit in lower yield.[88]



(34)

$ML_n = Fe(CO)_4$, $CpCo(CO)_2$, $(MeCp)Mn(CO)_2$, $(C_6H_6)Cr(CO)_2$

C. Transmetalation Reactions

The 19-electron cobalt(II) bisboryl compounds, which Nöth and Schmid reported, were found to be very reactive toward a wide variety of metal−halide compounds,[4,9,11,12,17] this reaction formally involving the σ-bond metathesis between cobalt−boron and metal−halide bonds (eqs 35 and 36).[9,11] The formation of tin−boryl compounds was also apparently achieved via σ-bond metathesis with cobalt−bisboryl compounds (eq 37),[12,17] although attempts to prepare BBr_2 derivatives were unsuccessful. It should be noted, however, that the majority of the products obtained from these σ-bond metathesis reactions were not completely characterized by modern methods, and some doubt therefore remains as to the true nature of these processes.

$$[Co(dppe)_2(BR_2)_2] + 2\,[L_nMX] \longrightarrow [CoX_2(dppe)_2] + 2\,[L_nM(BR_2)] \quad (35)$$

$R = Ph$, $L_nMX = AuCl(PPh_3)$, $MnBr(CO)_5$, $CpFeCl(CO)_2$;

$R = Br$, $L_nMX = RhCl(PPh_3)_3$, $CuCl(triars)$, $AgCl(triars)$
$triars = Me_2As(o\text{-}C_6H_4)As(Me)(o\text{-}C_6H_4)AsMe_2$

$$[Co(dppe)_2(BR_2)_2] + [L_nMX_2] \longrightarrow [CoX_2(dppe)_2] + 2\,[L_nM(BR_2)_2] \quad (36)$$

$R = Ph$, $L_nMX_2 = NiBr_2(dppe)_2$, $NiCl_2(dppe)_2$,

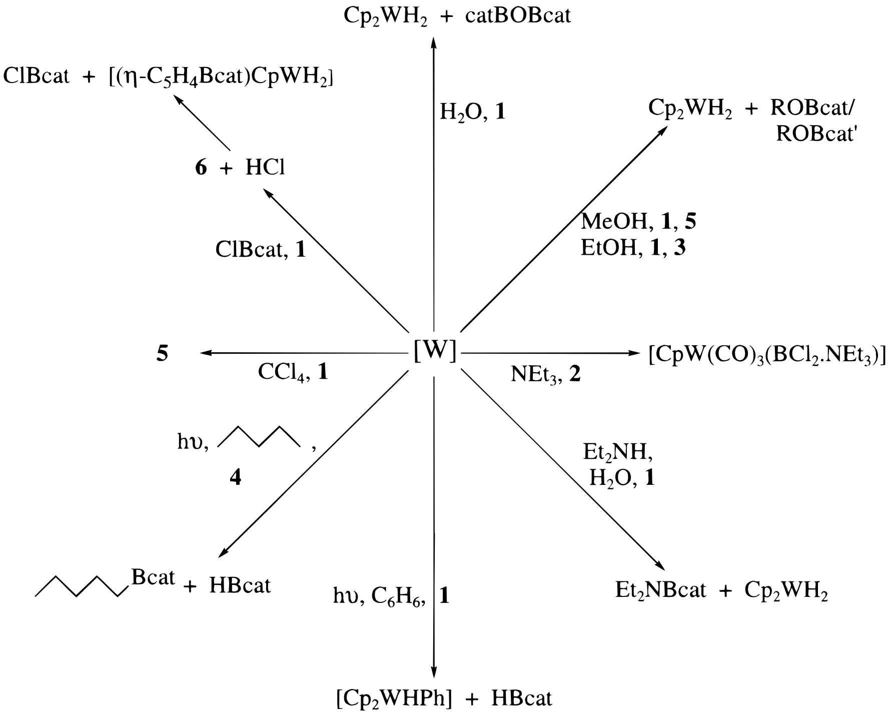
$$n/2\,[Co(dppe)_2(BPh_2)_2] + Me_{4-n}SnX_n \longrightarrow n/2\,[CoX_2(dppe)_2] + Me_{4-n}Sn(BPh_2)_n \quad (37)$$

$X = Cl, Br$
$n = 0, 1, 2, 3$

D. Reactions Involving Metal–Metal Bonds

The only other reported cobalt−boryl compounds were prepared from the reaction between $Co_2(CO)_8$ and BH_3X (X = thf,[91] SMe_2[92]) or $NaBH_4$.[93] The

Scheme 3. Reactivity of Tungsten–Boryl Compounds



[W] = $[Cp_2WH(Bcat)]$, **1**
$[CpW(CO)_3(BCl_2)]$, **2**
$[Cp_2W(Bcat')_2]$, **3** (cat' = 1,2-O_2-4-$Bu^tC_6H_3$; 1,2-O_2-3,5-$Bu^t{}_2C_6H_2$)
$[Cp^*W(CO)_3(Bcat)]$, **4**
$[Cp_2WCl(Bcat)]$, **5**
$[(\eta\text{-}C_5H_4Bcat)CpWH(Bcat)]$, **6**

products obtained were found to contain BH_2 ligands which were stabilized by solvent or phosphine coordination. The reactions of $(Me_2N)_2BCl$ with compounds containing a metal–metal bond giving the corresponding metal–boryl with cleavage of M–M bond were described in section II.A.

Reaction of BH_3·thf with $Co_2(CO)_8$ gives the corresponding metal–boryl compound with 1 equiv of $HCo(CO)_4$ (eq 38).[91] This compound contains one molecule of thf, which is believed to coordinate to the boron although this compound has only been characterized by NMR at low temperature. An analogous, but stable compound, containing a boron coordinated phosphine has been isolated and its structure determined by single-crystal X-ray diffraction (eq 39).[93]

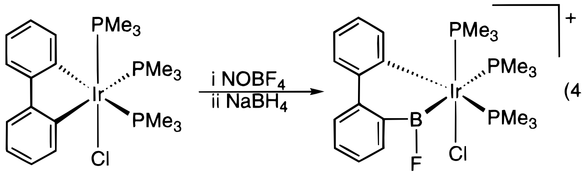
$$BH_3.thf + Co_2(CO)_8 \longrightarrow [Co(CO)_4(BH_2.thf)] + HCo(CO)_4 \qquad (38)$$

$$NaBH_4 + [CoBr_2(H_2O)_n] + CO + dppm \longrightarrow [(H_2B)(\mu\text{-}dppm)Co(CO)_2(dppm)] + [\{Co(CO)_2(\mu\text{-}dppm)\}_2] \qquad (39)$$

$(dppm = Ph_2PCH_2PPh_2)$

E. Miscellaneous Reactions

The formation of the $[Ir(PMe_3)_3(biphBF)Cl]^+$ (where biph = biphenyl-2,2-diyl) reported by Crabtree and co-workers represents the sole example of an iridium(IV)–boryl complex (eq 40).[94] The oxidation of $[IrCl(biph)(PMe_3)_3]$ with $NO[BF_4]$ effectively results in the insertion of BF into the Ir–C bond.



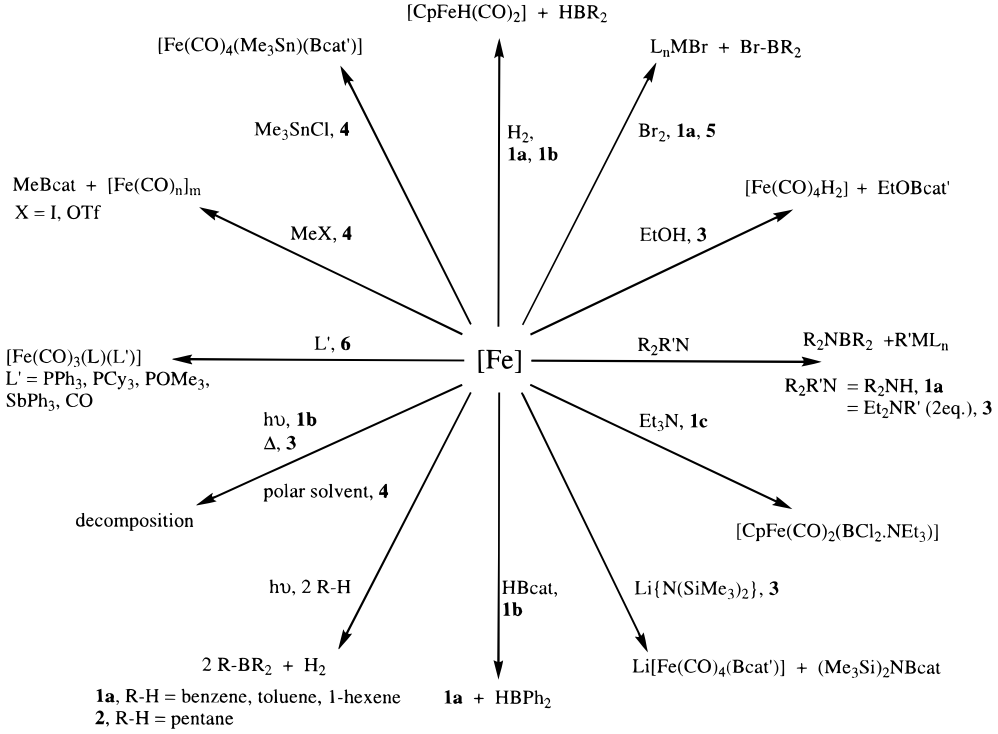
(40)

III. Reactivity of Metal–Boryl Compounds

A. Introduction

Until recently, studies concerning the reactivity of metal–boryl compounds have been limited. However, as interest increased in these compounds, due in large part to the development of related catalytic processes, such studies have become more prevalent. There are three possible sites for reactions involving

Scheme 4. Reactivity of Iron−Boryl Compounds



[Fe] = [CpFe(CO)$_2$(BR$_2$)], **1**
BR$_2$ = Bcat, **1a**
BR$_2$ = BPh$_2$, **1b**
BR$_2$ = BCl$_2$, **1c**
[Cp*Fe(CO)$_2$(Bcat)], **2**
[Fe(CO)$_4$(Bcat')$_2$], **3**
Li[Fe(CO)$_4$(Bcat')], **4**
[Fe(CO)$_4$Br{B(NR$_2$)Br}], **5**
[Fe(CO)$_3$(L)], **6**
L = η^2-amino-9-fluorenylideneborane

metal−boryl complexes. These can be classified as (i) reactions involving the M−B bond, (ii) reactions involving the metal center, and (iii) reactions occurring at the boryl ligand (BR$_2$) itself.

Reactions involving cleavage of the M−B bond have been further classified in terms of reactions in which the boryl moiety reacts with the incoming substrate and those in which it does not. Examples of the former include activation of saturated (alkanes) and unsaturated substrates such as alkynes and alkenes as well as metathetical reactions, while the latter includes processes involving the formation of new metal−boryl compounds with, for example, concomitant reductive elimination of the boryl group(s) in the presence of added diborane(4) compounds.

Reactions occurring at the metal center are often ligand substitution reactions, the majority involving phosphine exchange or coordination of incoming ligands to a vacant site on the metal. These reactions relate to the synthesis of new metal−boryl compounds not previously discussed. Recently, studies involving osmium−boryl derivatives prepared by coordination of an incoming ligand have shown an increased sensitivity to hydrolysis of the boryl substituent bonds. Reactivity of this type is relatively rare since the majority of reactions result in cleavage of the metal−boron bond. Examples of reactivity at the boryl ligand are discussed in the latter portion of this section. A series of schematic representations of reactivity observed in recent studies are also presented in Schemes 1−7. These include summaries of reactions involving tungsten, iron, ruthenium, osmium, rhodium, iridium, and platinum metal centers (Schemes 3−7). The reactivity of complexes incorporating manganese and cobalt have been summarized in a previous review.[22]

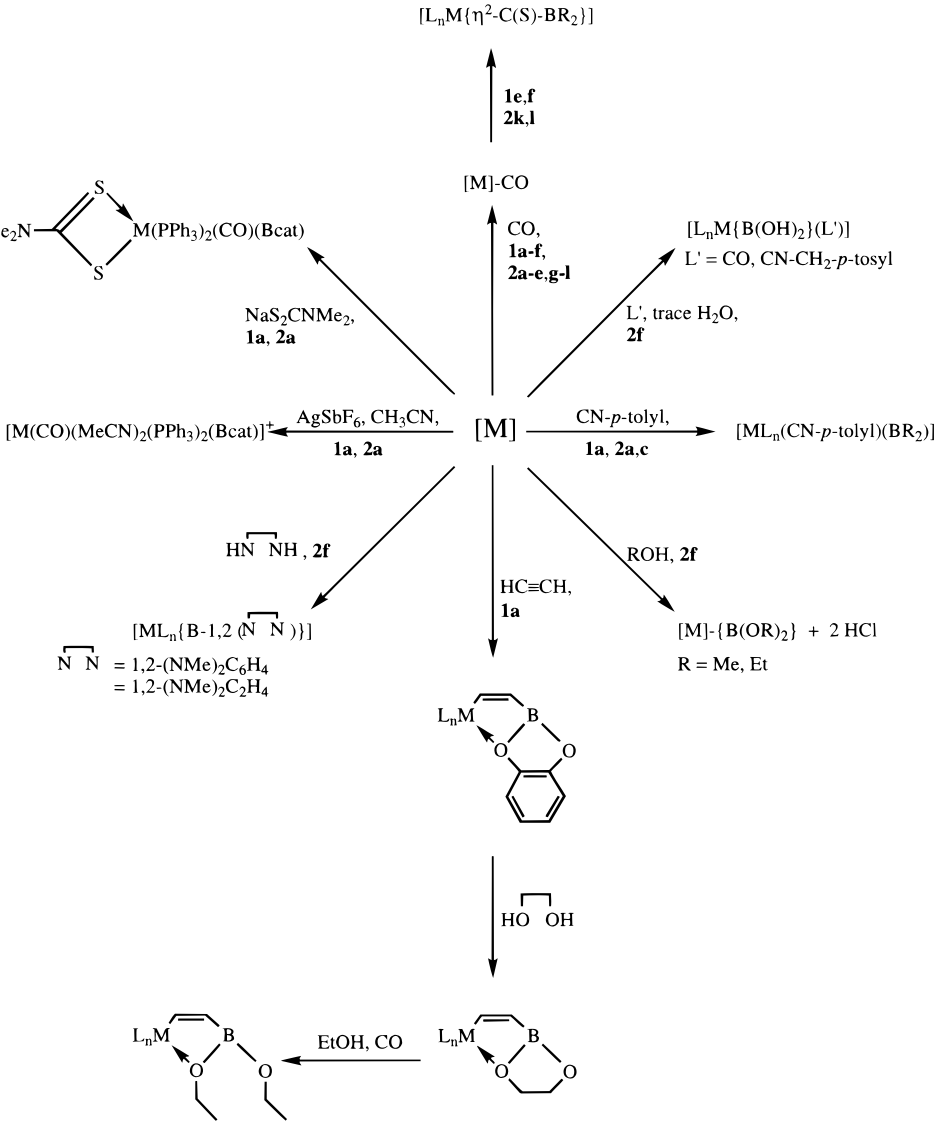
B. Reactions at the M–B Bond

1. Reactions with Incoming Substrates

i. Stability of M−BR$_2$. While most metal−boryl compounds exhibit instability in the presence of air or moisture leading to decomposition of the boryl groups, studies regarding the thermal stability and solvent effects have also been reported in which irreversible reactions occur to give similar products. Typically, donor solvents such as thf are not suitable in this regard while aromatic solvents and to a lesser extent halogenated solvents may be used to circumvent unwanted decomposition reactions.

The compound [Cp$_2$WH(Bcat)] (section II.A) was found to be stable in refluxing toluene for 12 h.[52] The

Scheme 5. Reactivity of Ruthenium– and Osmium–Boryl Compounds



1, [RuCl(CE)(PPh$_3$)$_2$(BR$_2$)]
1a, E = O; BR$_2$ = Bcat
1b, E = O; BR$_2$ = B-1,2-(NH)$_2$C$_6$H$_4$
1c, E = O; BR$_2$ = B-1-(NH)-2-SC$_6$H$_4$
1d, E = O; BR$_2$ = B-2,3-O$_2$C$_{10}$H$_6$
1e, E = S; BR$_2$ = Bcat
1f, E = S; BR$_2$ = B-1-(NH)-2-SC$_6$H$_4$

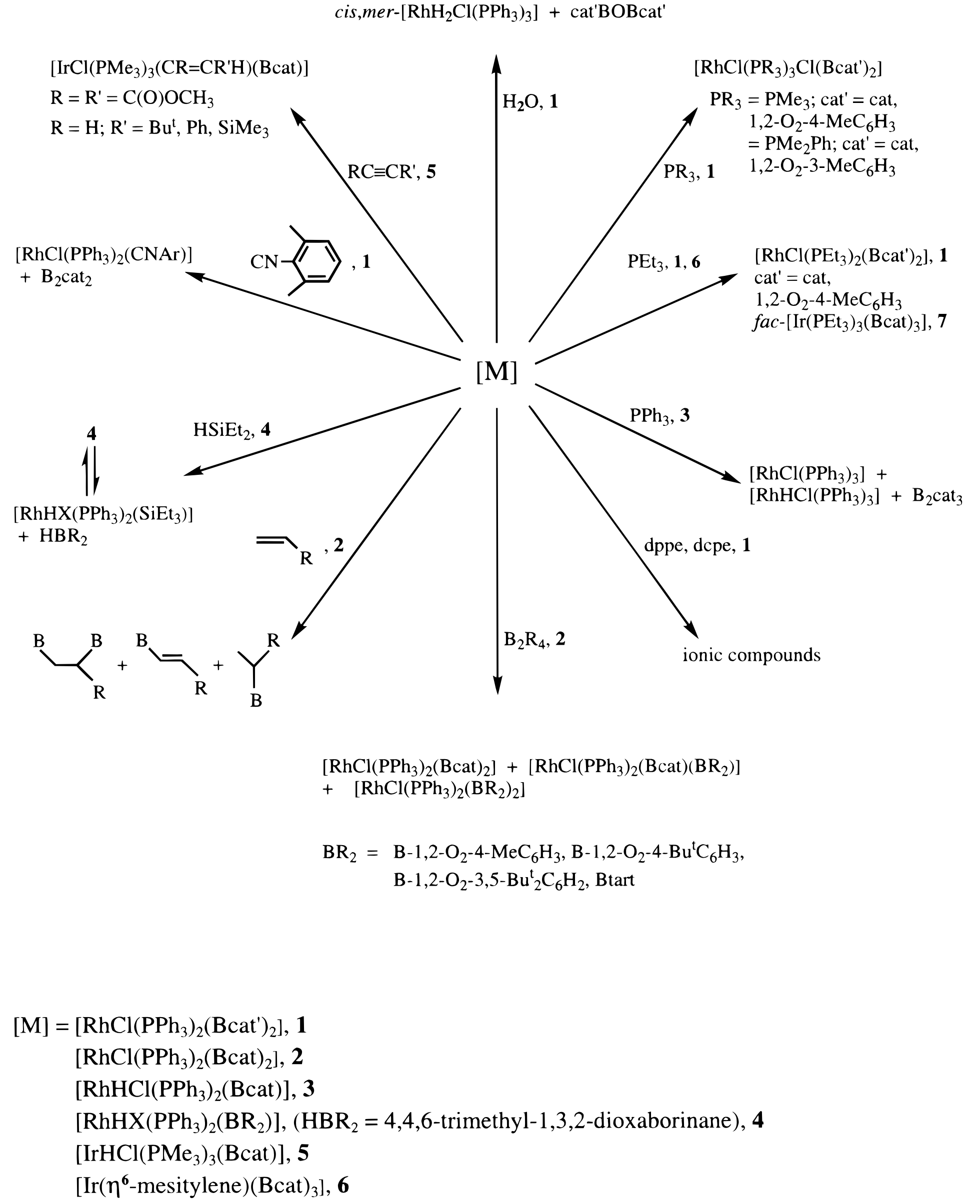
2, [OsCl(CE)(PPh$_3$)$_2$(BR$_2$)]
2a, E = O; BR$_2$ = Bcat
2b, E = O; BR$_2$ = B-1,2-(NH)$_2$C$_6$H$_4$
2c, E = O; BR$_2$ = B-1,2-(NMe)$_2$C$_6$H$_4$
2d, E = O; BR$_2$ = B-1-(NH)-2-SC$_6$H$_4$
2e, E = O; BR$_2$ = B-1,2-O$_2$-3-MeC$_6$H$_3$
2f, E = O; BR$_2$ = BCl$_2$
2g, E = O; BR$_2$ = B(OH)$_2$
2h, E = O; BR$_2$ = B(OMe)$_2$
2i, E = O; BR$_2$ = B(OEt)$_2$
2j, E = O; BR$_2$ = B-1,2-(NMe)$_2$C$_2$H$_4$
2k, E = S; BR$_2$ = Bcat
2l, E = S; BR$_2$ = B-1-(NH)-2-SC$_6$H$_4$

compound [CpFe(CO)$_2$(Bcat)] was stable under similar conditions for a day.[46] The related compound [CpFe(CO)$_2$(BPh$_2$)], however, was found to decompose when exposed to temperatures of 80 °C or under photolytic conditions.[46] Earlier studies with compounds formulated as [Mn(CO)$_5${B(NMe$_2$)$_2$}] (eq 41)[5] and [Mn(CO)$_4$(PPh$_3$){B(NMe$_2$)$_2$}] (eq 42)[6] described complex decomposition processes resulting in the formation of B$_2$(NMe$_2$)$_4$ as well as polymeric B–N–containing materials. The salts Li[Fe(CO)$_4$(Bcat′)] (section III.B.1.x) were found to decompose to [Bcat′$_2$]$^-$ in solution, a process which was accelerated in polar solvents.[49]

$$[\mathrm{Mn(CO)_5\{B(NMe_2)_2\}}] \xrightarrow[100^\circ\mathrm{C}]{\Delta} \mathrm{B_2(NMe_2)_4} + \mathrm{Mn_2(CO)_{10}} \quad (41)$$

$$[\mathrm{Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}}] \xrightarrow[200^\circ\mathrm{C}]{\Delta} \mathrm{B_2(NMe_2)_4} + \mathrm{PPh_3} + \mathrm{HNMe_2} + \text{polymers} \quad (42)$$

Scheme 6. Reactivity of Rhodium− and Iridium−Boryl Compounds



The bisboryl compounds $[Fe(CO)_4(Bcat')_2]$ (eq 29) were all found to be thermally sensitive decomposing in hours in solution or in days in the solid state.[49] In this case, polar solvents also accelerated the formation of $B_2cat'_3$ derivatives. Similar sensitivity has been noted for metal−boryl compounds incorporating the late transition metals. For example, the reaction of $[RhCl(PPh_3)_3]$ with HBcat in thf or CH_2Cl_2 was reported to yield several products including B_2cat_3 and $[RhHCl(PPh_3)_2(Bcat)]$. The rhodium−boryl complex in this case was unstable in the presence of free PPh_3 (eq 43).[69] The rhodium−bisboryl compounds (Scheme 1) were reported to be stable in CH_2Cl_2 for a period of one week in the absence of added phosphine or thf.

