

Synthesis and Structural Characterization of $[\kappa^3\text{-B,S,S-B(mim}^R)_3]\text{Ir(CO)(PPh}_3)_2\text{H}$ ($R = \text{Bu}^t, \text{Ph}$) and $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{M(PPh}_3)_2\text{Cl}$ ($M = \text{Rh, Ir}$): Analysis of the Bonding in Metal Borane Compounds

Victoria K. Landry, Jonathan G. Melnick, Daniela Buccella, Keliang Pang, Joseph C. Ulichny, and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

Received November 15, 2005

A series of iridium and rhodium complexes that feature $M \rightarrow B$ dative bonds, namely $[\kappa^3\text{-B,S,S-B(mim}^R)_3]\text{Ir(CO)(PPh}_3)_2\text{H}$ ($R = \text{Bu}^t, \text{Ph}$) and $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{M(PPh}_3)_2\text{Cl}$ ($M = \text{Rh, Ir}$), has been synthesized via (i) the reactions of $\text{Ir(PPh}_3)_2\text{(CO)Cl}$ with $[\text{Tm}^{\text{Bu}^t}]\text{I}$ and $[\text{Tm}^{\text{Ph}}]\text{Li}$ and (ii) the reactions of $(\text{COD})\text{M(PPh}_3)_2\text{Cl}$ with $[\text{Tm}^{\text{Bu}^t}]\text{K}$. The complexes have been structurally characterized by X-ray diffraction, thereby demonstrating the presence of a $M \rightarrow B$ dative bond in each complex. The nature of the $M \rightarrow B$ interaction in these complexes has been addressed by computational methods which indicate that the metal centers possess a d^6 configuration. The d^6 configuration is in accord with the value predicted by using a method that employs the valence to determine d^n , but is not in accord with the d^8 configuration that is predicted using the oxidation number. Thus, even though $\text{B(mim}^R)_3$ may be regarded as a neutral closed-shell ligand, coordination to a d^n transition metal via the boron results in the formation of a complex in which the metal center possesses a d^{n-2} configuration.

Introduction

Tris(2-mercapto-1- R -imidazolyl)hydroborato ligands, $[\text{HB(mim}^R)_3] = [\text{Tm}^R]$ (Figure 1),¹ which may be regarded as the sulfur counterparts to the well-known tris(pyrazolyl)hydroborato ligands, $[\text{Tp}^{\text{RR}'}]$,² have recently found widespread applications in coordination chemistry. For example, tris(2-mercapto-1- R -imidazolyl)hydroborato ligands have been employed in areas as diverse as bioinorganic chemistry and organometallic chemistry. In the vast majority of cases, the $[\text{Tm}^R]$ ligand coordinates in a tridentate manner via the three sulfur atoms (Figure 1a), although more complex coordina-

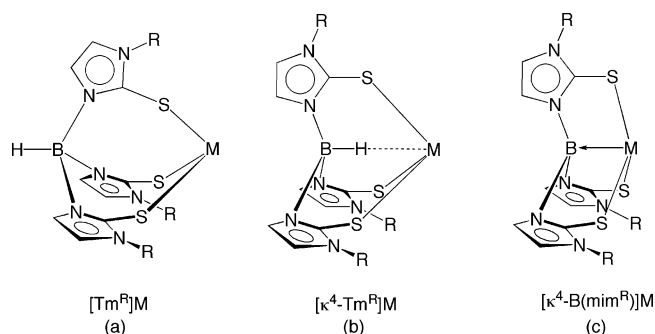


Figure 1. C_3 -symmetric coordination modes for $[\text{Tm}^R]$ and $[\text{B(mim}^R)_3]$ ligands.

tion modes have also been observed. A particularly interesting example is provided by the lead complex $[\text{Tm}^{\text{Ph}}]_2\text{Pb}$ in which one of $[\text{Tm}^{\text{Ph}}]$ ligands coordinates with an “inverted” κ^4 configuration (Figure 1b).³ Thus, in addition to interacting with the three sulfur donors, the lead center also participates in a $\text{Pb} \cdots \text{H} - \text{B}$ interaction along the 3-fold axis (Figure 1b). Further illustrations of the departure from simple κ^3 coordination via the three sulfur donors are provided by (i) $[\kappa^3\text{-}$