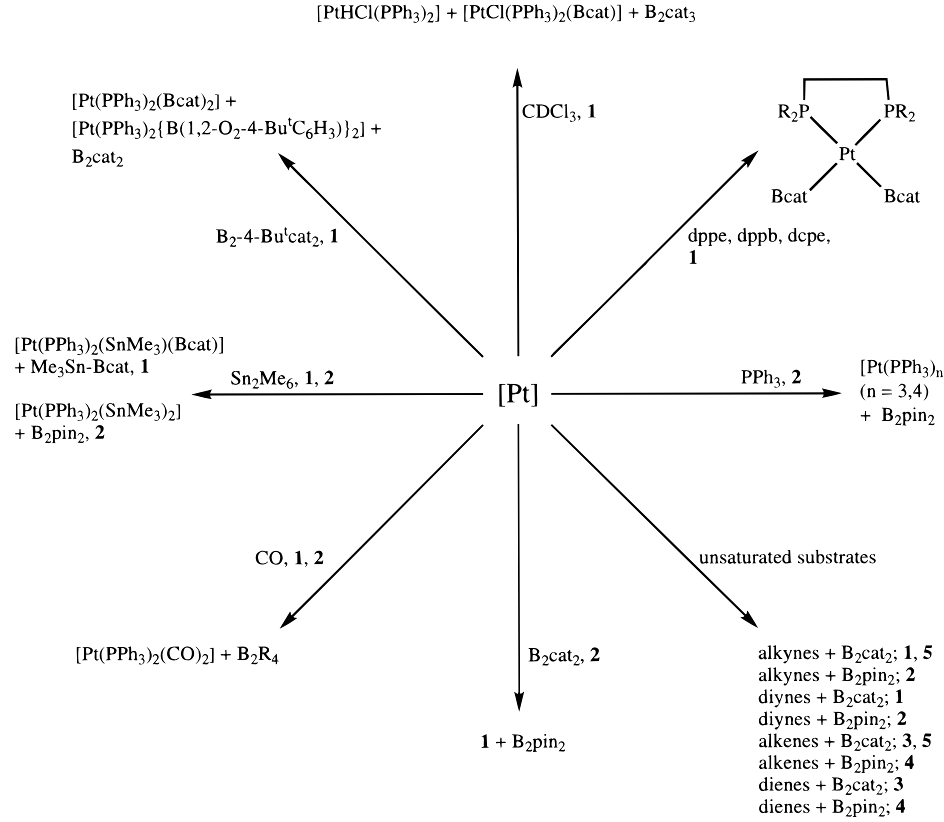
$$[RhHCl(PPh_3)_2(Bcat)] \xrightarrow[PPh_3]{} [RhCl(PPh_3)_3] + [RhH_2Cl(PPh_3)_3] + B_2cat_3 \quad (43)$$

The compound $[Pt(PPh_3)_2(Bcat)_2]$ (Scheme 2) was shown to decompose at 111 °C resulting in a red oil.[30] Solutions of this compound were also prone to decomposition yielding a red oil over time at room temperature. Solutions in C_6D_6 were stable for weeks at ambient temperature although solutions in $CDCl_3$ were shown to decompose within an hour and after 3 days several products were identified by ^{31}P NMR (eq 44). After one week, the sample contained *trans*-$[PtHCl(PPh_3)_2]$ and B_2cat_3 as the main constituents.

$$\textit{cis}\text{-}[Pt(PPh_3)_2(Bcat)_2] \xrightarrow[\text{3 days}]{CDCl_3} \textit{cis}\text{-}[Pt(PPh_3)_2(Bcat)_2] + \textit{trans}\text{-}[PtHCl(PPh_3)_2] + \textit{trans}\text{-}[PtCl(PPh_3)_2(Bcat)] + B_2cat_3 \quad (44)$$

ii. Hydrolysis. The hydrolysis of metal−boryl compounds has been shown to lead to activation of the M−B bond as well as the BR_2 ligand itself (section

Scheme 7. Reactivity of Platinum−Boryl Compounds



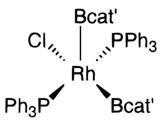
$[Pt] = [Pt(PPh_3)_2(Bcat)_2]$, **1**
$[Pt(PPh_3)_2(Bpin)_2]$, **2**
$[Pt(nbe)_3]/B_2R_4$, **3**
$[Pt(dba)_2]/B_2R_4$, **4**
$[Pt(COD)_2]/B_2R_4$, **5**

† Pt-boryl compounds derived from [Pt] = **3**, **4**, **5** have not been isolated. The compounds [Pt] = **1**, **2** have been prepared from $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$.

III.D). Thus, an aminoborane derivative formulated as $[Mn(CO)_5\{B(NMe_2)_2\}]$ was shown to react with water to yield boric acid as the main boron containing species (eq 45).[5]

$$[Mn(CO)_5\{B(NMe_2)_2\}] \xrightarrow{H_2O} B(OH)_3 + Mn_2(CO)_{10} + HNMe_2 + H_2 \quad (45)$$

Reactions with $[Cp_2WH(Bcat)]$ resulted in the formation of Cp_2WH_2 and catBOBcat.[52] Related products were obtained in reactions with the rhodium−bisboryl compounds described in Scheme 1 (eq 46).[79] Reactions involving the mixed rhodium−bisboryl compounds (section III.B.1.ix) resulted in the formation of mixed $R_2BOBR'_2$ compounds.



$$\xrightarrow[PPh_3]{H_2O} \textit{cis,mer}\text{-}[RhH_2Cl(PPh_3)_3] + cat'BOBcat' \quad (46)$$

iii. Reactions with ROH and R₂NH. The preference for boryl ligands to react with donor atoms such as oxygen and nitrogen is presumably a result of the enhanced stabilization of the vacant p_π orbital on boron. It is not surprising therefore that alcohols and secondary amines react with certain metal−boryl compounds in a related manner. The tungsten−boryl complexes prepared by Hartwig and co-workers have been examined for reactivity with alcohols and amines. The compound $[Cp_2WH(Bcat)]$ reacts with MeOH and EtOH to yield the respective ROBcat compounds and Cp_2WH_2 (eq 47),[52] although the same compound displayed no reaction with coordinating solvents such as NEt_3, thf, pyridine, and acetonitrile or the ligand PPh_3. The bisboryl compounds, $[Cp_2W(Bcat')_2]$ (eq 28), were also shown to react with EtOH albeit more slowly than with $[Cp_2WH(Bcat)]$.[51,52] The compound $[Cp_2WCl(Bcat)]$ also reacted slowly with

MeOH and steric constraints resulting from the Cl or increased π-bonding effects were suggested as possible sources of the observed reduction in reaction rates.

$$[\mathrm{Cp_2WH(Bcat)}] \xrightarrow[\mathrm{R = Me,\ Et}]{\mathrm{ROH}} \mathrm{Cp_2WH_2 + ROBcat} \qquad (47)$$

The tungsten−boryl compounds were relatively inert to reactions with amines, although the reaction of [$\mathrm{Cp_2WH(Bcat)}$] with diethylamine was found to proceed only in the presence of catalytic quantities of water. However, the iron−boryl compounds prepared by the same authors were considerably more reactive toward amination reactions. The compound [$\mathrm{CpFe(CO)_2(Bcat)}$] was reported to react rapidly with N−H bonds to give [$\mathrm{CpFeH(CO)_2}$] and the corresponding aminoborane as products.[46] Related behavior was also apparent in reactions involving the iron−bisboryl derivatives (eq 29) and substituted amines (eq 48).[49] When stoichiometric quantities of $\mathrm{HNEt_2}$ were used, 1 equiv of HBcat′ was also observed. The same compounds reacted immediately with excess EtOH to form [$\mathrm{Fe(CO)_4H_2}$] and EtOBcat′ with 1 equiv of HBcat′ formed under stoichiometric conditions.

$$[\mathrm{Fe(CO)_4(Bcat')_2}] \xrightarrow{\mathrm{(xs)\ Et_2NR}} 2\ \mathrm{Et_2NBcat'} + [\mathrm{Fe(CO)_4R_2}] \qquad (48)$$

cat′ = $\mathrm{1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3}$ and
$\mathrm{1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2\text{-}C_6H_2}$

R = H, $\mathrm{SiMe_3}$

iv. Reactions with H_2 and O_2. There are only a few reported reactions involving the action of H_2 and O_2 with metal−boryl compounds. Early studies described the reaction of the compound formulated as [$\mathrm{Co(dppe)_2(BPh_2)_2}$] with oxygen in thf in which the compounds [$\mathrm{(dppe)_2CoO}$]$_n$ and $\mathrm{Ph_2BOBPh_2}$ were apparently formed.[9] Prior to this, the compound [$\mathrm{Mn(CO)_5\{B(NMe_2)_2\}}$] had been reported to react with hydrogen yielding an amino borane and the corresponding metal hydride compound (eq 49).[5]

$$[\mathrm{Mn(CO)_5\{B(NMe_2)_2\}}] \xrightarrow{\mathrm{H_2}} \mathrm{HMn(CO)_5 + HB(NMe_2)_2} \qquad (49)$$

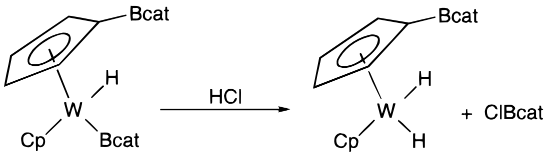
Recently, iron−boryl derivatives were examined by Hartwig and co-workers. The compound [$\mathrm{CpFe(CO)_2(BPh_2)}$] reacted within 30 min under 2 atm of hydrogen to yield $\mathrm{HBPh_2}$ which disproportionated to $\mathrm{BPh_3}$ and diborane ($\mathrm{B_2H_6}$) (eq 50).[46] Similar reactivity was noted for the FeBcat derivative (eq 51).[48]

$$[\mathrm{CpFe(CO)_2(BPh_2)}] \xrightarrow{\mathrm{H_2}} [\mathrm{CpFeH(CO)_2}] + \mathrm{HBPh_2} \qquad (50)$$

$$[\mathrm{CpFe(CO)_2(Bcat)}] \xrightarrow{\mathrm{H_2}} [\mathrm{CpFeH(CO)_2}] + [\{\mathrm{CpFe(CO)_2}\}_2] + \mathrm{HBcat} \qquad (51)$$

40-50%

v. Reactions with HCl. Two examples of the reaction with protic acids have been reported. Initially, [$\mathrm{Mn(CO)_5\{B(NMe_2)_2\}}$] reacted with HCl to form [$\mathrm{MnH(CO)_5}$], $\mathrm{BCl_3}$, and [$\mathrm{Me_2NH_2}$]Cl.[5] Related products were obtained in reactions involving [$\mathrm{Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}}$] with 5 equiv of HCl. The use of less than 5 equiv with the phosphine derivative resulted in reactions at the boryl ligand (section III.D.4). Recently, the formation of ClBcat was observed from the reaction between HCl and [(CpBcat)CpWH(Bcat)] (section III.B.2.iii) (eq 52).[52]



(52)

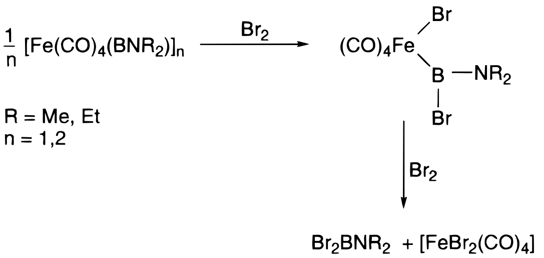
vi. Halogenation Reactions. Initial studies involving the bromination of metal−boryl compounds were reported by Nöth and Schmid. The manganese−boryl derivatives (eq 53) were reported to react with bromine to produce a Mn−Br bond and $\mathrm{BrB(NMe_2)_2}$.[5,6]

$$[\mathrm{Mn(CO)_4L\{B(NMe_2)_2\}}] \xrightarrow{\mathrm{Br_2}} [\mathrm{MnBr(CO)_4L}] + \mathrm{BrB(NMe_2)_2} \qquad (53)$$

L = CO, $\mathrm{PPh_3}$

The compound [$\mathrm{PtCl(PPh_3)_2(BPh_2)}$] reacted in a similar fashion to yield [$\mathrm{PtClBr(PPh_3)_2}$] and $\mathrm{BrBPh_2}$.[4] Recently, an anologous reaction with [$\mathrm{CpFe(CO)_2(Bcat)}$] has been reported in which BrBcat and [$\mathrm{CpFeBr(CO)_2}$] were formed.[46] The compound [$\mathrm{Cp_2WH(Bcat)}$] was shown to react with $\mathrm{CCl_4}$ to form [$\mathrm{Cp_2WCl(Bcat)}$] in 88% yield which, as mentioned previously, reacts slowly with alcohols.

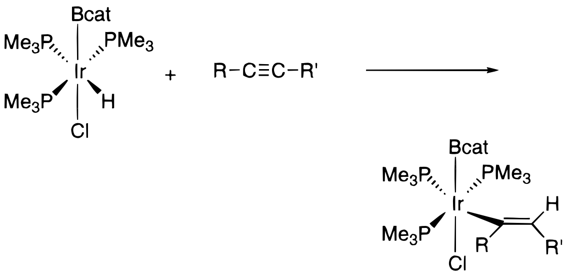
The borenyl compounds formulated as [$\mathrm{Fe(CO)_4(BNR_2)}$] (although the true nature of these compounds is open to question) were reported to react with 2 equiv of bromine. Initially, halogenation at the metal and boron center occurred which yielded a metal−boryl complex which reacted similarly to those compounds described above (eq 54).[13]



(54)

vii. Insertion Reactions. Several late transition metal−boryl compounds have been shown to undergo insertion reactions with small molecules and catalytically important substrates. Those to the left of these in the periodic table display different reactivity and catalytic processes which do not involve metal−boryl intermediates. For example, [$\mathrm{Cp_2WH(Bcat)}$] has been shown to be very reactive in previous examples, although the same compound was much less reactive in reactions involving 1-hexyne, 1-hexene, CO, $\mathrm{CO_2}$, and H_2, as well as with acetone and boranes.[47,52] In this respect, [$Cp_2WH(Bcat)$] may be considered approximately intermediate in reactivity between these two extremes. The following section describes insertion reactions including information derived from catalytic processes. These include reactions with sp- and sp^2-hybridized substrates and a brief description of insertions involving other small molecules.

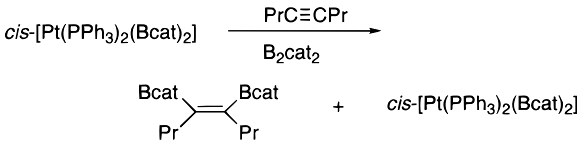
a. Insertion of Alkynes. Initial studies regarding the insertion of alkynes into metal−boryl bonds involved the use of [$IrHCl(PMe_3)_3(Bcat)$].[73] In this case, however, a preference for insertion into the Ir−H bond was observed (eq 55). When electron-withdrawing substituents were present on the alkyne, the authors observed reductive elimination of the B−C bond, yielding vinylboronate esters. This behavior can be rationalized by taking into account recent calculations of the relative stability of Ir−H (60 kcal mol^{-1}) and Ir−B bonds (66 kcal mol^{-1}).[44] Clearly, a small difference exists between barriers to insertion for Ir−H and Ir−B bonds, with which thermodynamic factors are consistent. The compounds [$IrH_2Cl(CO)(PPh_3)_2$] and [$IrHCl(CO)(PPh_3)_2(Bcat)$] were used as model complexes.



(55)

R = R' = C(O)OMe
R = H; R' = Bu^t, Ph, $SiMe_3$

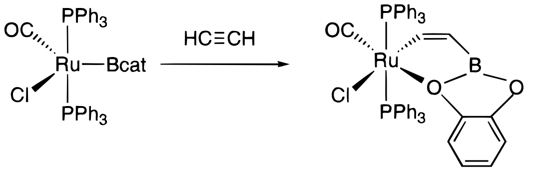
Recently, several reports describing the stoichiometric and catalytic diboration of alkynes and diynes have appeared. A common feature in all of these reports is the necessity for insertion of alkyne substrates into the Pt−B bond resulting from the observation of Smith and co-workers that [$Pt(PPh_3)_2(\eta^2$-4-octyne)] reacts stoichiometrically with B_2cat_2 to give [$Pt(PPh_3)_2(Bcat)_2$] and 4-octyne.[28] The reaction of [$Pt(PPh_3)_2(Bcat)_2$] with 4-octyne, however, resulted in diboration of the alkyne (eq 56), indicating the importance of insertion into the Pt−B bond. Kinetic investigations revealed that the process was first-order overall in concentration of the platinum−bisboryl species.[29]



(56)

A number of alkynes[25,26,29,30] and diynes[30] have been catalytically diborated, or tetraborated in the case of diynes, via insertion into Pt−B bonds. Recent theoretical studies have estimated the Pt−B bond energy of [$Pt(PH_3)_2\{B(OH)_2\}_2$] and [$Pt(PH_3)_2(BH_2)_2$] to be 62.9 and 64.8 kcal mol^{-1}, respectively.[43] In addition, a detailed examination of the alkyne diboration reaction was also reported[42] which showed that insertion of acetylene into the $Pt-B(OH)_2$ bond was exothermic by 28.1 kcal mol^{-1} with the overall reaction being exothermic by 60.8 kcal mol^{-1}. With the rate-determining step in the catalysis calculated to be phosphine dissociation from [$Pt(PH_3)_2\{B(OH)_2\}_2$],[42] it is not surprising that the insertion proceeds readily when a monophosphine catalyst was prepared using [$Pt(cod)_2$].[30] It should be noted that phosphine dissociation occurs prior to the rate-determining step when platinum−PPh_3 complexes are used, these results providing good confirmation of these theoretical studies.[29]

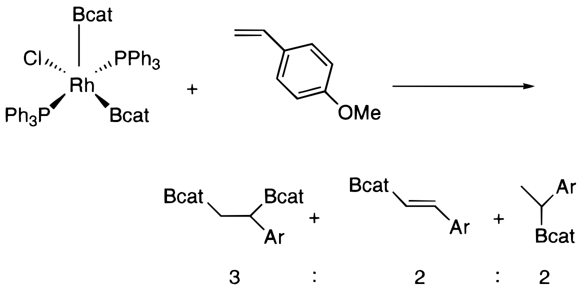
Recently, the isolation and structural characterization of the insertion product derived from the reaction between acetylene and [$RuCl(CO)(PPh_3)_2(Bcat)$] has been reported (eq 57).[76] This is the first example of the isolation of such an intermediate. Attempts to isolate similar products from the reactions between alkynes and *trans*-[$PtX(PPh_3)_2(Bcat)$] (X = Cl, Br) have thus far proven unsuccessful.[63]



(57)

b. Insertion of Alkenes. The insertion of alkenes into metal−boron bonds is a common feature in catalyzed hydroboration and diboration reactions. Similar reactivity is presumed to account for the activation of related sp^2-hybridized substrates such as dienes[32−34] and α,β-unsaturated ketones.[36]

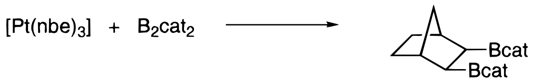
The insertion of alkenes into Rh−B bonds has been reported by Marder and co-workers (eq 58).[67] The product distribution using 4-vinylanisole was attributed to β-hydride elimination occurring after the insertion reaction leading to the formation of the vinylboronate ester. Hydrogenated products such as the monoborated aryl species in eq 58 were attributed to reactions with Rh−H species also formed in the β-hydride elimination reaction. This type of behavior is common with rhodium-catalyzed hydroboration reactions[24] where competition of incoming substrates with M−H versus M−B bonds is apparent in the distribution of products. Evans et al. [95] have reported a preference for the insertion of alkenes into Rh−H bonds and this has been complemented by theoretical studies,[40] although other theoretical studies have also



(58)

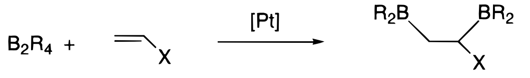
been described[42] which support insertion into Rh–B bonds as indicated by some experimental studies.[60,96,97] Although alkene insertion using rhodium compounds may give rise to multiple products, a catalyst fashioned from gold precursors was found to be effective for the diboration of alkenes since the β-hydride elimination reaction pathway was excluded.[31]

Initial studies involving phosphine-containing platinum–bisboryl compounds indicated no activity for the diboration of alkenes.[25] Subsequently however, Smith and co-workers demonstrated an immediate reaction between [Pt(nbe)$_3$] (nbe = norbornene) and B_2cat_2 (eq 59), yielding the norbornene diboration product in 88% yield.[28] In this case, oxidative addition of B_2cat_2, followed by insertion of norbornene into the Pt–B bond is a likely mechanism although there is no experimental data to support this. Theoretical studies[42] indicated that insertion of ethylene into the Pt–B bonds in [Pt(PH$_3$){B(OH)$_2$}$_2$] was less favorable energetically (≈13 kcal mol^{-1}) compared to the reaction involving acetylene. The substitution of a π-bound ligand for a phosphine ligand should result in an overall reduction of the activation barrier to insertion of alkenes by destabilizing the platinum–bisboryl complex prior to the insertion step.



(59)

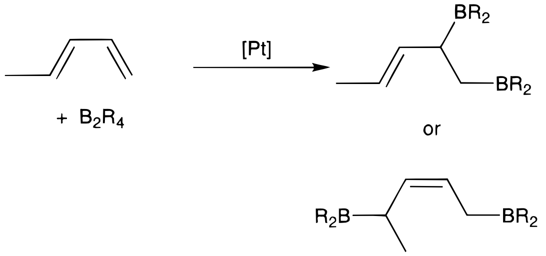
Recent experimental results have also demonstrated the utility of compounds such as [Pt(dba)$_2$] (dba = dibenzylideneacetone), [Pt(cod)$_2$], and [Pt(nbe)$_3$] as catalyst precursors for the diboration of terminal and strained cyclic alkenes (eq 60)[33,34] and dienes (eq 61).[32–34] With alkene diboration, reactions involving [Pt(cod)$_2$] and B_2cat_2 gave optimal yields compared to the [Pt(dba)$_2$]/B_2pin_2 system. Higher reactivity has been noted for B_2cat_2 compared to B_2pin_2 in previous studies.[30,77]



(60)

[Pt] = [Pt(COD)$_2$]
R_2 = cat; X = H, Bu, 1-ClBu,1-MeC(O)OBu,C_6H_4-*p*-OMe, C_6H_4-*p*-CF_3
[Pt] = [Pt(nbe)$_3$]
R_2 = cat; (C=CX) = nbe
[Pt] = [Pt(dba)$_2$]
R_2 = pin; X = C_8H_{17}, Ph, C_6H_4-*p*-OMe

In reactions of dienes, dimerization in the presence of [Pt(dba)$_2$] occurred prior to diboration when 2 equiv of isoprene were used.[32] In reactions with B_2pin_2 and penta-1,5-diene, variation in catalytic conditions gave rise to different products.[34] For example, reactions with [Pt(dba)$_2$] in toluene at room temperature resulted in the formation of a 1,2-diboration product while in the presence of [Pt(PPh$_3$)$_4$] at 80 °C, the 1,4-diboration product was obtained (eq 61). Reactions involving B_2cat_2 and norbornadiene (nbd) were found to yield tetraboration products while reactions with hexa-1,5-diene enabled the isolation of diborated and tetraborated products.[33]



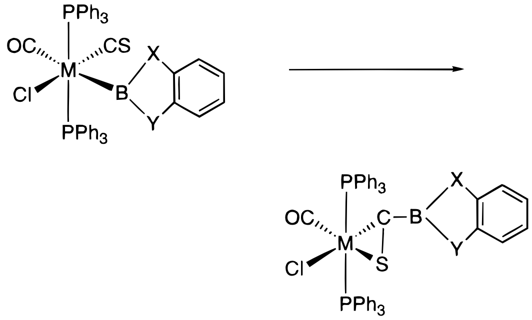
(61)

c. Insertion of Other Molecules. The insertion of other small molecules such as CO into M–B bonds has received limited attention. Nöth and Schmid reported the insertion of SO_2[6] and CS_2[22] into Mn–B (eq 62) and Co–B (eq 63) bonds respectively although the compounds are not well characterized.

$$[Mn(CO)_5\{B(NMe_2)_2\}] + SO_2 \longrightarrow [Mn(CO)_5\{(SO_2)B(NMe_2)_2\}] \quad (62)$$

$$[Co(dppe)_2(BPh_2)] + CS_2 \longrightarrow [Co(dppe)_2\{(CS_2)BPh_2\}] \quad (63)$$

The only additional example of this type of behavior which has been reported is that the unstable, six-coordinate compound [MCl(CO)(CS)(PPh$_3$)$_2${B-1,2-XYC$_6H_4$}] (section III.C.2), spontaneously inserted a CS ligand into the M–B bond (eq 64).[76]



(64)

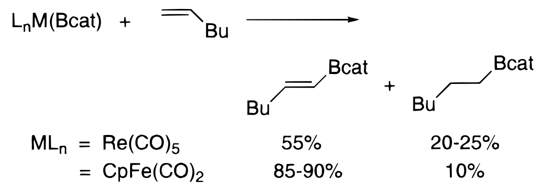
M = Ru; X = Y = O, X = NH, Y = S
M = Os; X = Y = O

viii. Photolytic Hydrocarbon Activation Reactions. Hartwig and co-workers have examined several metal–boryl compounds under photolytic conditions and demonstrated the activation of aromatic, olefinic, and aliphatic compounds.[48,53] Although the exact mechanism and whether it involves insertion into M–B bonds or radical reactions is unclear, these workers have provided strong evidence against boryl radicals being involved namely k_H/k_D data for benzene activation varies with the metal system.[53] Reactions in benzene proceeded rapidly with [CpFe(CO)$_2$(Bcat)] yielding 80–90% of PhBcat in an hour (eq 65).[48] The rhenium derivative reacted in 3 h to give a 50% yield while the manganese complex required 6 h of irradiation to achieve 43% conversion. In reactions involving rhenium, the compound $Re_3H_3(CO)_{12}$ was also observed in the products.

$$L_nM(Bcat) \longrightarrow PhBcat + [\{ML_n\}_2] \quad (65)$$

ML_n = CpFe(CO)$_2$ (80-90 %)
= Re(CO)$_5$ (50 %)
= Mn(CO)$_5$ (43 %)

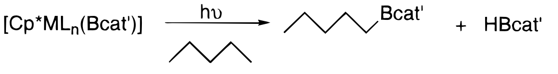
The more reactive rhenium and iron derivatives were also examined in toluene and 1-hexene. Reactions in toluene yielded mixtures of meta and para borylated products with small but significant differences in the meta/para ratio. (Re, 1.6:1.0; Fe, 1.1: 1.0). Reactions with 1-hexene (eq 66) yielded *trans*-borylalkene and borylalkane products. The iron boryl derivative underwent dehydrogenative borylation producing the borylalkene product selectively. The latter process was attributed to activation of C−H bonds following reductive elimination of the B−C bond.



(66)

ML_n = $Re(CO)_5$ 55% 20-25%
= $CpFe(CO)_2$ 85-90% 10%

Recently, Waltz and Hartwig have described the activation of alkanes using metal−boryl compounds in which both the boryl and cyclopentadienyl ligands were methylated (eq 67).[53] The borylation of pentane was much more efficient in the presence of a third row transition metal derivative. In fact, the tungsten−boryl derivative was also shown to actively borylate 2-methylbutane (55% at the terminal 4 position), cyclohexane (22%), and ethyl-cyclohexane (74% at the Et terminus).

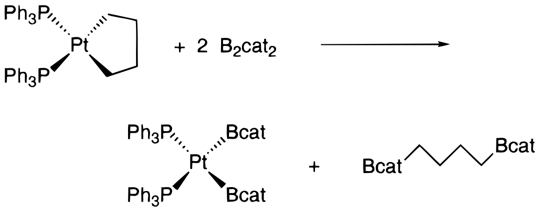


(67)

$Cp^* = C_5Me_5$ Bcat' = 1,2-O_2-3,5-$Me_2C_6H_2$
$ML_n = Fe(CO)_2$ 28% 10%
$= Ru(CO)_2$ 40% trace
$= W(CO)_3$ 85%

ix. Reactions Involving σ-Bond Metathesis. The use of cobalt−bisboryl compounds for the synthesis of a series of additional L_nM−boryl species has been discussed in section II.D (eqs 35 and 36). Recent studies have revealed similar metathetical behavior although in some cases a metal−boryl complex may not be involved.

Iverson and Smith initially reported a metathetical reaction between a platinum−metallocyclopentane complex and B_2cat_2 (eq 68).[28] Whether or not a metal−boryl intermediate was formed before B−C bond formation is not known. The compound *cis*-[Pt-$(PPh_3)_2(Bcat)_2$] was also shown to react with Sn_2Me_6, yielding $Me_3SnBcat$ which definitely demonstrated Pt−Bcat participation (eq 69).[29] Similar products were reported from reactions with the cobalt−bisboryl compounds and Sn halides (eq 37). Related reactions of B_2cat_2 and B_2pin_2 with $Me_3Si−C≡C−SiMe_3$ were also reported to give rise to R_2BSiMe_3 and $R_2BC≡CSiMe_3$ apparently by similar processes under catalytic conditions.[30] Reactions of platinum−bisboryl compounds with other diborane(4) compounds have been investigated although the products were shown not to contain mixed-boryl complexes which would have been consistent with a metathetical reaction.[29,30]



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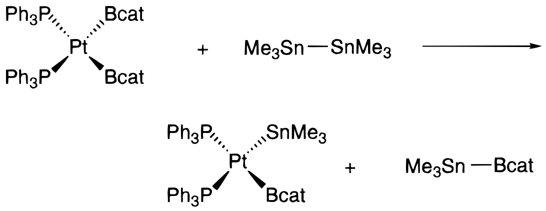
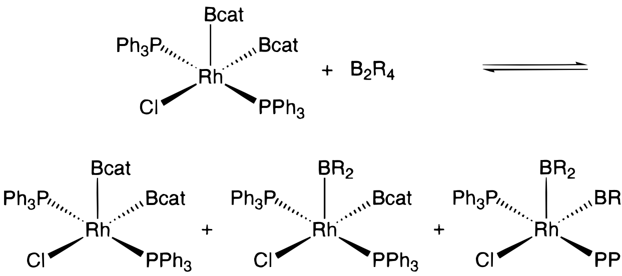


(69)

Thus, a reductive elimination/oxidative addition sequence was proposed.

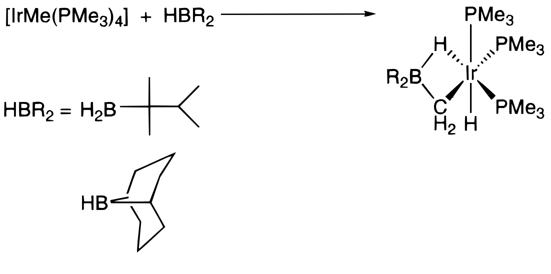
Metathesis involving rhodium−bisboryl compounds with diborane(4) compounds have been reported to yield equilibrium mixtures of bisboryl compounds, including those of the metathetical mixed-boryl products (eq 70).[78]



(70)

$B_2R_4 = B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$, $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$, $B_2(1,2\text{-}O\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_2$, $B_2(tart)_2$

Reactions of HBcat with some metal−Me bonds result in the formation of metathetical products but these may also not involve metal−boryl intermediates. The reaction between HBcat and [CpRuMe-$(PPh_3)_2$] resulted in the formation of [CpRuH$(PPh_3)_2$] and MeBcat.[98] Reactions of [IrMe$(PMe_3)_4$] with thexylborane or 9-BBN have also been shown to result in boraethyl−metal compounds which could be indicative of metathetical intermediates (eq 71),[70] B−H oxidative addition, or alkyl anion abstraction followed by C−H oxidative addition.

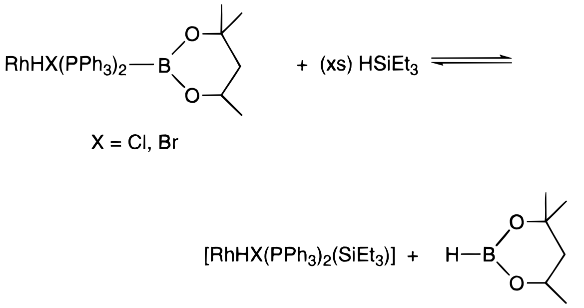


(71)

x. Miscellaneous. The Lewis acidity of the boryl ligand with regard to incoming substrates may dictate observed reactivity patterns. For example, [CpFe$(CO)_2(BPh_2)$] reacts with HBcat (eq 72).[46] The lack of B−X π-stabilization of the BPh_2 ligand, or the steric requirements of the Ph groups could result in a higher reactivity compared to the weaker Lewis acid moiety Bcat, but the reaction could also be driven by the formation of B—H—B bridges in $HBPh_2$ or any number of other factors.

$$[CpFe(CO)_2(BPh_2)] + HBcat \longrightarrow \underset{90\ \%}{[CpFe(CO)_2(Bcat)]} + HBPh_2 \qquad (72)$$

The photolytic activation of $[Cp_2WH(Bcat)]$ in benzene on the other hand, results in the formation of $[Cp_2WHPh]$ with elimination of HBcat.[52] Early studies involving rhodium—boryl complexes with $HSiEt_3$ indicated the existence of an equilibrium between the metal—boryl and metal—silyl compounds (eq 73).[65] It was postulated that a lack of sufficient π-stabilization of the boryl moieties may be responsible for the activities observed with the reagents described since the π-bonding in such metal—boryl compounds has been noted to be weak. However, differences in the bond dissociation energies of the Si—H and B—H bonds may account for the observed equilibria. There is as yet no definitive data concerning M—B π-bonds but see section IV.C.



(73)

The iron—bisboryl compounds (eq 29) react with lithium amides resulting in the cleavage of the $M—BR_2$ bond, yielding the anionic iron boryl complex shown in eq 74.[49] This anionic metal—boryl compound reacts with sources of CH_3^+ resulting in the cleavage of the remaining $Fe—BR_2$ bond (eq 75). When the triflate derivative was used, a 60% yield of MeBcat was obtained.

$$[Fe(CO)_4(Bcat)_2] + Li[N(SiMe_3)_2] \longrightarrow Li[Fe(CO)_4(Bcat)] + (Me_3Si)_2NBcat \qquad (74)$$

$$Li[Fe(CO)_4(Bcat)] + MeX \xrightarrow{-LiX} MeBcat + [\{Fe(CO)_n\}_m] \qquad (75)$$

The palladium-catalyzed reaction of aryl halides with diborane(4) compounds has recently been shown to produce a variety of aryl—boryl compounds.[27]

2. Ligand Substitution Involving M–BR$_2$

The cleavage of $M—BR_2$ bonds does not necessarily involve a direct reaction with the incoming molecules. Examples of reactivity of this type have been observed with diborane(4) compounds, π-acids, and Sn reagents with metal—boryl compounds on the right-hand side of the periodic table.

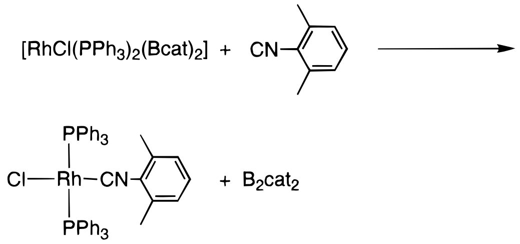
i. Reactions with Diborane(4) Compounds. In section III.B.1.ix, the platinum—bisboryl compounds were discussed in respect to the lack of metathetical reactions with other diborane(4) compounds. As mentioned, these compounds react via reductive elimination/oxidative addition of B—B bonds. For example, *cis*-$[Pt(PPh_3)_2(Bcat)_2]$ reacts with $B_2(4\text{-}Bu^tcat)_2$ to give a mixture of the symmetrical platinum—bisboryl compounds presumably via a dissociative mechanism although detailed studies have not yet been carried out.[30] No reaction was observed with B_2pin_2, although the compound *cis*-$[Pt(PPh_3)_2(Bpin)_2]$ did react with B_2cat_2 with elimination of B_2pin_2 (eq 76).[29] Both steric and electronic factors may account for the instability of the Pt—Bpin bond. The inability to form $[RhCl(PPh_3)_2(Bpin)_2]$ via oxidative addition to $[RhCl(PPh_3)_3]$ or $[\{RhCl(PPh_3)_2\}_2]$ provides further evidence of differing inherent M—B bond strengths or steric constraints.[77]

$$[Pt(PPh_3)_2(Bpin)_2] + B_2cat_2 \underset{X}{\rightleftarrows} [Pt(PPh_3)_2(Bcat)_2] + B_2pin_2 \qquad (76)$$

ii. Reactions with π-Acids. The platinum—bisboryl compounds were also found to react with CO resulting in the formation of B_2R_4 and $[Pt(CO)_2(PPh_3)_2]$ (eq 77).[29] The use of π-acids to displace B_2cat_2 from $[RhCl(PPh_3)_2(Bcat)_2]$ has been demonstrated with *o*-xylyl isocyanide (eq 78),[67] the reduced electron density at rhodium caused by the π-acceptor presumably being the driving force for reductive elimination. Strong donors such as PEt_3 result in phosphine exchange reactions which are discussed in the following section.

$$[Pt(PPh_3)_2(BR_2)_2] \underset{-CO}{\overset{+CO}{\rightleftarrows}} [Pt(PPh_3)_2(CO)_2] + B_2R_2 \qquad (77)$$

BR_2 = Bpin, Bcat



(78)

iii. Miscellaneous. The compound *cis*-$[Pt(PPh_3)_2(Bpin)_2]$ also reacts with Sn_2Me_6 and PPh_3 via reductive elimination of the B—B bond.[29] No metathetical products related to the reaction of Sn_2Me_6 with *cis*-$[Pt(PPh_3)_2(Bcat)_2]$ were observed. The reaction with PPh_3 (eq 79) resulted in an equilibrium mixture of products. The reactivity in the presence of added phosphine presumably accounts for the requirement of a large excess of B_2pin_2 in the original synthesis of *cis*-$[Pt(PPh_3)_2(Bpin)_2]$ from $[Pt(PPh_3)_4]$.[25,26]

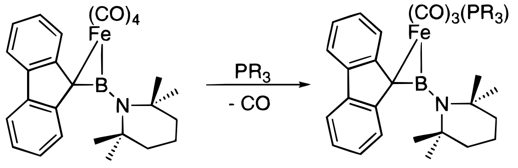
$$[Pt(PPh_3)_2(Bpin)_2] \underset{-PPh_3}{\overset{+PPh_3}{\rightleftarrows}} [Pt(PPh_3)_4] + [Pt(PPh_3)_3] + B_2pin_2 \qquad (79)$$

C. Reactions at the Metal Center

Many examples of ligand substitution reactions do not involve cleavage of the metal—boron bond and substitution reactions of this type involving phosphines have been reported for metal–boryl compounds of manganese,[6] tungsten,[53] iron,[89,90] rhodium,[67,79] iridium,[74] and platinum.[30] Reactions with Lewis bases such as CO and CN-*p*-tolyl do not always result in the reductive elimination of the boryl fragment in reactions involving ruthenium and osmium derivatives.[76] In addition, substitution with amines and reactions involving ionic substrates have also been reported.