(1) For example, derivatives with $R = \text{Me},^{\text{a-c}} \text{Ph},^{\text{d}} \text{Mes},^{\text{d}} \text{Cum},^{\text{e}} \text{Bu}^t,^{\text{e}} \text{CH}_2\text{Ph},^{\text{f}}$ and $p\text{-Tol}^{\text{f}}$ are known. See: (a) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *J. Chem. Soc., Chem. Commun.* **1996**, 1975–1976. (b) Reglinski, J.; Garner, M.; Cassidy, I. D.; Slavin, P. A.; Spicer, M. D.; Armstrong, D. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2119–2126. (c) Santini, C.; Lobbia, G. G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. *Inorg. Chem.* **1998**, *37*, 890–900. (d) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **1999**, 2301–2302. (e) Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 4022–4029. (f) Bakbak, S.; Bhatia, V. K.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Polyhedron* **2001**, *20*, 3343–3348.

(2) (a) Trofimenko, S. *Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Polyhedron* **2004**, *23*, 197–203.

(3) Bridgewater, B. M.; Parkin, G. *Inorg. Chem. Commun.* **2000**, *3*, 534–536.

$H,S,S\text{-Tm}^{\text{Me}}\text{Ru}(\text{CO})(\text{PPh}_3)\text{H}$,⁴ $[\kappa^3\text{-}H,S,S\text{-Tm}^{\text{p-Tol}}]\text{Ni}(\text{dppe})\text{-Cl}$,⁵ and $[\text{Tm}^{\text{Bu}}]_2\text{Co}$,⁶ in which the B–H group coordinates to the metal via a 3-center-2-electron interaction, and (ii) $\{[\text{Tm}^{\text{Ph}}\text{Ti}]_2\}$ ⁷ and $\{[\text{Tm}^{\text{Bu}}]_2\text{Co}_2\text{Br}\}[\text{PF}_6]$,⁶ in which the $[\text{Tm}^{\text{R}}]$ ligands bridge two metal centers.

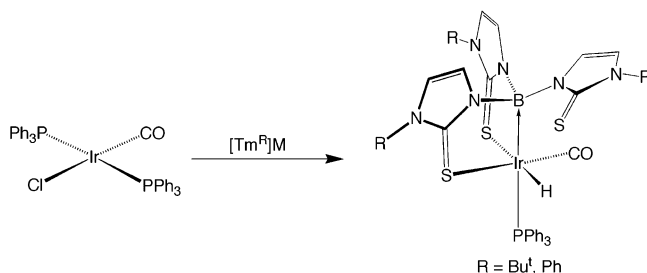
An important recent development in the application of $[\text{Tm}^{\text{R}}]$ ligands is concerned with the discovery by Hill that the B–H entity is reactive and may be cleaved by a metal center to generate so-called metallaboratrane⁸ complexes which feature the $[\text{B}(\text{mim}^{\text{R}})_3]$ ligand (Figure 1c). Examples of such complexes include $[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Ru}(\text{CO})(\text{PPh}_3)$,^{4,9} $[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Os}(\text{CO})(\text{PPh}_3)$,¹⁰ $\{[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Co}(\text{PPh}_3)\}\text{-}[\text{BPh}_4]$,⁶ $[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Rh}(\text{PPh}_3)\text{Cl}$,¹¹ $\{[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Rh}(\text{PPh}_3)(\text{CNR})\}^+$,¹¹ $\{[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Rh}(\text{PMe}_3)_2\}^+$,^{11,12} $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Me}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$,¹³ $\{[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Pt}(\text{PPh}_3)\text{-H}\}\text{Cl}$,¹⁴ and $[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Pt}(\text{PPh}_3)$.¹⁴ Examination of this series of $[\text{B}(\text{mim}^{\text{R}})_3]$ complexes indicates that they are largely restricted to those of the parent $[\text{B}(\text{mim}^{\text{Me}})_3]$ derivative,¹⁵ with only one report of a structurally characterized complex that incorporates bulky substituents.⁶ In this paper, we (i) describe the synthesis and structural characterization of rhodium and iridium complexes of $[\text{B}(\text{mim}^{\text{Bu}})_3]$ and $[\text{B}(\text{mim}^{\text{Ph}})_3]$ ligands which feature $\text{M}\rightarrow\text{B}$ dative bonds and (ii) provide a theoretical analysis of the nature of the bonding in these derivatives.