1. Substitution with Phosphine

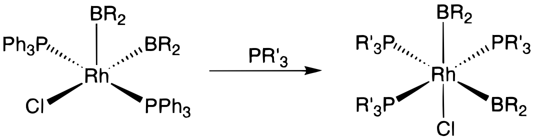
A variety of photolytic reactivity has been described in section III.B.1.viii. The compound [Cp*W(CO)$_3$(Bcat′)][53] also reacted with PMe$_3$ under similar conditions, yielding [Cp*W(CO)$_2$(PMe$_3$)(Bcat′)] with loss of CO. The photolytic activation of CO ligands has also been examined for the compound [Mn(CO)$_5$(Bcat)] which reacted with PPh$_3$ to give [Mn(CO)$_4$(PPh$_3$)(Bcat)], which itself displayed a large range of reactivity.[44] Recently, several phosphines were substituted for CO under photolytic conditions using the Fe(CO)$_4$-η^2-boryl derivative described in section II.B.4. This compound underwent further photolysis in the presence of ligands to give a series of [Fe(CO)$_3$(L)(L′)] complexes where L′ = η^2-amino-9-fluorenylideneborane and L = PPh$_3$, P(C$_6$H$_{11}$)$_3$, P(OCH$_3$)$_3$, SbPh$_3$ and CO (eq 80).[89]



(80)

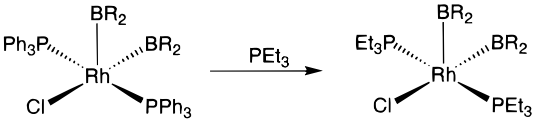
PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PCl$_3$, PCl$_2$Ph, P(OMe)$_3$

Phosphine substitution may also be carried out in the absence of photolytic conditions when more readily dissociating ligands are present. Substitution of the PPh$_3$ ligands in [RhCl(PPh$_3$)$_2$(Bcat′)$_2$] compounds (Scheme 1) has been shown to result in the formation of either five-coordinate (eq 81) or six-coordinate (eq 82) rhodium–bisboryl products.[67,79] No



(81)

PR'$_3$ = PMe$_3$; BR$_2$ = Bcat, B(1,2-O$_2$-4-MeC$_6$H$_3$)
PR'$_3$ = PMe$_2$Ph; BR$_2$ = Bcat, B(1,2-O$_2$-3-MeC$_6$H$_3$)

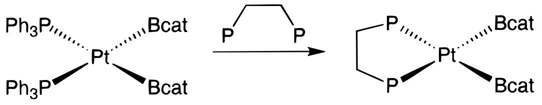


(82)

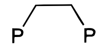
BR$_2$ = Bcat, B(1,2-O$_2$-4-MeC$_6$H$_3$)

reaction was observed with PCy$_3$ or PPr$^i_3$ and reactions involving bidentate ligands such as dppe and dcpe (1,2-dicyclohexylphosphinoethane) resulted in the formation of ionic products with cleavage of the metal–boryl bond.

Replacement of PPh$_3$ with the bidentate phosphines dppe,[30] dppb,[30] and dcpe[99] in *cis*-[Pt(PPh$_3$)$_2$(Bcat)$_2$] proceeded without formation of ionic metal compounds (eq 83). The dppe derivative was relatively inactive toward alkyne diboration consistent with a monophosphine–platinum complex being the active catalyst in related processes.



(83)



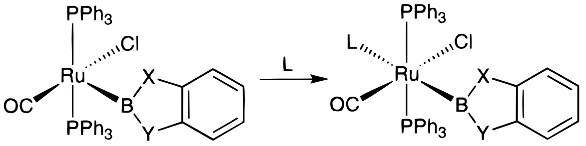
= dppe, dppb, dcpe

Related reactivity has been reported for the iridium–trisboryl compound containing a π-bound mesitylene ligand. In this case, the weakly bound mesitylene ligand is rapidly replaced with three PEt$_3$ ligands to yield *fac*-[Ir(PEt$_3$)$_3$(Bcat)$_3$].[74]

2. Substitution with Lewis Base Ligands

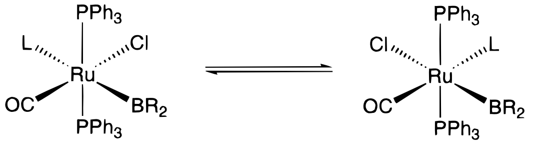
Nöth and co-workers were the first to report ligand substitution with CO at the metal center. The compound [Fe(CO)$_3$(η^4-amino-9-fluorenylideneborane)] described in eq 80 also reacted with CO to produce [Fe(CO)$_4$(η^2-amino-9-fluorenylideneborane)].[88] Ligand addition with Lewis bases has also been demonstrated for a variety of coordinatively unsaturated ruthenium and osmium complexes. Coordination of CO or CN-*p*-tolyl has been observed for several derivatives,[76] the six-coordinate products of which in turn display a wide variety of reactivity.

The five-coordinate ruthenium boryl compounds shown in eq 84 were found to bind Lewis bases yielding a coordinatively saturated product. The products obtained were unstable with regard to isomerization when Bcat or the 2,3-dioxynaphthalene derivative (B-2,3-O$_2$C$_{10}$H$_6$) were present (eq 85). Related behavior has been noted for the complex [IrHBr(CO)(dppe)(Bcat)] (eq 86).[72]



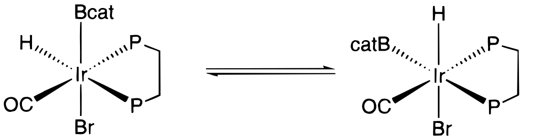
(84)

L = CO; X = Y = O, NH; X = S, Y = NH
L = CO; B-1,2-XYC $_6$H$_4$ = B-2,3-O$_2$C$_{10}$H$_6$
L = CN-*p*-tolyl; X = Y = O



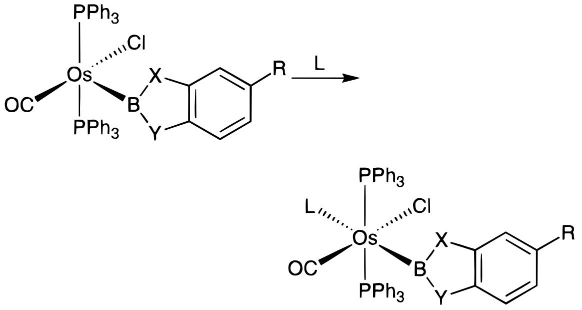
(85)

L = CO; R$_2$ = cat, 2,3-O$_2$C$_{10}$H$_6$, 1,2-(NH)$_2$C$_6$H$_4$, 1-S-2-(NH)C$_6$H$_4$
L = CN-*p*-tolyl; R$_2$ = cat



(86)

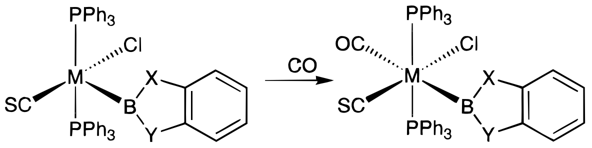
Similar reactivity was observed with five-coordinate osmium boryl compounds (eq 87) although these



(87)

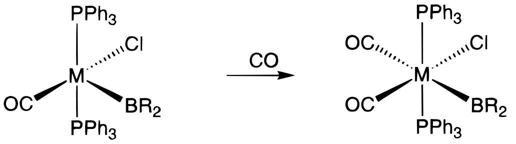
L = CO; R = H; X = Y = O, NH, NMe; X = S, Y = NH
L = CO; R = Me; X = Y = O
L = CN-*p*-tolyl; R = H; X = Y = O, NMe

were not prone to isomerization in solution. Coordination was also achieved with osmium derivatives containing thiocarbonyl ligands (eq 88) and in the presence of a variety of boryl substituents (eq 89).



(88)

M = Ru; X = Y = O; X = S, Y = NH
M = Os; X = Y = O



(89)

$BR_2 = B(OH)_2, B(OMe)_2, B(OEt)_2,$
$B(1,2\text{-}(NMe)_2C_2H_4), B(1,2\text{-}(NMe)_2C_6H_4)$

The coordinatively saturated products obtained from eq 88 were found to undergo insertion of the CS ligand into the metal–boryl bond resulting in $M\{\eta^2\text{-}C(S)(BR_2)\}$ compounds as shown in eq 64 (section III.B.1.vii). Stable derivatives of six-coordinate osmium–boryl compounds were obtained when certain boryl ligands were present (eq 89), the only exception being the $Os\{B\text{-}1,2\text{-}(NMe)_2C_6H_4\}$ derivative which existed in an equilibrium with the five-coordinate species. For $BR_2 = BCl_2$, reactivity with CO and tosylmethyl isocyanide ($CNCH_2$-*p*-tosyl) was found to result in the formation of hydrolysis products at the boryl ligand (section III.D.1).

3. Miscellaneous

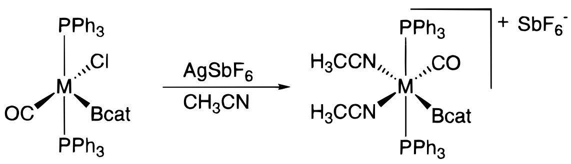
Metal–boryl compounds have also been examined for reactivity with a variety of other reagents not yet described. In the following section, no evidence for cleavage of the M–B bond was noted in the products obtained from the reactions. In most cases, the M–B bond is unusually stable.

Initial studies with $[Co(PPh_3)(BPh_2)(dmg(BPh_2))]$ in pyridine indicated the dissociation of PPh_3 and formation of a Co–pyridine complex.[10] The compound $[Co(dppe)_2(BPh_2)_2]$, which apparently displayed remarkable metathetical behavior, was reportedly reduced to the 20-e$^-$ anion in the presence of Na/Hg amalgam by the same authors (eq 90).[9] The formation of additional ionic metal–boryl compounds has been reported which incorporate the stabilized Bcat′ moiety. The synthesis of $Li[Fe(CO)_4(Bcat')]$ was discussed previously. This ionic derivative reacts further with Me_3SnCl to give a new metal–boryl compound (eq 91).[49]

$$[Co(dppe)_2(BPh_2)_2] \xrightarrow{Na/Hg} Na[Co(dppe)_2(BPh_2)_2] \quad (90)$$

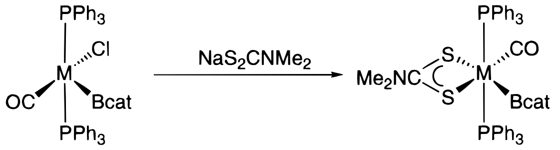
$$Li[Fe(CO)_4(Bcat)] + Me_3SnCl \xrightarrow{-\ LiCl} \underset{90\%}{[Fe(CO)_4(SnMe_3)(Bcat)]} \quad (91)$$

Metal–boryl compounds of ruthenium and osmium were also found to react with silver salts in acetonitrile, yielding cationic metal–boryl compounds (eq 92),[76] the acetonitrile coordinating to the two vacant coordination sites on the metal. Reactions with a dimethyldithiocarbamate salt resulted in the formation of the (η^2-S_2CNMe_2)–metal compounds (eq 93).



(92)

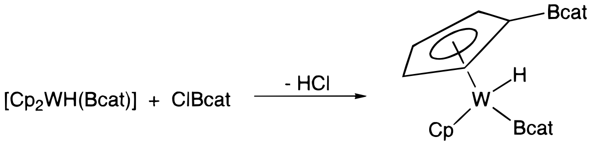
M = Ru, Os + AgCl



(93)

M = Ru, Os + NaCl

Unusual reactivity has been noted for the compound $[Cp_2WH(Bcat)]$ in the presence of added ClBcat. In this example, the reaction occurred at one of the bound Cp ligands with elimination of HCl (eq 94).[52] Related reactivity has also been noted for reactions of Cp_2WH_2 with $RBCl_2$ ($R = Pr^i, Bu^t$) which resulted in zwitterionic complexes incorporating $[Cp_2WH_3]^+$ and $[CpBCl_2R]^-$ moieties.[100]



(94)

D. Reactions at the Boron Center

Reactions occurring directly at the boryl ligand itself are relatively rare, and in most cases, this reactivity is only observed when the boryl ligand contains groups which are not efficient at stabilizing the vacant p orbital on boron such as chlorine. The reactivities of organic hydroboration or diboration products are quite different and have been well-documented. For example, synthetic methodology involving hydrolysis of the boryl products and coupling with aryl halides is well-known due in large part to efforts by Suzuki and co-workers.[27]

1. Hydrolysis

The reactivity of five-coordinate osmium−boryl compounds toward incoming π-acids was illustrated in eq 87. When the compound $[OsCl(CO)(PPh_3)_2(BCl_2)]$ (section II.B.2) reacted with CO and tosylmethyl isocyanide, the reaction products were quite different (eq 95).[76] In this case, coordination of the incoming ligand to the vacant site appeared to activate the boryl ligand toward hydrolysis with trace amounts of water. This process was accelerated in strongly coordinating solvents such as thf and acetonitrile. The five-coordinate compound $[OsCl(CO)(PPh_3)_2(BCl_2)]$ also reacted in a similar fashion with water to give the corresponding $Os{-}B(OH)_2$ product. Both of the derivatives involving CO ligands were structurally characterized.

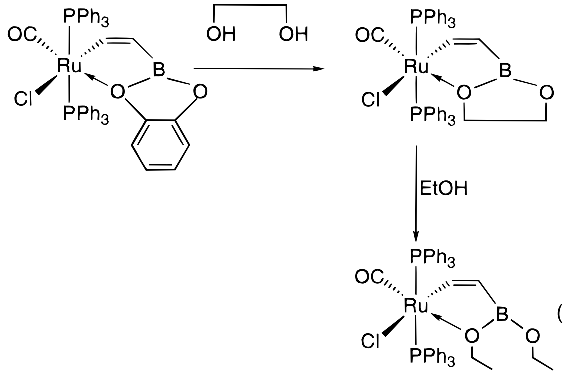
$$[OsCl(CO)(PPh_3)_2(BCl_2)] \xrightarrow[H_2O]{L} [OsCl(CO)(PPh_3)_2(L)\{B(OH)_2\}] \quad (95)$$

L = CO, $CNCH_2$-*p*-tosyl

2. Reactions with Alcohols

The first example of alcoholysis of a boryl ligand was described for a compound formulated as $[Mn(CO)_4(PPh_3)(BCl_2)]$ with sodium methoxide. Sodium methoxide was used because the reaction with alcohols liberated HCl which was known to cleave the Mn−B bond and result in the formation of BCl_3 (section III.D.4).[6]

Recent examples of related reactivity include those of alcohols with the alkyne insertion product of $[RuCl(CO)(PPh_3)_2(Bcat)]$ (eq 57; section III.B.1.vii) shown in eq 96, and $[OsCl(CO)(PPh_3)_2(BCl_2)]$ (eq 97).[76] Although the ruthenium compound is not a true metal−boryl complex, the succession of substitutions for the catecholato and ethylene glycolato moieties are rare and worth mentioning. The presence of a Ru−O bond has been confirmed by cystallographic studies and may result in increased Lewis acidity of the boryl ligand leading to the enhanced substitution chemistry observed.



(96)

The osmium−dichloroboryl compound was shown to react with MeOH and EtOH yielding the alkoxy boryl derivatives (eq 97). No products could be isolated with pinacol, ethylene glycol, or the thiol derivatives, 1,2-ethanedithiol and toluenethiol.

$$[OsCl(CO)(PPh_3)_2(BCl_2)] \xrightarrow{ROH} [OsCl(CO)(PPh_3)_2\{B(OR)_2\}] \quad (97)$$

R = Me, Et

3. Reactions with Amines

All of the known reactions of amines with boryl ligands have been reported for metal−BCl_2 derivatives. Reactions with primary and secondary amines have been examined for complexes of manganese and, more recently, osmium. Reactions with tertiary amines generally result in the formation of adducts at the boryl ligand.

Nöth and Schmid examined the reactivity of the compound described as $[Mn(CO)_4(PPh_3)(BCl_2)]$ with primary, secondary, and tertiary amines. Reactions with $1,2\text{-}(NH_2)_2C_6H_4$ in NEt_3 reportedly afforded a new metal−boryl compound incorporating the $B\text{-}1,2\text{-}(NH)_2C_6H_4$ ligand while the reaction with $HNMe_2$ was said to result in the formation of a $Mn{-}B(NMe_2)Cl$-containing compound.[6] Reaction with NEt_3 in the absence of a primary amine resulted in an adduct formulated as $[Mn(CO)_4(PPh_3)(BCl_2{\cdot}NEt_3)]$. The same reactivity with NEt_3 was noted in reactions with a variety of metal−boryl compounds (eq 98).

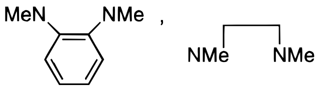
$$[ML_n(BCl_2)] \xrightarrow{NEt_3} [ML_n(BCl_2.NEt_3)] \quad (98)$$

ML_n = $CpMo(CO)_3$, $CpW(CO)_3$, $Mn(CO)_4(PPh_3)$, $CpFe(CO)_2$

Related reactivity has been observed with the compound $[OsCl(CO)(PPh_3)_2(BCl_2)]$ (eq 99).[76] Reactions were found to occur with secondary amines although no products could be isolated with pyrazole, 2,2,6,6-tetramethylpiperidine, *p*-toluidine, 2,6-diisopropylaniline, or *N*-methylethanolamine.

$$[OsCl(CO)(PPh_3)_2(BCl_2)] \xrightarrow{HNR_2} [OsCl(CO)(PPh_3)_2\{B(NR_2)_2\}] \quad (99)$$

$(NR_2)_2$ =



4. Miscellaneous

The use of tertiary amines gave rise to adducts with metal−boron bonds as discussed. The reactivity of $[Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}]$ with 5 equiv of HCl was described in section III.B.1.v. The cleavage of the metal−boron bond was apparent with the formation of BCl_3. When only 2 equiv of HCl were added, the product was described as a metal−boryl adduct of the type $Mn{-}(BCl_2{\cdot}HNMe_2)$ similar to the above reactions although the compound was not well-characterized. When 4 equiv of HCl were added, the $Mn{-}BCl_2$ compound was the product reportedly obtained (eq 100).[5]

$$[Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}] \xrightarrow{4\ HCl} [Mn(CO)_4(PPh_3)(BCl_2)] \quad (100)$$

IV. Structure and Bonding in Transition Metal–Boryl Compounds

Until recently, the bonding in metal−boryl compounds has largely been rationalized on the basis of observed NMR chemical shifts, IR data, and reactivity studies. Care must be taken, however, when correlating spectroscopic data with structural models since there are limitations in the accuracy of such methods. Currently, several structural studies are available which enable a clearer description of the bonding in these compounds together with related properties such as the boryl group trans influence and any orientational preferences. In numerous examples, the boryl ligands have been noted to display a geometry suitable for π-bonding with high lying filled molecular orbitals of the respective metal fragments. In addition, the M−B bond distances in several examples are shorter than the predicted value derived from the sum of covalent radii ($\sum r_{\mathrm{cov}}$) also indicative of π-bonding. However, in more recent studies, the stabilization of the vacant p orbital on the boron atom derived from alkoxy or amino groups attached to the boron atom appears to be the predominant source of this stabilization. Thus, the importance of π-bonding effects involving the metal atom in these compounds has not yet been fully resolved.