Results and Discussion

1. Syntheses and Structures of $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ and $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Ph}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$.

The iridium borane complexes $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ and $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Ph}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ may be obtained via reaction of Vaska's complex $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ with $[\text{Tm}^{\text{Bu}}]\text{M}$ ($\text{M} = \text{K}, \text{Ti}$) and $[\text{Tm}^{\text{Ph}}]\text{Li}$, respectively (Scheme 1). While the formation of $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{R}})_3]\text{Ir}$

Scheme 1



$(\text{CO})(\text{PPh}_3)\text{H}$ necessarily involves a reaction sequence that comprises metathesis of Cl by $[\text{Tm}^{\text{R}}]$ and cleavage of the B–H bond,¹⁶ details of the mechanism are otherwise unknown. The analogue $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Me}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ has been previously synthesized, but efforts to obtain crystals suitable for X-ray diffraction were unsuccessful and the existence of an Ir–B bond was inferred from the observation of a broad $^31\text{P}\{^1\text{H}\}$ NMR signal.¹³ It is, therefore, noteworthy that we have been able to determine the molecular structures of both $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ and $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Ph}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ by X-ray diffraction, as illustrated in Figures 2 and 3, which clearly indicate the $\kappa^3\text{-B,S,S}$ coordination mode of the ligand. In accord with these structures, ^1H NMR spectroscopy indicates that the three mim^{R} groups are chemically inequivalent, as illustrated by the ^1H NMR spectrum of $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ (Figure 4).

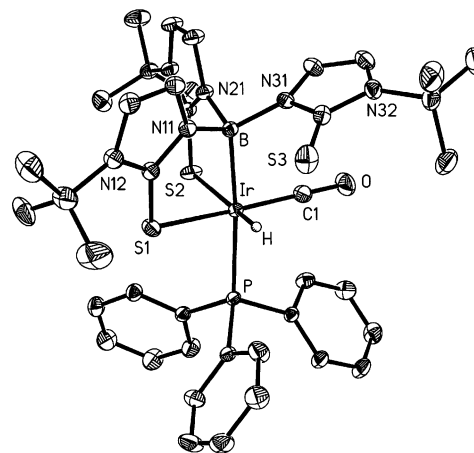


Figure 2. Molecular structure of $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$.

2. Syntheses and Structures of $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{PPh}_3)\text{-Cl}$ and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Rh}(\text{PPh}_3)\text{Cl}$.

Whereas the carbonyl compounds $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{R}})_3]\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ exhibit tridentate coordination of the $[\text{B}(\text{mim}^{\text{R}})_3]$ ligand, tetradentate coordination is observed in the carbonyl-free complexes $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{PPh}_3)\text{Cl}$ and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Rh}(\text{PPh}_3)\text{Cl}$, which are obtained via the reactions of $(\text{COD})\text{M}(\text{PPh}_3)\text{Cl}$ with $[\text{Tm}^{\text{Bu}}]\text{K}$ (Scheme 2). The molecular structures of $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Ir}(\text{PPh}_3)\text{Cl}$ and $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}})_3]\text{Rh}(\text{PPh}_3)\text{Cl}$ have been determined by X-ray diffraction, as illustrated in Figures