A. Covalent Bonding in Metal–Boryl Compounds

The covalent bonding between boron and a transition metal center is very similar in nature to that between boron and nonmetals. Complexes in which an sp^2-hybridized boron atom is bonded directly to a metal center, X_2B-ML_n [where ML_n is a suitable metal ligand fragment] can be envisaged as analogues of boranes. As is the case with metal carbonyls, considerable controversy concerning the relative importance of the σ- and π-components of the metal−boron bonding model has appeared in the literature. Attempts have been made to address the nature and magnitude of ligand and/or metal fragment participation in stabilizing the electron-deficient boron center. The stability of the metal−boron bond is influenced strongly by the ligands attached to boron, the nature of those completing the coordination sphere of the metal, the metal itself, and its oxidation state. The description of metal−boron bonding also has features in common with metal carbenes. σ-Bonding between the boron and metal center can be viewed simplistically as overlap between the filled sp^2-hybridzed orbital centered on boron and an empty σ-hybrid orbital of appropriate symmetry on the metal (Figure 1a). Furthermore the possibility of a π-interaction between the boron and metal exists in the form of π-back-donation from a metal-based frontier orbital, which possesses appropriate symmetry, to the boron p orbital (Figure 1b).

In light of these bonding relationships described above, the following would be anticipated to effectively stabilize a transition metal−boryl linkage: low valent, late transition metal centers whose coordination sphere is completed by good σ-donor ancillary ligands and π-donating heteroatom substituents on boron. These stabilizing requirements in fact correlate well with the observed properties and reactivity of reported transition metal−boryl complexes with few exceptions. For example, the stability of the covalent metal−boron bonds of the late transition metals platinum and iridium is dramatically enhanced compared with the M−B bonds in boryl−metal carbonyl compounds.

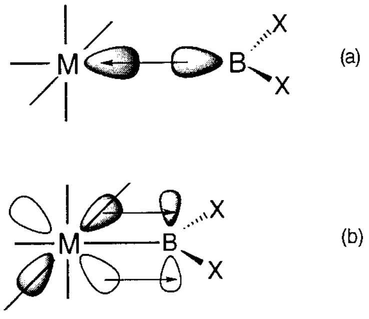


Figure 1. Covalent bonding in metal−boryl compounds.

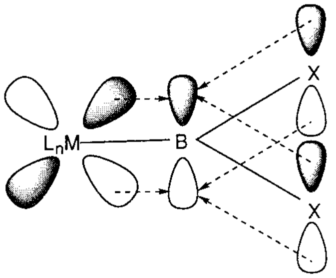


Figure 2. Bonding model for stabilization of the vacant p orbital on boron.

Substituent effects play an integral role in the stabilization of the boron atom. Trivalent boron possesses an empty p orbital which can also interact with the substituents X. Analogous to metal carbenes, the filled nonbonding orbitals of these substituents can donate electron density to the vacant p orbital on boron. If the substituents cannot participate in back-bonding to provide stabilization, the metal must be able to satisfy the electron deficiencies at the boron center. The synergistic nature of this model is best represented in Figure 2.

Clearly competition between the metal fragment and the substituents on boron for stabilization of the boron center will affect the nature of the bond between boron and the metal. This will in turn influence its reactivity.

B. Spectroscopic Studies

Experimentally, the presence of π-bonding between the metal and boron has been tested. Early studies on the role of π-back-bonding in these complexes relied heavily on the use of IR and ^{11}B NMR spectroscopies as the primary tools. Numerous spectroscopic analyses of infrared stretching frequencies have been used to ascertain bonding and structural features of metal−boryl compounds.

1. IR Spectroscopy

The stretching vibrations of π-acceptor ligands such as CO, CS, NO, and CNR in metal complexes are very sensitive to ancillary ligand effects. This effect is well-known and perhaps best exemplified in studies involving metal polycarbonyl complexes. Replacement of CO by a better σ-donor, poorer π-acceptor phosphine ligand results in a lowering of the remaining carbonyl stretching frequencies.[101-104] Ligands such as arsines, amines, and isonitriles also show similar trends.[105] This effect arises because the relative charge on the metal has become more negative.

From a molecular orbital perspective, higher basicity leads to greater donation of electron density into the CO π*-orbitals resulting in a lowering of the C−O bond order. The incorporation of the boryl group into the metal ligand manifold has also been found to have a pronounced effect on CO vibrations in a manner similar to that described above. This effect has been exploited for the study of boryl, carbonyl transition metal compounds by comparison of the CO stretching frequencies within a series of isostructural examples possessing different boron substitution patterns or which bear ligands other than a boryl group. Schmid argued that this indirectly afforded proof of a π-contribution to the metal−boron bond.[22] The increased CO bond order implied by a higher stretching frequency is ascribed to a less electron-rich metal center which is less able to contribute electron density to the π*-orbitals of the CO ligand. Increased metal acidity can be interpreted as a consequence of greater electron acceptance into the boron−metal π-MO manifold.

Nöth and Schmid[5-7,13,22] studied several series of related compounds using IR spectroscopy although some of these results must be treated with caution since there is some doubt as to the true nature of the compounds. The carbonyl stretching frequencies for the compounds $[Mn(CO)_5\{B(NMe_2)_2\}]$ and $[Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}]$ were found to decrease upon addition of the phosphine, consistent with previous results regarding phosphine substitution of metal−carbonyl complexes.[5] This however may not be the most productive method of comparing carbonyl stretching frequencies since the phosphine should coordinate trans to the boryl ligand. A more direct comparison has been made by examining related compounds containing methyl ligands which are strong σ-donors and incapable of π-back-bonding unlike the related boryl complexes.[7] Comparison of the carbonyl stretching frequencies for $[CpMo(CO)_3(X)]$ and $[CpW(CO)_3(X)]$ (X = Me, BPh_2, BCl_2) indicated a shift to lower energy for the boryl derivatives compared to the methyl analogues of tungsten, while the opposite trend was observed for the molybdenum derivatives indicative of stronger π-back-bonding to the carbonyl ligands in the tungsten boryl complexes. This is clearly due to an increase in electron density from the strong σ-donor boryl group. The CO stretching frequency would be expected to increase if the boryl ligands were significantly contributing to the π-back-bonding in the molecule as in the case of the molybdenum boryl derivatives. Hartwig et al.[46] have reported that the CO stretching frequencies are higher for $[CpFe(CO)_2(Bcat)]$ compounds relative to the $[CpFe(CO)_2(alkyl)]$ compounds which are incapable of π-interactions. By similar arguments, this suggests that π-interactions are present in the M−B bonds although the values for the BPh_2 compound are lower.

The combined σ- and π-effects of the boryl ligands X have been found to affect the CO bond order in an analogous fashion to that described above for substitution of CO by phosphines in metal−carbonyl complexes. Linear relationships were observed between the inductive effects of boryl groups (with varying substituents X) and CO stretching frequencies. Taft[106] constants, σ*, for X versus CO stretching frequencies were plotted for $[Mn(CO)_4(PPh_3)(BX_2)]$ and $[Co(CO)_4(BX_2)]$, giving straight lines, but these data should be treated with caution in view of the doubt surrounding the formulation of the compounds.[22] This result corroborates the synergistic bonding model proposed earlier (Figure 2) where σ-donation of the boryl group is accompanied by π-back-bonding from the metal to the boron p orbital which in turn is moderated by boron substituent participation. Similar effects were noted for the compounds $[CpW(CO)_3(BR_2)]$ and $[CpMo(CO)_3(BR_2)]$ mentioned earlier when comparisons were made between the BPh_2 versus BCl_2 ligands. Although information gained from IR spectroscopy contributes to the bonding picture, these relationships are of limited value with regard to the electronic environment at boron.

2. NMR Spectroscopy

i. ^{11}B NMR. A particularly sensitive probe into the electronic environment at boron and elucidation of structure is the use of ^{11}B NMR spectroscopy. The ^{11}B chemical shifts of those metal−boryl compounds prepared to date are summarized in Table 1. Although any resolution of structural ambiguity still rests with X-ray methods, this is nonetheless a powerful tool and has been used extensively in the development of bonding arguments and to afford structural information for boron compounds without boron−transition metal bonds.[107] The chemical shift of the signal corresponds directly to the number and type of substituents attached to the boron. As with other nuclei, the chemical shift therefore may be characteristic for certain groups. ^{11}B chemical shifts for trigonal boron depend on the σ-polarization and π-acceptor strength of boron. Therefore, both σ- and π-bonding effects contribute to the chemical shift, with the two contributions not readily separable. However to a large extent the π-electron density dominates, hence shifts may appear at considerably higher field than would otherwise be expected if based purely on electronegativity grounds.[107]

The consequence of this is the use of ^{11}B NMR to measure the level of π-electron density and hence π-acceptance onto the boron atom from its three substituents. Generally the higher the charge density localized on the boron center, the greater the shielding and the higher field the chemical shift. In view of this, increased basicity at a trigonal boron center can be achieved by efficient π-overlap of its ligands with the vacant p orbital. For example, relationships have been developed which demonstrate for related series of compounds, R_3B, R_2BX, RBX_2, BX_3 (where R = H or Me which have no expected π-donating contribution), that comparison of their chemical shifts reveals an increasing high field shift in traversing the series R_3B to BX_3. This observation is attributed to π-back-donation from X to boron.[107]

It would not seem unreasonable to assume a similar effect in metal−boryl complexes when the metal is considered a π-donor fragment. For example, changes of metal ancillary ligands, and hence changes in metal electron density, are reflected in changes of the boron chemical shift among isostructural examples involving compounds of cobalt and manganese indicating that π-bonding has a significant role in the metal−boron bond.[22] Hartwig et al., however, have noted that interpretation of the ^{11}B NMR chemical shifts of metal−boryl compounds and correlation with the degree of π-back-bonding should be approached with caution since the paramagnetic shielding effects of the metal exert a dominant influence on the chemical shifts of atoms bound directly to the metal.[49] In addition, the ^{11}B shifts for the titanium[56,57] and niobium[47] borane adducts are virtually identical to those in structurally dissimilar boryl complexes. For example, the anionic species, Li[Fe(CO)$_4$(Bcat)], shows a single resonance in the ^{11}B NMR spectrum at δ 55 ppm. This resonance is downfield of the related neutral species, *cis*-[Fe(CO)$_4$(Bcat)$_2$], (δ 45 ppm), which cannot be explained in terms of electron density on boron. In addition, predictions of chemical shift based solely on the relative π-donor capacity of the boryl substituents, among a series of related compounds, is not necessarily reflected in an increasingly lower field chemical shift. The chemical shifts for the three chloroboranes $ClBPh_2$, $ClBCl_2$, and $ClB(NMe_2)_2$ are 61.0, 46.5, and 27.9 ppm, respectively. Thus, the π-donor ability of the substituents may be ranked $NMe_2 > Cl > Ph$. The replacement of the chloride substituent by Co(CO)$_4$ leads to a change in boron chemical shift which is not anticipated on the basis of boron substituent π-donor characteristics alone. The observed chemical shifts for the cobalt boryl compounds were 34.2, 20.6, and 26.9 ppm such that the π-donor ability of the substituents is now ranked $Cl > NMe_2 > Ph$.

Within the domain of δ, trigonal boryl complexes which possess negative chemical shifts are rare and questionable. The chemical shift values ranging from −6.5 to −23.5 ppm are in unusually high-field regions when compared with those typically found. Furthermore, these complexes exhibit unusual chemical reactivity. These shifts are those typically associated with tetracoordinate boron. An upfield shift of the ^{11}B resonances would be expected if there is significant donation into the vacant p orbital on boron as illustrated recently with a series of Lewis base adducts of diborane(4) compounds. Coordination of pyridines and the subsequent change from three- to four-coordinate geometries resulted in an upfield shift of the ^{11}B resonance.[108] Similarly, as the metal donates into the vacant orbital, the chemical shift would be expected to shift upfield as well. The compound formulated as a borylene species [Fe(CO)$_4${B(NMe$_2$)}] prepared by Nöth and Schmid gave a clear example of this with a chemical shift of 18 ppm, far upfield of any metal−boryl compound known to date. Similarly, the same authors concluded that carbene-like canonical forms often referred to as “borenes” could be used to rationalize the high field chemical shifts. As mentioned, this type of approach to bonding involving metals bound to boron may be misleading. In addition, a reexamination of [CpFe(CO)$_2$(BPh$_2$)] has recently resulted in a revised chemical shift value (δ 121 ppm)[46] differing by almost 100 ppm compared to the initial reports.[1] The possibility of decomposition processes and subsequently misleading chemical shifts cannot be ruled out in the older reports without further structural evidence.

In examples involving catecholato-substituted derivatives, the ^{11}B chemical shifts in Table 1 are reasonably consistent with values ranging from approximately 30 to 70 ppm. Examples which incorporate Bcat ligands which are trans disposed to a halide ligand exhibit chemical shifts which are slightly upfield of this. The related alkyl- and aryl-substituted boryl complexes are shifted downfield relative to this range, indicative of the poorer stabilization of the vacant p orbital on boron by the attached groups. More details of these compounds will be discussed in conjunction with structural results.

ii. ^1H and ^{13}C NMR. While several metal−boryl derivatives have been characterized by ^1H and ^{13}C NMR spectroscopy, these techniques have had limited use for studies involving bonding in metal−boryl compounds. For example, the ^1H and ^{13}C-{^1H} NMR spectra of [CpFe(CO)$_2$(Bcat)][46] showed no signs of hindered rotation about the M−B bond at −90 °C. The authors noted that the rotational barrier did not give a direct indication of the π-bond energy because the second highest occupied molecular orbital (SHOMO) on iron with π-symmetry is orthogonal to the HOMO. The structural results were nonetheless interpreted as suggesting an overall weak, π-interaction. The same authors have also demonstrated the use of deuterium labeling and isotopic substitution studies to determine the presence of a continuum between metal−boryl and metal−hydridoborate structures in solution. The use of ^{11}B NMR spectroscopy was proposed as a simple test to determine the position on the continuum of the respective species in these systems.[47]

iii. ^{31}P NMR. ^{31}P (natural abundance 100%, spin $= {}^1/_2$) resonances have been crucial to the understanding of the bonding in square planar platinum(II) compounds and related systems. The magnitude of the coupling with ^{195}Pt (natural abundance 34%, spin $= {}^1/_2$) gives valuable information regarding the σ-bonding which directly reflects the trans influence of ligands. The coupling constant, ($|^1J_{Pt-P}|$) for a series of *cis*-[PtX$_2$(PPh$_3$)$_2$] compounds would be expected to increase with a decrease in the trans influence of X. The strong trans influence of the boryl ligands weakens the metal−phosphine bond resulting in a small coupling constant (ca. 1600 Hz).[25,26,28,30] The weakening of the M−P bond is the result of strong σ-donation from the boryl groups. The compound *cis*-[PtCl$_2$(PPh$_3$)$_2$], ($J_{Pt-P} = 3675$ Hz), displays much stronger coupling due to the stronger overlap

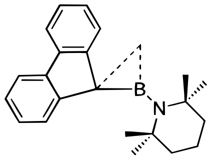
Table 1. ^{11}B NMR Data for Metal−Boryl Complexes^a

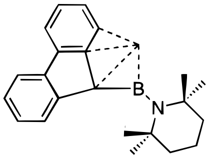
formula	δ (ppm)	ref(s)	formula	δ (ppm)	ref(s)
Group 5					
$[CpNbH_2(Bcat)]$	59.0	47	*endo*-$[Cp_2TaH_2(Bcat)]$	70.0	54
			exo-$[Cp_2TaH_2(Bcat)]$	64.7	54
Group 6					
$[Cr(\eta-C_6H_6)(CO)_2(\eta^2-tmp'BCR_2)]$	57.2	90	$[Mo(tpb')(CO)_2\{B(Et)CH_2-p-tolyl\}]$	−9.3 (BH-tpb′), 76.0 (MoB)	64
$[Cp_2WH(BPh_2)]$	114	47	$[Cp^*W(CO)_2(PMe_3)\{B(1,2-O_2-3,5-Me_2C_6H_2)\}]$	58.0	53
$[Cp_2WH(Bcat)]$	57.0	47, 52			
$[Cp_2W\{B(1,2-O_2-4-Bu^tC_6H_3)\}_2]$	59.3	51	$[CpW(CO)_2\{B(NMe_2)BCl(NMe_2)\}]$	40.3 (BCl), 62.7 (BW)	55
$[Cp_2WCl(Bcat)]$	49.0	52	$[(tpb')W(CO)_2\{B(Et)CH_2Me\}]$	−9.3 (BH-tpb′), 77.0 (WB)	64
$[Cp_2W\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}_2]$	58.2	52			
$[Cp^*W(CO)_3\{B(1,2-O_2-3,5-Me_2C_6H_2)\}]$	53.0	53	$[(tpb')W(CO)_2\{B(Et)CH_2-p-tolyl\}]$	−9.3 (BH-tpb′), 78.0 (WB)	64
Group 7					
$[Mn(CO)_5\{B(NMe_2)_2\}]$	27.1*	6	$[Mn(CO)_5(Bcat)]$	42.8	48
$[Mn(CO)_4(PPh_3)\{B(NMe_2)_2\}]$	20.0*	6	$[\{CpMn(CO)_2\}_2\{\mu-B(NMe_2)\}]$	103.0	84
$[Mn(CO)_4(PPh_3)(BPh_2)]$	28.5*	6	$[\{(\eta-C_5H_4Me)Mn(CO)_2\}_2\{\mu-B(NMe_2)\}]$	102.8	84
$[Mn(CO)_5(BPh_2)]$	42.8*	9	$[\{CpMn(CO)_2\}_2\{\mu-BBu^t\}]$	170.0	84
$[Mn(CO)_4(PPh_3)(BCl_2)]$	16.0*	6	$[(\eta-C_5H_4Me)Mn(CO)_2\{\eta^2-tmp'BCR_2\}]$	58.0	90
Group 8					
$[Fe(CO)_4\{B(NEt_2)\}]_n$	−13.8*	13	$[Cp^*Fe(CO)_2\{B(1,2-O_2-3,5-Me_2C_6H_2)\}]$	54.0	53
$[Fe(CO)_4(BBr)]_n$	−15.3*	13	$[CpFe(CO)_2\{B(NMe_2)BCl(NMe_2)\}]$	39.0 (BCl), 69.5 (BFe)	55
$[CpFe(CO)_2(BPh_2)]$	121.0	46	$[Fe(CO)_3(\eta^4-tmp'BCR_2)]$	55.4	89
	37.0*	107	$[Fe(CO)_4(\eta^2-tmp'BCR_2)]$	58.5	88, 89
$[Fe(CO)_3(NO)(BPh_2)]$	45.5*	107	$[Fe(CO)_3(PMe_3)(\eta^2-tmp'BCR_2)]$	58.7	90
$[CpFe(CO)_2(Bcat)]$	51.8	46	$[Fe(CO)_3(PMe_2Ph)(\eta^2-tmp'BCR_2)]$	61.0	90
$[Fe(CO)_4(Bcat)_2]$	45.0	49	$[Fe(CO)_3(PMePh_2)(\eta^2-tmp'BCR_2)]$	58.2	90
$[Fe(CO)_4\{B(1,2-O_2-4-Bu^tC_6H_3)\}_2]$	45.0	49	$[Fe(CO)_3(PPh_3)(\eta^2-tmp'BCR_2)]$	60.4	89
$[Fe(CO)_4\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}_2]$	45.0	49	$[Fe(CO)_3(PCy_3)(\eta^2-tmp'BCR_2)]$	58.9	89
$[Fe(CO)_4(SnMe_3)\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}]$	47.0	49	$[Fe(CO)_3\{P(OMe)_3\}(\eta^2-tmp'BCR_2)]$	59.0	89
			$[Fe(CO)_3(PCl_3)(\eta^2-tmp'BCR_2)]$	59.4	90
$Li[Fe(CO)_4(Bcat)]$	55.0	49	$[Fe(CO)_3(PCl_2Ph)(\eta^2-tmp'BCR_2)]$	59.1	90
$Li[Fe(CO)_4\{B(1,2-O_2-4-Bu^tC_6H_3)\}]$	54.8	49	$[Fe(CO)_3(SbPh_3)(\eta^2-tmp'BCR_2)]$	62.1	89
$Li[Fe(CO)_4\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}]$	54.3	49	$[Cp^*Ru(CO)_2\{B(1,2-O_2-3,5-Me_2C_6H_2)\}]$	48.0	53
Group 9					
$[CpCo(CO)(\eta^2-tmp'BCR_2)]$	61.2	90	$[Co(CO)_3(AsPh_3)(BPh_2)]$	42.8*	22
$[Co(Me_2P-o-C_6H_4-PMe_2)_2(BPh_2)_2]$	−23.5*	9	$[Co(CO)_3\{P(OPh)_3\}(BPh_2)]$	42.5*	22
$[Co(Me_2P-o-C_6H_4-PMe_2)_2(BC_{12}H_8)_2]$	−15.0*	9	$[Co(PF_3)_4(BPh_2)]$	44.9*	21, 22
$[Co(dppe)_2(BPhCl)]$	−10.0*	11	$[Co(PF_3)_4\{B(NMe_2)\}_2]$	21.4*	21, 22
$[Co(CO)_4(BCl_2)]$	20.6*	22	$[Co(dppe)_2(BPh_2)_2]$	−23.0*	22
$[Co(CO)_4(BPh_2)]$	34.2*	22	$[Co(dppe)_2(BBr_2)]$	−23.0*	22
$[Co(CO)_4\{B(NMe_2)_2\}]$	25.5*	22	$[Co(PMe_3)_3(Bcat)_2]$	paramagnetic	83
$[Co(CO)_3(PPh_3)(BCl_2)]$	17.3*	22	$[Co(CO)_4(BH_2\cdot THF)]$	7.9	91
$[Co(CO)_3(PPh_3)(BPh_2)]$	21.6*	22	$[Co(CO)_4(BH_2\cdot SMe_2)]$	−10.0	91
$[Co(CO)_3(PPh_3)\{B(NMe_2)_2\}]$	26.9*	22	$[Co(CO)_4(BH_2\cdot NEt_3)]$	3.6	91
$[Co(CO)_3(PBu^n_3)(BPh_2)]$	42.7*	22	$[Co(CO)_4(BH_2\cdot bipy)]$	−2.2	91
$[Co(CO)_3(AsPh_3)(BCl_2)]$	17.5*	22	$[Co(CO)_2(dppm)(\mu-dppm)(BH_2)]$	−25.9	93
$[Rh(PPh_3)_3(BBr_2)]$	−6.5*	11	$[RhCl(PPh_3)_2\{B(1,2-O_2-3-MeC_6H_3)\}_2]$	40.3	79
$[Rh(CO)_4(BPh_2)]$	32.5*	107	$[RhCl(PPh_3)_2\{B(1,2-O_2-4-MeC_6H_3)\}_2]$	37.0	79
$[RhHCl(PPh_3)_2(Bcat)]$	35.8	66	$[RhCl(PPh_3)_2(Btart)_2]$	36.3	79
$[RhHCl(PPr^i_3)_2(Bcat)]$	37.7	68	$[RhCl(PPh_3)_2\{B(1,2-S_2C_6H_4)\}_2]$	56.1	79
$[RhHCl(PMe_3)_3(Bcat)]$	42.8	69	$[RhCl(PMe_2Ph)_3(Bcat)_2]$	40.3	79
$[RhCl_2(PMe_3)_3(Bcat)]$	40.1	121	$[RhCl(PMe_3)_3(Bcat)_2]$	44.1, 40.8	79
$[RhCl(PPh_3)_2(Bcat)_2]$	38.2	67	$[RhCl(PMe_3)_3\{B(1,2-O_2-3-MeC_6H_3)\}_2]$	44.2, 41.4	79
	38.4	79	$[RhCl(PMe_3)_3\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}_2]$	42.0	79
$[RhCl(PEt_3)_2(Bcat)_2]$	39.7	67, 79	$[RhCl(PMe_3)_3(Btart)_2]$	43.3, 38.2	79
$[RhCl(PPh_3)_2\{B(1,2-O_2-4-Bu^tC_6H_3)\}_2]$	38.9	77, 79	$[RhCl(PMe_3)_3(Bneopentylglycolate)_2]$	39.0	79
$[RhCl(PPh_3)_2\{B(1,2-O_2-3,5-Bu^t_2C_6H_2)\}_2]$	42.6	77	$[Rh(PMe_3)_4(Bcat)]$	49.0	80
	39.1	79	$[Rh(PMe_3)_3(Bcat)_3]$	46.8	80
$[IrH_2(PMe_3)_3\{B(CMe_2CHMe_2)\}]$	107.8	70	$[Ir(\eta-C_6D_6)(Bcat)_3]$	37.9	74
$[IrH_2(PMe_3)_3(BC_8H_{14})]$	106.2	70	$[Ir(\eta-C_6H_5Me)(Bcat)_3]$	37.7	74
$[IrHCl(CO)(PPh_3)_2(Bcat)]$	30.8	71	$[Ir(\eta-1,3,5-Me_3C_6H_3)(Bcat)_3]$	37.8	74
$[IrHCl(PEt_3)_2(Bcat)]$	33.5	71	$[Ir(PEt_3)_3(Bcat)_3]$	44.7	74
$[IrHCl(PPr^i_3)_2(Bcat)]$	40.1	71	$[IrCl(PEt_3)_2(Bcat)_2]$	32.6, 41.7	81
$[IrHCl(PMe_3)_3(Bcat)]$	32.8	73	$[IrCl(PMe_3)_3(biphBF)]^+$	paramagnetic (EPR g_{xy} 2.15, g_z 1.96)	94
$[Ir(\eta-C_6H_6)(Bcat)_3]$	37.7	74			

Table 1 (Continued)

formula	δ (ppm)	ref(s)	formula	δ (ppm)	ref(s)
			Group 10		
$[Ni(PPh_3)_2(BPh_2)]\cdot 0.5Et_2O$	−45.4*	16	$[Pd(dmpe)(SnMe_3)\{B(1,2\text{-}(NMe)_2C_2H_4)\}]$	46.9	87
$[Pt(PPh_3)_2\{B(OMe)_2\}_2]$	47.2	82	$[Pt(dppe)(Bcat)_2]$	48.9	30
$[Pt(PPh_3)_2(Bpin)_2]$	46.0	26	$[Pt(dppb)(Bcat)_2]$	48.9	30
$[Pt(PPh_3)_2(Bcat)_2]$	47.0	30	$[Pt(dcpe)(Bcat)_2]$	53.5	99
$[Pt(PPh_3)_2\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2]$	50.1	30, 63	$[Pt(PPh_3)_2(Bped)_2]$	48.2	113
$[Pt(PPh_3)_2\{B(1,2\text{-}S_2C_6H_4)\}_2]$	72.0	63	$[Pt(PPh_3)_2(Btart)_2]$	48.1	113
$[Pt(PPh_3)_2\{B(1,2\text{-}O_2C_6Cl_4)\}_2]$	51.5	63	$[PtCl(PPh_3)_2(Bcat)]$	28.7	63
$[Pt(PPh_3)_2\{B(1,2\text{-}O_2C_6Br_4)\}_2]$	48.0	63	$[PtBr(PPh_3)_2(Bcat)]$	30.9	63
			Group 11		
$[Cu(triars)(BBr_2)]$	−15.8*	11	$[Ag(triars)(BBr_2)]$	−14.2*	11
			Group 14		
$SnMe_3\{B(NMe_2)Cl\}$	44.5	19	$SnMe_3\{B(NEt_2)Cl\}$	45.2	19

[a] Notes: Chemical shift values marked with an asterisk (*) are taken from the early reports of Nöth and Schmid and, as stated in the text, should be treated with caution; cat = 1,2-$O_2C_6H_4$; pin = 1,2-$O_2C(CH_3)_2C(CH_3)_2$; ped = *S*-1,2-$O_2CH(Ph)CH_2$; tart = *R*,*R*-1,2-$O_2CH(CO_2Me)CH(CO_2Me)$; tpb′ = tris(3,5-dimethylpyrazol-1-yl)hydroborate; triars = $Me_2As(o\text{-}C_6H_4)As(Me)(o\text{-}C_6H_4)AsMe_2$;

{η^2-tmp'BCR$_2$} =


; {η^4-tmp'BCR$_2$} =


All ^{11}B chemical shifts are quoted relative to $BF_3\cdot Et_2O$ with positive shifts to high frequency.

of the Pt−P bond, as would be expected from the weak trans influence of Cl ligands. In the ^{31}P spectra of a series of cis-platinum−bisboryl compounds, the presence of the boryl ligand also results in drastic broadening of the resonances most likely due to quadrupolar effects of the boron nucleii. This broadening of the resonances is not observed in the ^{31}P spectra of several rhodium−bisboryl compounds, however, since the phosphorus atoms are trans to each other rather than being trans to boron. Spectroscopic examination of the phosphorus environments has proved very useful for the elucidation of metal−boryl compounds derived from σ-bond metathesis processes.[78]

C. Structural Studies

The metal−boryl compounds which have been structurally characterized to date are listed in Table 2. In general, the compounds to the left and center of the periodic table display M−B bond distances which are close to the value that the sum of covalent radii ($\sum r_{cov}$) would predict (Ti, Nb, Ta, W, Mn, Fe), whereas for metals to the right, M−B bond distances are generally shorter than the sum of the covalent radii would predict (Os, Co, Rh, Ir, Pt).[109] The covalent radius for a number of the boryl ligands can be determined accurately from structural data of the corresponding diborane(4) compounds.[77,110−113] For example, the value for Bcat may be taken as $^1/_2(D_{B-B})$ in B_2cat_2 = 1.678/2 = 0.84 Å. Comparison with isoelectronic sp^2-hybridized carbon ligands in related metal compounds has also been used as a basis for determining the expected metal−boryl bond distances when the difference between the covalent radii of B vs C are taken into account.

Several structures also exhibit boryl ligand orientations consistent with the correct alignment for π-back-bonding. In addition, several new modes of binding for boranes and diborane(4) compounds have been demonstrated using X-ray crystallography. In the following section the structural information such as orientation of the boryl ligands and modes of binding in boranes and diborane(4) compounds will be described.

1. Group 4

The compound $[Cp_2Ti(\eta^2\text{-}HBcat)_2]$ displayed a ^{11}B chemical shift of 45 ppm almost 20 ppm downfield of HBcat (27 ppm). Accordingly, this compound may have been interpreted as a metal−boryl complex but structural data indicated that this was not the case. In fact, structural analysis of this compound indicated that two HBcat ligands were complexed in an η^2-H−B fashion to the metal center. The Ti−B bond length [2.335(5) Å] was too long to be a true metal−boryl bond and the B−Ti−B angle (55°) was too small for the compound to be a cosidered a Ti(IV) complex when compared to typical angles in metallocene systems. In addition, the Ti−H distance (1.779 Å) was typical for a bridging hydride complex. The separation between the two boron atoms (2.11 Å) was also too long for a strong interaction between these atoms. The angle formed from the midpoint of the two HBcat ligands and the titanium in this case, was consistent with that expected for a d^0 Cp_2ML_n compound consistent with a bis(η-HBcat) structure. The observed alignment of the Bcat ligand was consistent with that expected for maximum π-back-bonding from titanium to boron according to ab initio calculations.

2. Group 5

The compound $[Cp_2NbH_2(Bcat)]$ was described as a genuine metal−boryl compound, while $[Cp_2Nb(H_2\text{-}BC_8H_{14})]$, was reported to be a hydridoborate complex.[47] The Ta−B bond distances for the *endo* and

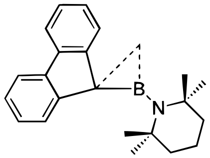
Table 2. Structurally Characterized Metal−Boryl and Related Compounds[a]

compound	Σr_{cov}[b]	M−B (Å)	B−B (Å)	B−M−B (deg)	ref(s)
$[\mathrm{Cp_2Ti\{\eta^2\text{-}(HBcat)\}_2}]$	2.16	2.335(5)	2.11	53.8(2)	56
$[\mathrm{Cp_2NbH_2(Bcat)}]$ (Figure 3)	2.18	2.292(5)			47
$[\mathrm{Cp_2Nb(\eta^2\text{-}H_2BC_8H_{14})}]$[c]	2.22	2.40(1)			47
endo-$[\mathrm{Cp_2TaH_2(Bcat)}]$	2.18	2.263(6)			54
exo-$[\mathrm{Cp_2TaH_2(Bcat)}]$	2.18	2.295(11)			54
$[\mathrm{Cp_2WH(Bcat)}]$ (Figure 4)	2.14	2.190(7)			47, 52
$[\mathrm{Cp_2W\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3\}_2}]$	2.14	2.19(1), 2.23(1)	2.78	78.0(4)	51, 52
$[\mathrm{(tpb')W(CO)_2\{B(Et)CH_2C_6H_4CH_3\}}]$	2.18	2.07(1)			64
$[\mathrm{CpW(CO)_3\{B(NMe_2)B(NMe_2)Cl\}}]$	2.18	2.370(8)	1.69(1)		55
$[\mathrm{Mn(CO)_5(Bcat)}]$ (Figure 5)	2.01	2.108(6)			48
$[(\eta\text{-}\mathrm{C_5H_4Me)Mn(CO)_2(L)}]$[d]	2.05	2.162(5)			90
$[\{\mathrm{CpMn(CO)_2\}_2(\mu\text{-}BNMe_2)}]$	2.05	2.03(1), 2.03(1)			84
$[\mathrm{CpFe(CO)_2(Bcat)}]$	2.004	1.959(6)			46
$[\mathrm{CpFe(CO)_2(BPh_2)}]$ (Figure 6)	2.045	2.034(3)			46
$[\mathrm{Fe(CO)_4\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2}]$ (Figure 7)	2.009	2.028(7)	2.68	82.8(4)	49
$[\mathrm{Fe(CO)_3(L)}]$[e]	2.045	2.080(4)			89
$[\mathrm{Fe(CO)_4(L)}]$[d]	2.045	2.125(5)			88
$[\mathrm{Fe(CO)_3(PMe_3)(L)}]$[d]	2.045	2.091(4)			90
$[\mathrm{Fe(CO)_3\{P(OMe)_3\}(L)}]$[d]	2.045	2.109(9)			89
$[\mathrm{CpFe(CO)_2\{B(NMe_2)B(NMe_2)Cl\}}]$	2.045	2.090(3)	1.683(3)		55
$[\mathrm{OsCl(CO)(PPh_3)_2\{B(OH)_2\}}]$	2.14	2.046(7)			76
$[\mathrm{OsCl(CO)(PPh_3)_2\{B(OEt)_2\}}]$ (Figure 8)	2.14	2.076(5)			76
$[\mathrm{OsCl(CO)(PPh_3)_2\{B(1,2\text{-}(NMe)_2C_6H_4)\}}]$	2.14	2.082(10)			76
$[\mathrm{OsCl(CO)_2(PPh_3)_2\{B(OH)_2\}}]$	2.14	2.20(4)			76
$[\mathrm{OsCl(CO)_2(PPh_3)_2(Bcat)}]$	2.10	2.177(14)			76
$[\mathrm{OsCl(CO)_2(PPh_3)_2\{B(1,2\text{-}(NH)_2C_6H_4)\}}]$	2.14	2.201(9)			76
$[\mathrm{OsCl(CO)_2(PPh_3)_2\{B(1\text{-}S\text{-}2\text{-}(NH)C_6H_4)\}}]$	2.14	2.200(22)			76
$[\mathrm{Co(dppm)(\mu\text{-}dppm)(CO)_2(BH_2)}]$[f]	2.04	2.227(6)			93
$[\mathrm{CpCo(CO)(L)}]$[d]	2.04	2.011(8)			90
$[\mathrm{CpCo(CO)(L)}]$[d]	2.04	1.989(10)			90
$[\mathrm{Co(PMe_3)_3(Bcat)_2}]$ (Figure 9)	2.00	1.945(11), 1.970(11)	2.185	67.9(4)	83
$[\mathrm{RhHCl(PPr^i_3)_2(Bcat)}]$ (Figure 10)	2.09	1.961(7)			68
$[\mathrm{Rh(PMe_3)_4(Bcat)}]$ (Figure 11)	2.09	2.047(2)			80
$[\mathrm{RhCl(PEt_3)_2(Bcat)_2}]$	2.09	1.973(2), 1.994(2)	2.423	75.29(10)	79
$[\mathrm{RhCl(PPh_3)_2(Bcat)_2}]\cdot\mathrm{3ClCH_2CH_2Cl}$	2.09	2.008(7), 1.956(8)	2.521	79.0(3)	67
$[\mathrm{RhCl(PPh_3)_2(Bcat)_2}]\cdot\mathrm{4CH_2Cl_2}$ (Figure 12)	2.09	2.008(4), 1.954(4)	2.541	79.8(2)	79
$[\mathrm{RhCl(PPh_3)_2\{B(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3\}_2}]$	2.13	2.034(12), 1.906(13)	2.556	80.9(5)	79
cis,mer-$[\mathrm{RhCl_2(PMe_3)_3(Bcat)}]$ (Figure 13)	2.09	2.012(2)			121
$[\mathrm{Rh(PMe_3)_3(Bcat)_3}]\cdot\mathrm{C_7H_8}$ (Figure 14)	2.09	2.055(4), 2.053(4), 2.061(4)	2.622 to 2.700	79.34(14) to 82.05(14)	80
$[\mathrm{IrBr_2(CO)(PMe_3)_2(B_5H_8)}]$	2.14	2.071(14)			122
mer-$[\mathrm{IrHCl(PMe_3)_3(Bcat)}]$ (Figure 15)	2.10	2.023(10)			73
fac-$[\mathrm{IrH_2(PMe_3)_3(BC_8H_{14})}]$	2.14	2.093(7)			70
$[\mathrm{IrCl(PMe_3)_3\{B(F)C_{12}H_8\}}]^+$	2.14	2.00(1)			94
$[\mathrm{IrClBr(PMe_3)_3(Bcat)}]$	2.10	2.035(7)			121
trans-$[\mathrm{IrHCl(CO)(PPh_3)_2(Bcat)}]\cdot\mathrm{CH_2Cl_2}$ (Figure 16)	2.10	2.045(5)			71
cis,mer-$[\mathrm{IrCl(PMe_3)_3(Bcat)_2}]$	2.10	2.024(6), 2.080(6)	2.94	91.6(2)	81
$[\mathrm{IrCl(PEt_3)_2(Bcat)_2}]$	2.10	1.991(6) 2.004(6)	2.476	76.6(3)	79
$[\mathrm{Ir(\eta^6\text{-}C_6H_5Me)(Bcat)_3}]$ (Figure 17)	2.10	2.036(4), 2.018(5), 2.024(5)	2.618, 2.689, 2.715	80.3(2), 83.1(2), 84.4(2)	74

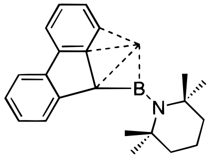
$[Ir(\eta^6\text{-}C_6H_3Me_3)(Bcat)_3]$	2.10	2.016(3)			74
$[Pd(dmpe)(SnMe_3)\{B\text{-}1,2\text{-}(NMe)_2CH_2CH_2\}]$	2.16	2.077(6)			87
trans-$[PtCl(PPh_3)_2(Bcat)]$ (Figure 18)	2.13	2.008(8)			63
cis-$[Pt(PPh_3)_2\{B(OMe)_2\}_2]$	2.15	2.098(4), 2.100(4)	2.494	72.9(2)	82
cis-$[Pt(PPh_3)_2(Bpin)_2]$	2.15	2.076(6), 2.078(6)	2.537	75.3(3)	26
cis-$[Pt(PPh_3)_2(Bcat)_2]\cdot C_7H_8$	2.13	2.07(2), 2.08(2)	2.61	77.9(7)	28
cis-$[Pt(PPh_3)_2(Bcat)_2]\cdot C_7H_8$ (Figure 19)	2.13	2.040(6), 2.058(6)	2.552	77.1(2)	30
cis-$[Pt(PPh_3)_2\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2]$	2.13	2.045(11), 2.046(13)	2.554	77.2(4)	30
cis-$[Pt(PPh_3)_2\{B(1,2\text{-}S_2C_6H_4)\}_2]$	2.13	2.056(4), 2.075(4)	2.612	78.5(2)	63
cis-$[Pt(PPh_3)_2(Btart)_2]$	2.14	2.052(7), 2.067(5)	2.451	73.0(4)	35
cis-$[Pt(PPh_3)_2(Bped)_2]$	2.14	2.054(4), 2.070(3)	2.525	75.5(2)	35
cis-$[Pt(PPh_3)_2\{B(1,2\text{-}O_2C_6Cl_4)\}_2]$	2.17	2.04(2), 2.03(2)	2.616	80.0(8)	63
cis-$[Pt(dppe)(Bcat)_2]$	2.13	2.058(8), 2.048(8)	2.667	81.0(3)	30
cis-$[Pt(dppb)(Bcat)_2]$	2.13	2.031(8)	2.514	76.5(4)	30

[a] Abbreviations: cat = 1,2-$O_2C_6H_4$; pin = 1,2-$O_2C(CH_3)_2C(CH_3)_2$; tart = *R*,*R*-1,2-$O_2CH(CO_2Me)CH(CO_2Me)$; ped = *S*-1,2-$O_2CH(Ph)CH_2$. [b] Where available, covalent radii for BR_2 calculated according to $r_{cov} = {}^1/_2(D_{B-B})$ in B_2R_4, refs 77 and 110−113. Other values taken from ref 109. [c] Substituted hydridoborate complex.

[d] L =



[e] L =



[f] Contains a phosphine group complexed to the BH_2 unit.

exo isomers of $[Cp_2TaH_2(Bcat)]$ [2.263(6) and 2.295(11) Å][54] are quite similar to that in the niobium boryl derivative [2.2292(5) Å], indicative of a Ta−boron bond as opposed to a hydridoborate structure. In metal d^0 complexes where there are no d electrons to participate in π-back-bonding to boron, observed bond lengths match rather closely those expected for single bonds based on simple covalent radii predictions. This is clearly demonstrated in the d^0 boryl complexes of Nb(V) and Ta(V) in which the values have been shown to be quite similar to the calculated value of 2.22 Å. The Nb−H bond distances in the compound $[Cp_2NbH_2(Bcat)]$ were reported to be consistent with known niobium hydride values although the H−Nb−H angle is more acute than in Cp_2NbH_3 which may therefore be an indication of some H−B interaction. In the compound $[Cp_2Nb(H_2BC_8H_{14})]$, longer Nb−H bond lengths, shorter H−B distances and a smaller H−Nb−H angle are also consistent with a hydridoborate structure. The H−Ta−H angles [113(3)°] were closer to $[Cp_2TaH_3]$ [126°] than those for the Nb−Bcat [92(2)°] or $Nb-H_2BC_8H_{14}$ [70(3)°] derivatives and the Ta−H bond lengths [1.75(5) Å and 2.11(6) Å] were longer than expected for typical borohydride complexes [1.10−1.20 Å] consistent with a tantalum−boryl compound.

3. Group 6

In the structures of $[Cp_2WH(Bcat)]$[47,52] and $[Cp_2W\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2]$[51,52] the tungsten−boron bond distances were slightly longer than predicted from covalent radii although the W−B distances in these compounds are significantly shorter than their alkyl counterparts. The boryl groups were oriented to allow overlap between the HOMO (highest occupied molecular orbital) on tungsten and the boron p orbitals, even though this orientation was sterically unfavorable which was attributed to weak $d\pi-p\pi$-back-bonding. The tungsten−bisboryl compound showed a B−W−B bond angle of 78(2)° which was equivalent to the B−W−H angle in the former structure, as well as the calculated ideal angle for a Cp_2ML_2 compound with two d electrons.[114] An examination of Table 2 reveals that in most cases the B−M−B angle in structurally characterized bisboryl compounds is quite small.

The structure of $[(tbp')W(CO)_2\{B(Et)CH_2C_6H_4\text{-}CH_3\}]$ (tbp′ = tris(3,5-dimethylpyrazol-1-yl)hydroborate) exhibited the shortest W−B bond distance known but also contained an agostic interaction with the methylene group attached to the benzene ring. This compound was thought to contain significant π-bonding between the metal and boron based on structural data, as well as spectroscopic results.[64]

The compound $[CpW(CO)_3\{B(NMe_2)B(NMe_2)Cl\}]$ displayed the longest W−B bond distance. This compound represented the first example of a structurally characterized metal−diboran(4)yl compound.[55] The B−B bond distance is consistent with other known diborane(4) compounds which have been structurally characterized.[77,110−113] The ^{11}B chemical shifts were also consistent with one boron atom in a typical diborane(4) environment (δ = 40.3 ppm) and the other bound to a transition metal center (δ = 62.7 ppm).

4. Group 7

The Mn−B bond length in the structure of $[Mn(CO)_5(Bcat)]$[48] was longer than that expected from the sum of the covalent radii; however, the Mn−CO bond distance for the carbonyl ligand trans to the boryl ligand was within the range of other Mn−CO bonds. Therefore, even though the covalent radii predict a shorter Mn−B bond distance, there may still be π-back-bonding since the additional electron density at manganese is not reflected in any variation of the Mn−CO bond distances. Hartwig et al. have also noted that the Mn−CO bond distances are shorter than those of the related alkyl− and hydrido−$M(CO)_5$ (M = Re, Mn) compounds in which no π-interaction is possible which indicates that π-bonding effects may be minimal.

Nöth et al. have reported a series of compounds in which the metal center is bound to a 9-fluorenylidene(2,2,6,6-tetramethylpiperidino)borane ligand.[88−90] The manganese derivative displays a pseudo-tetrahedral geometry at the Mn center with a CO−Mn−CO angle of 103.4(2)°. In this example, as with others described below, the fluorenylidene moiety also binds to the metal through the central carbon atom. The Mn−B bond distance [2.162(5) Å] is longer than the Mn−C bond distance [2.148(4) Å] as would be expected since boron has a larger covalent radius than carbon. The analogous iron and cobalt structures exhibit the opposite trend to this and the difference in the manganese structure is attributed to the number of ancillary ligands.

Braunschweig and Wagner reported the first example of a structurally characterized transition metal−borylene complex $[\{CpMn(CO)_2\}_2(\mu\text{-}BNMe_2)]$ in which the borylene ligand bridges two mutually bonded manganese atoms. The short Mn−B bond distances [2.03(1) Å for both] observed are no doubt a result of this unique bonding environment as evidenced by ^{11}B NMR (δ = 103 ppm) and distinctive B−N double-bond character (B−N = 1.39(1) Å).

5. Group 8

The observed Fe−B bond distances in all of the structurally characterized examples are similar to those predicted from covalent radii calculations. Slightly longer distances have been observed for the bora-olefin compounds prepared by Nöth and coworkers, as well as, the diboran(4)yl derivative. In the latter example, the structure is quite similar to the tungsten derivative described earlier as are the ^{11}B NMR chemical shifts (δ 39.0, 69.5 ppm).

Hartwig and co-workers have reported the structures of $[CpFe(CO)_2(Bcat)]$ and $[CpFe(CO)_2(BPh_2)]$.[46] The main difference existed in the orientation of the boryl ligands as evidenced by the dihedral angles between the Cp−centroid−Fe−B and O−B−O or C−B−C planes (7.9° and 75°, respectively). The geometry of the Bcat moiety was consistent with the alignment of the vacant p orbital (LUMO) on boron with the $CpFe(CO)_2$ HOMO most suitable for π-bonding similar to observations made for carbene and olefin binding in related systems.[115,116] The orientation of the BPh_2 ligand was also consistent with a π-interaction albeit through alignment with the $CpFe(CO)_2$ SHOMO. The lengthening of the Fe–B bond in the BPh_2 derivative (2.034(4) Å) versus the Bcat derivative [1.959(6) Å] may also be attributed to steric factors.

In the structure of $[Fe(CO)_4\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2]$,[49] the Fe–B bond distances are longer than in the structure of $[CpFe(CO)_2(Bcat)]$ but this may be interpreted in terms of variations of ancillary ligands and hence, electron density at the $CpFe(CO)_2$ versus $Fe(CO)_4$ center. The Fe–C bond distances for the carbonyl ligands trans to a boryl ligand [1.832(6) Å] are slightly longer than those for trans-disposed carbonyl ligands [1.795(9), 1.803(9) Å]. The values obtained are close to 3σ indicating only slight differences but also suggesting that π-back-bonding to boron may be present. The boryl ligands are cis-disposed about the Fe center and oriented to reduce their mutual steric repulsion. The B–M–B angle [82.8(4)°] is larger relative to other metal–bisboryl compounds presumably due to a lack of steric constraints imposed by the small CO ligands.

Unlike the manganese derivative discussed previously, the iron and cobalt bora-olefin compounds displayed M–B bond distances which were shorter than the M–C bond distances even though boron has a larger covalent radius. Additional derivatives were structurally characterized from phosphine or phosphite substitution or elimination of CO as in the case of the $Fe(CO)_3$ derivative. In the latter compound, the vacant coordination site generated by elimination of CO was occupied through additional bonding with the fluorenyl moiety resulting in a slight shortening of the Fe–B bond distance [2.080(4) Å].[89]

The inference from the structural asymmetry in the bora-olefin complexes of iron, cobalt, and manganese is that boron plays an important role as a π-acceptor. Extended Hückel calculations on the model compound $[Fe(CO)_4(\eta^2\text{-}H_2NB{=}CH_2)]$ revealed that the bora-olefin has an asymmetrical ethylene-like π-system which possesses a donor and an acceptor end. Moreover, the minimum energy structure calculated for the model compound closely matched the structure of $[Fe(CO)_4(\eta^2\text{-tmpB}{=}CR_2)]$ (CR_2 = 9-fluorenylidene) determined by a diffraction study. Both structures adopted a geometrical disposition of the ligands around the metal which, according to the authors, allowed the boron acceptor end to adopt the electronically preferred “quasi” equatorial site affording good π-back-bonding to the boron.[89] These geometries are also found to be in accord with ligand site preference rules for pentacoordinate trigonal-bipyramidal d^8 complexes.[117]

Several examples of structurally characterized osmium–boryl compounds have been reported for which the predicted and observed Os–B bond distances show reasonable agreement.[76] In general, the five-coordinate complexes display slightly shorter Os–B bond distances when compared to the six-coordinate analogues. The five-coordinate derivatives all display a distorted square-based pyramidal structure with the boryl ligands in the apical position and two mutually trans phosphines in the basal plane. The Cl ligands were noted to be slightly distorted from the basal plane presumably due to steric interaction with the boryl ligands. The six-coordinate derivatives display a distorted octahedral geometry with the additional carbonyl ligands coordinated trans to the boryl ligand. The phosphines are mutually trans lying in the plane with Cl and the other CO ligand.

The Os–B bond distance was found to be relatively insensitive to differing heteroatom substitution at boron and suggests the π-component of the Os–B bond may be very small.

The effects of both intermolecular and intramolecular hydrogen bonding were noted in the osmium derivatives. The structure of $[OsCl(CO)(PPh_3)_2\{B(OH)_2\}]$ revealed the presence of weak intramolecular H-bonding between the O–H and the cis-coordinated metal bound Cl. The O–H···Cl distance of 3.355 Å was slightly longer than typical values observed of 2.92–3.18 Å.[118] Strong intermolecular H-bonding was observed between adjacent molecules (O–H···O = 2.765 Å which falls in the range of typical values of 2.48–2.90 Å.[118] In the structure of $[OsCl(CO)(PPh_3)_2\{B(1,2\text{-}(NMe)_2C_6H_4)\}]$, the plane of the benzodiazaborole ligand was slightly tilted with respect to the equatorial plane of the metal. This was attributed to both intermolecular packing forces and intramolecular steric interactions associated with the N-methyl groups and those between adjacent metal bound ligands. In this case, no intramolecular H-bonding was apparent.

The six-coordinate compound $[OsCl(CO)_2(PPh_3)_2\{B(OH)_2\}]$ contained two molecules in the asymmetric unit which were similar in all aspects within the 3σ range. In this structure there was evidence for strong intramolecular H-bonding (O–H···Cl = 3.07 Å) and weak intermolecular H-bonding (O–H···O = 2.95 and 2.84 Å).

In the structure of $[OsCl(CO)_2(PPh_3)_2(Bcat)]$, there was disorder for the mutually trans CO and Cl ligands. The CO bond distance for the ligand trans to the Bcat moiety was 0.167 Å longer than that for the CO trans to the Cl ligand. The meridional plane defined by Os, Cl, and the CO ligands was tilted with respect to the plane defined by the Os and Bcat ligand by 29.3°. In the structures of $[OsCl(CO)(PPh_3)_2\{B(1,2\text{-}(NH)_2C_6H_4)\}]$ and $[OsCl(CO)(PPh_3)_2\{B(1\text{-}(NH)\text{-}2\text{-}SC_6H_4)\}]$, the boryl ligand planes were coplanar with the meridional planes defined by the Os, and Cl atoms, and the two CO ligands. The difference with respect to the Bcat derivative was attributed to the influence of intermolecular H-bonding in the solid state. In both examples the Cl···H–N distances [3.060 and 3.102 Å, respectively] were within the range typically observed for such interactions [3.00–3.20 Å].[118]

6. Group 9

The structure of $[Co(CO)_2(\eta^1\text{-dppm})(\mu\text{-dppm})(BH_2)]$ represents a unique example of a boryl substituent containing hydrogen ligands and is stabilized by the coordination of a phosphorus ligand which bridges the metal center. The coordination around the cobalt was reported to be that of a distorted trigonal bipyramid with the boryl and monodentate phosphine ligands occupying the axial positions. The Co−B bond distance [2.227(6) Å] was substantially longer than in other examples due to the tetrahedral environment around the boron.

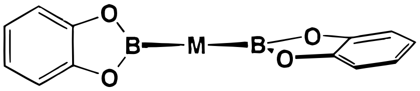
The cobalt derivatives involving the bora-olefin ligand described earlier are very similar to the iron derivatives and are within the range of expected Co−B bond distances. The Co−B bond distances are shorter than the Co−C bond distances to the bora-olefin ligand as described above. Two molecules were observed in the unit cell.

The compound [Co(PMe$_3$)$_3$(Bcat)$_2$] was reported to have a distorted square-pyramidal structure with one phosphine occupying the apical position. The unusually small B−Co−B angle [67.9(4)°] gave rise to a B−B separation of 2.185 Å which when compared to the structure of B$_2$cat$_2$ [B−B = 1.678(3) Å] suggested the possibility of some remaining B−B interaction. Thus, the (Bcat)$_2$ moiety could be considered as a single ligand resulting in a distorted tetrahedral geometry. Comparison with the structure of [CoCl(PMe$_3$)$_3$] showed considerable similarities in the cobalt ligand sphere with this pseudo-tetrahedral complex. The compound [Co(PMe$_3$)$_3$(Bcat)$_2$] was therefore suggested to lie part way along an oxidative addition reaction coordinate with some residual B−B interaction possibly still present, but whether there is a B−B interaction is still unknown.

Metal−boron bond length contraction may also be observed when the metal coordination sphere is completed by non-π-acidic ligands, effectively enhancing the metals ability to participate to a greater degree in dπ−pπ-interactions with boron. Representative of this category is the short bond length reported for [RhHCl(PPr$^i_3$)$_2$(Bcat)] of 1.962(7) Å.[68] This 16-electron Rh(III) species was described as having a distorted trigonal-bipyramidal geometry around rhodium with axial PPr$^i_3$ ligands and a planar Bcat ligand. The BO$_2$ plane was rotated through 14.9° with respect to the RhBCl plane and the presence of the hydride ligand was indicated by the B−Rh−Cl angle of 137.5°.

Orientational preferences in the solid state are often given as evidence for π-accepting character in related boryl ligands. Recent structural studies for [Rh(PMe$_3$)$_4$(Bcat)][80] show that the boryl ligand is located in an axial position in the trigonal-bipyramidal structure. Theoretical studies of ML$_5$ compounds[117] indicate that σ-donors prefer to occupy an axial site, while π-acceptors prefer to occupy an equatorial site in this geometry. Thus, it has been proposed that Bcat and related ligands are very strong σ-donors which result in a strong trans-influence with the π-accepting ability being rather weak and making a lesser contribution, if any, to the strong trans-influence of these boryl ligands. The Rh−B bond distance [2.047(2) Å] is shorter than that expected on the basis of calculations as are the remaining rhodium−boryl complexes and iridium analogues. Although the geometric features discussed above suggest a lack of significant π-bonding in these systems, there is a distinct possibility that weak interactions are present especially when the electron density at the metal center is high and metal orbitals suitable for such interactions are populated. More studies are clearly needed to resolve this matter.

Lack of metal ligation trans to the boryl group by π-acids would also be expected to enhance metal boron π-interactions because of the absence of competition for π-electron density. This characteristic is observed in the bisboryl complex [RhCl(PPh$_3$)$_2$(Bcat)$_2$] whose molecular structure is described as a distorted square-based pyramid with mutually trans phosphines in the basal plane.[67,79] The boryl ligand occupying the apical site has one of the shortest metal−boron bond lengths (1.954(4) Å) reported to date. Two structural determinations have been performed for this compound with differing solvents of crystallization, more accurate results being obtained for the dichloromethane example. In comparison, the boryl ligand in the basal plane exhibits a metal−boron bond length of 2.008(4) Å. Both these Rh−boron bond distances are substantially shorter than the covalent single bond distance of 2.09 Å predicted on the basis of covalent radii. The two boryl moieties were essentially perpendicular in both structures, as shown in **A**, which precluded any residual B···B interaction between the boron p orbitals.



A

The compound [RhCl(PPh$_3$)$_2${B(1,2-O$_2$-3-MeC$_6$H$_3$)}$_2$] also crystallized as a solvate with 3 equiv of CH$_2$Cl$_2$ and one-half molecule of *n*-hexane per asymmetric unit.[79] In this case, the structure is similar to the Bcat derivative described above. The Rh−B bond distance [1.906(13) Å] for the apical boryl ligand is the shortest metal−boryl value reported to date.

The structure of [RhCl(PEt$_3$)$_2$(Bcat)$_2$][79] is best described in terms of the discussion of Y- and T-type structures presented by Eisenstein and co-workers for d^6 ML$_5$ complexes.[119,120] The structure is actually quite similar in nature to other rhodium−bisboryl compounds structurally characterized although the geometry in this case is best described as Y-shaped. Unlike the compound [RhCl(PPh$_3$)$_2$(Bcat)$_2$] which has a distorted square-pyramidal structure, the Cl−Rh−B angles are closer to each other indicative of the Y-shaped structure. The boryl ligands still remain in different environments as reflected in the bond lengths [Rh−B = 1.973(2) and 1.994(2) Å] and the mutually perpendicular arrangement in space (type **A**).

The structure of *cis,mer*-[RhCl$_2$(PMe$_3$)$_3$(Bcat)][121] is consistent with the expected structure predicted from trans-influence arguments. The boryl ligand is situated trans to the weak σ-donor chlorine ligand. The Rh−B bond distance (2.012(2) Å) shows reasonable agreement with other structurally characterized examples containing a boryl ligand coordinated in the same plane as the halide ligand such as [RhCl(PPh$_3$)$_2$-

(Bcat)$_2$] and [RhCl(PEt$_3$)$_2$(Bcat)$_2$]. In this case, the six-coordinate derivative was obtained when the less sterically demanding PMe$_3$ ligand was used.

The compound [Rh(PMe$_3$)$_3$(Bcat)$_3$] is the only example of a structurally characterized trisboryl derivative of rhodium.[80] The *fac* arrangement of the three Bcat ligands is evidence of the strong trans influence which in turn is a reflection of their strong σ-donating ability. The three boryl ligands in this case are aligned such that all are mutually perpendicular.

The Ir−B bond distances in *mer*-[IrHCl(PMe$_3$)$_3$-(Bcat)][73] and *fac*-[IrH$_2$(PMe$_3$)$_3$(BC$_8$H$_{14}$)][70] were reported to be consistent with values expected from covalent radii together with that in the related Ir−B bond distance in *cis,trans*-[IrBr$_2$(CO)(PMe$_3$)$_2$(σ-2-B$_5$H$_8$)] [2.071(14) Å].[122] Similar values are displayed by other Ir(III) compounds described in Table 2. The relative trans influence of the Cl, H, and Bcat ligands can be determined from a comparison between the structures of *mer*-[IrHCl(PMe$_3$)$_3$(Bcat)] and *mer,cis*-[IrCl(PMe$_3$)$_3$(Bcat)$_2$].[81] The compound *mer*-[IrHCl-(PMe$_3$)$_3$(Bcat)] displays an octahedral arrangement of the ligands with the three phosphine ligands in a meridional plane and mutually trans Cl and Bcat ligands. The structure of *mer,cis*-[IrCl(PMe$_3$)$_3$(Bcat)$_2$] is essentially the same with the hydride in this case being replaced with another Bcat ligand. In the former structure, the Ir−P bond distance for the phosphine ligand trans to the hydride [2.351(2) Å] is greater than those values for a phosphine trans to another phosphine [2.307(2), 2.304(2) Å], indicating the stronger trans influence of the hydride versus PMe$_3$. In the iridium−bisboryl compound, the hydride ligand is replaced by a Bcat ligand and this results in a further lengthening of the Ir−P bond distance [2.3989(13) Å]. This is consistent with a stronger trans influence for Bcat vs hydride. In addition, the Ir−B bond distances for Bcat ligands trans to Cl [2.024(6) Å] and PMe$_3$ [2.080(6) Å], suggest a weak trans influence, as expected, for the weak σ-donor ligand, Cl. In fact, as expected, all of the compounds in Table 2 which contain a Cl ligand, also contain a boryl group in the trans position. The respective M−B and M−Cl bond distances are also reasonably consistent.

The compound *fac*-[IrH(PMe$_3$)$_3$(η^2-CH$_2$BHC$_8$H$_{14}$)] was obtained from the reaction of 9-BBN with [IrMe-(PMe$_3$)$_4$]. The Ir−B bond distance in the boraethyl derivative was 2.50(2) Å, consistent with a lack of covalent Ir−B bonding. The ^{11}B NMR resonances were also consistent with structural results with a low-field shift for the iridium boryl complex *fac*-[IrH$_2$-(PMe$_3$)$_3$(BC$_8$H$_{14}$)] (δ 106.2 ppm) and a high-field shift for the bora-ethyl complex (δ 20.6 ppm) which has a bridging Ir−H−B interaction.

The cationic Ir(IV) compound [IrCl(PMe$_3$)$_3${B(F)-C$_{12}$H$_8$}]$^+$ contained a B−F bond inserted into one of the Ir−C bonds of the biphenyl-2,2′-diyl ligand.[94] This represents the sole example of an Ir(IV)−boryl complex. The boryl group was planar as expected.

The structure of *trans*-[IrHCl(CO)(PPh$_3$)$_2$(Bcat)] consists of an octahedral arrangement of the ligands with trans phosphine ligands and the Bcat ligand *trans* to chloride. The Ir−B bond distance and angles around the iridium center were consistent with expected values.

The structure of [IrCl(PEt$_3$)$_2$(Bcat)$_2$] is isomorphous with the Rh analogue described above and will not be discussed in further detail. The novel trisboryl compounds of iridium were also similar to the rhodium analogue described above in that the orientation of the boryl ligands is such that the mutually cis-boryl ligands were all mutally perpendicular. The Ir−B bond distances were as expected from comparison with other iridium boryl compounds.

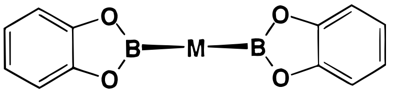
7. Group 10

Tanaka and co-workers have reported the only example of a structurally characterized palladium−boryl complex.[87] In this case, the *cis*-Pd(II)−stannyl-(boryl) complex exhibited a square-planar geometry around the palladium. The repulsion between ligands is minimized by the arrangement of the diazaborolane ring which is nearly perpendicular to the BSn-PdP$_2$ mean plane resulting in only minor distortions from planarity. The Pd−P bond distance trans to the boryl ligand [2.338(2) Å] is slightly longer than that for the phosphine trans to the stannyl ligand [2.280-(2) Å] indicative of a larger trans influence for the boryl ligand.

The value of a covalent radius for platinum in Pt-(II) compounds has been reported as 1.29 Å,[109] giving a predicted Pt−Bcat bond distance of 2.17 Å. However, this value is larger than any experimentally determined Pt−Bcat bond length.[28,30,63] In addition, structural analysis indicates that the boryl ligands are oriented to allow overlap between the filled Pt, d$_{xy}$ orbital and the empty p orbitals on the boron atoms. Thus, the possibility of dπ−pπ-back-bonding does exist. Iverson and Smith[28] reported similar arguments based on a comparison of Pt−B bond distances with those for related Pt−C bond lengths in aryl compounds. By predicting a difference between bond distances for sp^2-hybridized M−C and M−B bonds and using a Pt−C bond distance of 2.08 Å, a value of 2.16 Å was obtained for the theoretical Pt−B bond distance. Examination of the structures of *trans*-[PtClMe(PPh$_3$)$_2$][123] and *trans*-[PtCl(PPh$_3$)$_2$-(Bcat)] provide a means for a more accurate comparison of covalent radii for the determination of π-back-bonding effects. The methyl derivative is incapable of π-bonding and subtraction of the covalent radius for the methyl group [0.77 Å] from the Pt−C bond length [2.08(1) Å] yields a covalent radius for the *trans*-[PtCl(PPh$_3$)$_2$] fragment of 1.31 Å. This value can be compared directly with that of the Bcat derivative since the ligands substitution at platinum and the oxidation state are the same. Changes in the ligand coordination and oxidation state can often lead to quite different values for covalent radii.[124] The sum of the covalent radii for the compound *trans*-[PtCl(PPh$_3$)$_2$(Bcat)] then becomes 2.15 Å which is significantly larger than the observed value of 2.008-(8) Å indicative of substantial π-back-bonding in this compound. Furthermore the trans influence of the Bcat ligand may also be assumed to be similar to that of a methyl ligand in this case since the Pt−Cl bond distances of are equal within 3σ [2.4446(16) Å and 2.431(3) Å, respectively]. The true measure of the trans influence of the Bcat ligands can also be determined from a comparison between the structures of *trans*-[PtHCl(PPh$_3$)$_2$][125] and *trans*-[PtCl(PPh$_3$)$_2$(Bcat)].[63] In this case, the Pt−Cl bond distance increases from 2.36(1) Å to 2.4446(14) Å when the Cl ligand is trans to H and Bcat, respectively. This is consistent with Bcat having a stronger trans influence than a hydride ligand as demonstrated in the iridium structures described above.

The structures of the platinum−bisboryl compounds display the expected square planar coordination geometry around the platinum center with the boryl groups in a cis configuration. The observed parameters for this series of compounds are reasonably consistent. The Pt−B bond distances range from 2.031 to 2.100 Å, the B−Pt−B angles fall in the range of 72.9−81.0° and the P−Pt−P angles range from 100.72 to 107.14° (the P−Pt−P angle for *cis*-[Pt(PPh$_3$)$_2${B(OMe)$_2$}$_2$] was not available). In the compound containing the chelating diphosphine ligand dppe, the P−Pt−P angle [85.36°] is somewhat reduced as expected.

Although the origin of the acute B−Pt−B angles remains unclear, the observation of B−Pt−B angles less than 90° and P−Pt−P angles greater than 90° seems to be a general feature of *cis*-bisboryl complexes of platinum. Steric factors certainly favor such a distortion in that while PPh$_3$ is a very three-dimensional ligand, the boryl groups are much more two-dimensional such that when they are oriented approximately perpendicular to the platinum square plane (type **B** structure), they are probably able to approach one another quite closely. For example in several derivatives[30] the interplanar angles between the boron trigonal plane and the mean square plane around the platinum centers range from 71.3 to 88.8° (with the exception of one Bcat group in [Pt(dppe)(Bcat)$_2$] for which the angle is 55.1°). It is also possible that an electronic origin exists for the observed structural distortion (it should be noted that the boryl ligand orientations are such as to maximize any Pt−B π-back-bonding, although any such orientational preference in this situation is expected to be slight) and a recent study by Sakaki and Kikuno[43] on model Pt^{II}(PH$_3$)$_2$−*cis*-bisboryl complexes does reproduce the experimentally observed geometries, although no explicit comment is made concerning the B−Pt−B angles. Any further insight into this matter will have to await a more detailed theoretical analysis, but appreciable B···B interactions would seem to be relatively unimportant, however, in the view of the long B···B distances observed (~2.5 Å).



B

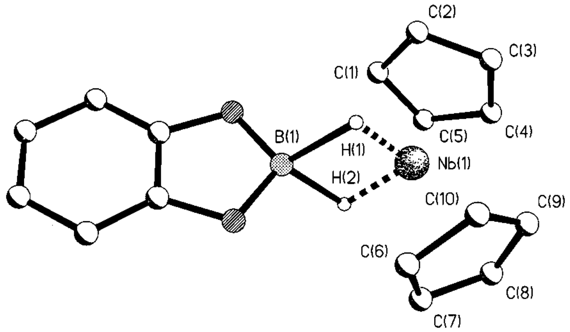


Figure 3. Structure of [Cp$_2$NbH$_2$(Bcat)].

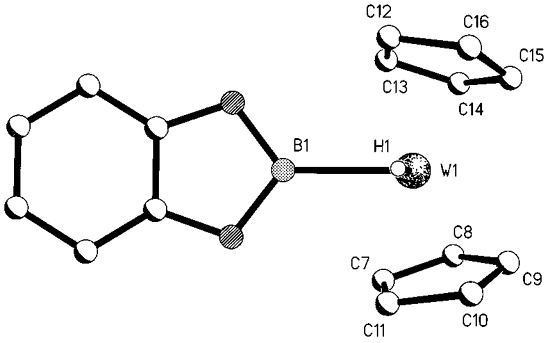


Figure 4. Structure of [Cp$_2$WH(Bcat)].

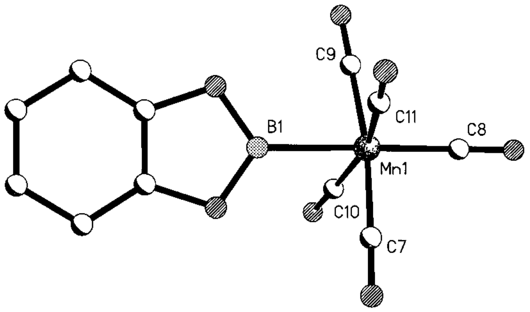


Figure 5. Structure of [Mn(CO)$_5$(Bcat)].

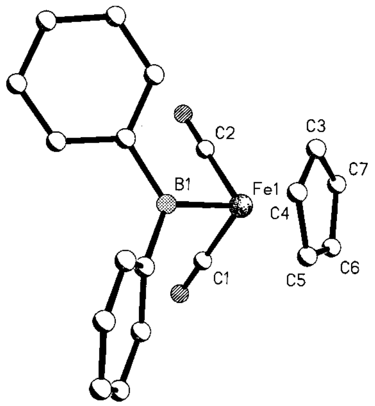


Figure 6. Structure of [CpFe(CO)$_2$(BPh$_2$)].

In considering the nature of metal−boryls in more detail, the cis configuration observed for the platinum(II) complexes is also found in all other structurally characterized examples of metal−bisboryl and −trisboryl compounds and is presumed to be due to the high trans influence of the boryl group. It is of interest to note that the bissilyl, bisgermyl, and bisstannyl complexes of platinum(II), which result from the oxidative addition of Si−Si, Ge−Ge, and Sn−Sn bonds respectively,[126−128] are also cis but in cases where Si−X (X = halide) bond oxidative addition occurred, the resulting [PtX(PR$_3$)$_2$(SiR′$_3$)] com-

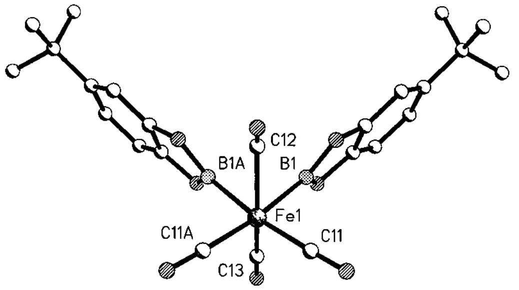


Figure 7. Structure of $[\mathrm{Fe(CO)_4\{B(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)\}_2}]$.

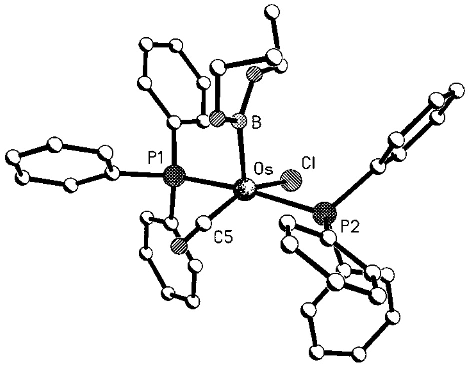


Figure 8. Structure of $[\mathrm{OsCl(CO)(PPh_3)_2\{B(OEt)_2\}}]$.

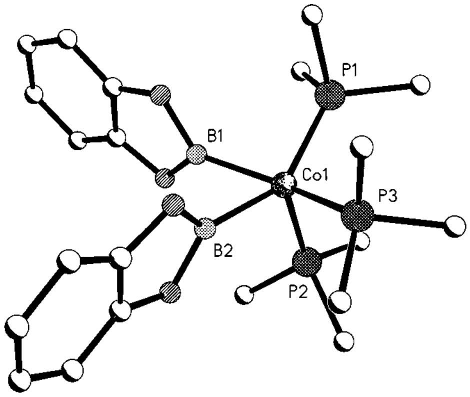


Figure 9. Structure of $[\mathrm{Co(PMe_3)_3(Bcat)_2}]$.

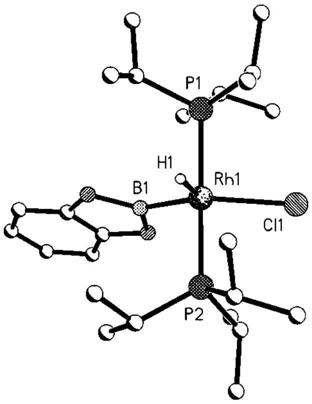


Figure 10. Structure of $[\mathrm{RhHCl(PPr^i_3)_2(Bcat)}]$.

plexes adopt a trans geometry. These data are consistent with a relative ordering of trans influence for the various ligands as $\mathrm{BR_2} \approx \mathrm{SiR_3} > \mathrm{PR_3} > \mathrm{X}$, and we should therefore expect that a complex with the general formula $[\mathrm{PtX(PR_3)_2(BR'_2)}]$ would also have a trans geometry as has been observed.

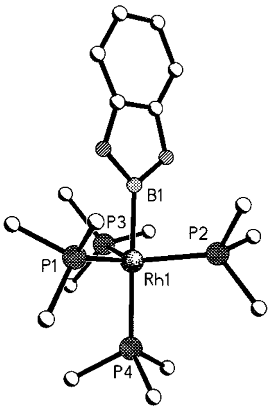


Figure 11. Structure of $[\mathrm{Rh(PMe_3)_4(Bcat)}]$.

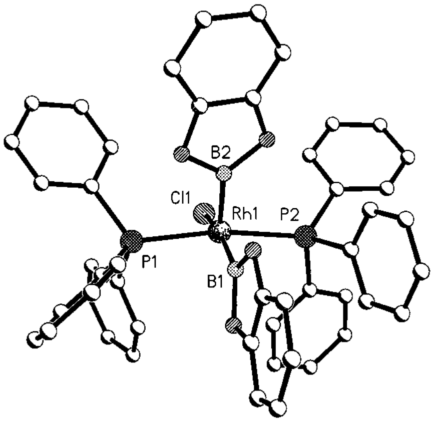


Figure 12. Structure of $[\mathrm{RhCl(PPh_3)_2(Bcat)_2}]$.

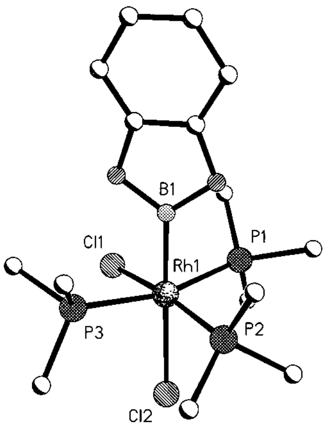


Figure 13. Structure of *cis,mer*-$[\mathrm{RhCl_2(PMe_3)_2(Bcat)}]$.

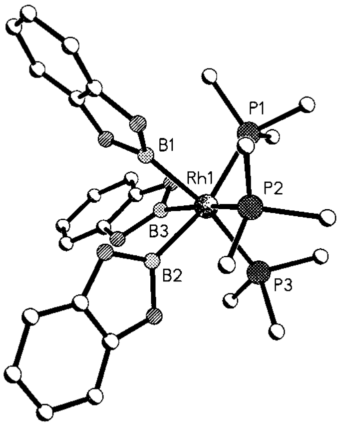


Figure 14. Structure of $[\mathrm{Rh(PMe_3)_3(Bcat)_3}]$.

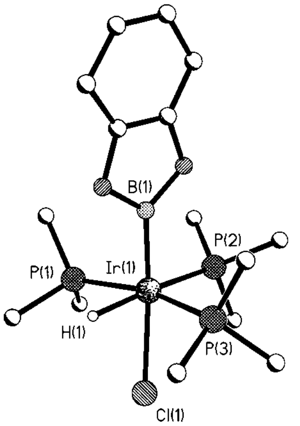


Figure 15. Structure of *mer*-[IrHCl$(PMe_3)_3$(Bcat)].

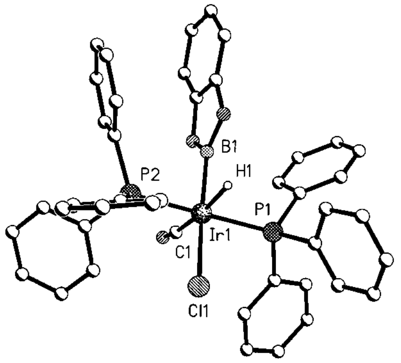


Figure 16. Structure of *trans*-[IrHCl(CO)$(PPh_3)_2$(Bcat)].

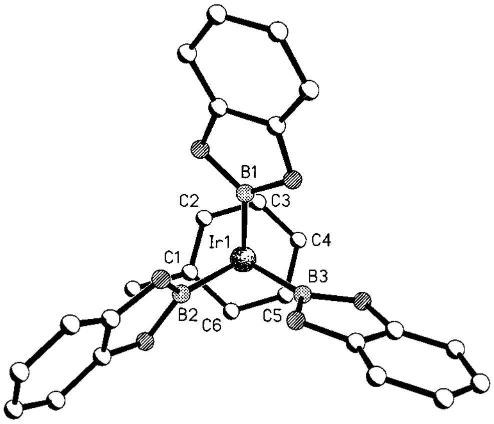


Figure 17. Structure of [Ir(η^6-C_6H_5Me)$(Bcat)_3$].

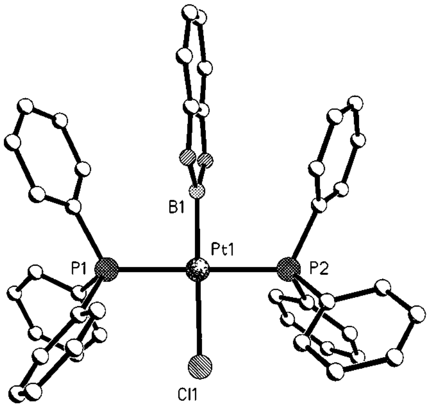


Figure 18. Structure of *trans*-[PtCl$(PPh_3)_2$(Bcat)].

A selection of metal−boryl structures derived from X-ray crystallography are shown in Figures 3−19.

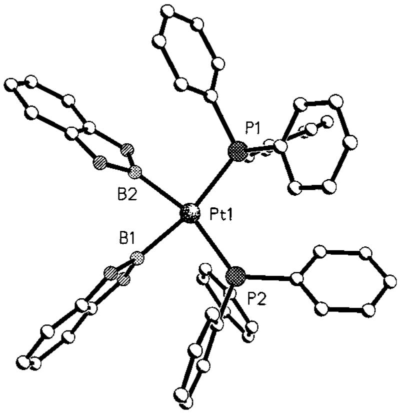


Figure 19. Structure of *cis*-[Pt$(PPh_3)_2$$(Bcat)_2$].

V. Acknowledgments

First, we would like to thank all our various group members whose names appear in the references. In addition, T.B.M. thanks NSERC of Canada and N.C.N. thanks the EPSRC, Laporte plc and The Royal Society for research support. T.B.M. and N.C.N. also thank NSERC, The Royal Society and The British Council for supporting this collaboration via a series of Bilateral Exchange Awards.

Note Added at Proof

Since this work was finished and submitted for publication, a number of papers relevant to this topic have appeared. The titles (in italics), full reference and a brief sentence describing the work (where appropriate) are listed below.

Preparation and Structure of cis-[Pt$(BF_2)_2$$(PPh_3)_2$]: the First Crystallographically Characterised Complex Containing the BF_2 Ligand. Kerr, A.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Timms, P. L.; Whittell, G. R. *Chem. Commun.* **1998**, 319.

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