- (4) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446–4450.
 (5) Alvarez, H. M.; Tanski, J. M.; Rabinovich, D. *Polyhedron* **2004**, *23*, 395–403.
 (6) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2004**, 1626–1634.
 (7) Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 1267–1274.
 (8) The term “atrane” is traditionally used to describe molecules in which two bridgehead atoms are bridged by three three-atom moieties.^{a–c} As such, it is not completely appropriate for $[\kappa^3\text{-}B,S,S\text{-B}(\text{mim}^{\text{R}})_3]$ derivatives in which the third ligand arm does not coordinate. (a) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233–295. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483–489. (c) Woronkow, M. G.; Seltshan, G. I.; Lapsina, A.; Pestunowitschich, W. A. *Z. Chem.* **1968**, *8*, 214–217.
 (9) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759–2761.
 (10) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913–916.
 (11) (a) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221–223. (b) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289–299.
 (12) For a binuclear $\{[\kappa^4\text{-B}(\text{mim}^{\text{Me}})_3]\text{Rh}\}$ derivative, see: Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083–4086.
 (13) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062–1064.
 (14) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656–5658.
 (15) $\text{B}(\text{mim}^{\text{Me}})_3$ is often abbreviated as $\text{B}(\text{mt})_3$ in view of the trivial name of methimazolyl for mim^{Me} .

- (16) For other examples of B–H addition to $\text{Ir}(\text{PR}_3)_2(\text{CO})\text{X}$ derivatives, see: (a) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930–936. (b) Cleary, B. P.; Eisenberg, R. *Organometallics* **1995**, *14*, 4525–4534.

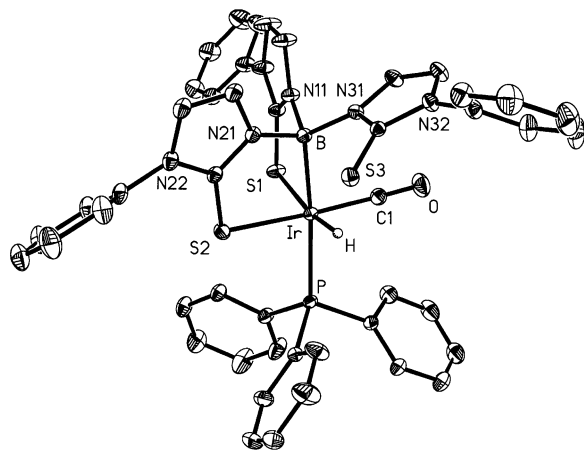


Figure 3. Molecular structure of $[\kappa^3\text{-B,S,S-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Ir(CO)(PPh}_3\text{)H}$.

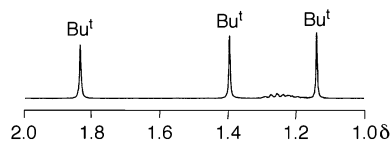
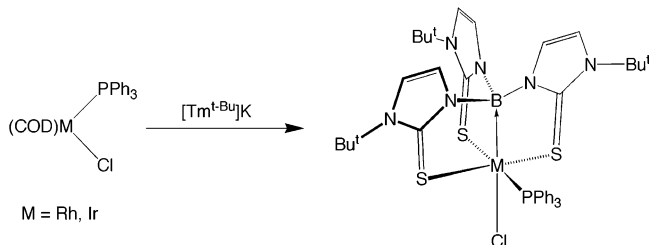


Figure 4. ^1H NMR spectrum of $[\kappa^3\text{-B,S,S-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Ir(CO)(PPh}_3\text{)H}$ showing the chemical inequivalence of the three *tert*-butyl groups of the $\text{B(mim}^{\text{Bu}^t}\text{)}_3$ ligand.

Scheme 2



5 and 6. The formation of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{M(PPh}_3\text{)Cl}$ is undoubtedly complex, and the nature of the byproducts is not known. In the case of the rhodium system, however, an intermediate which is tentatively characterized as the hydride derivative $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)H}$ has been observed in solution prior to crystallization of $\text{B(mim}^{\text{Bu}^t}\text{)}_3\text{Rh(PPh}_3\text{)Cl}$.¹⁷ Evidence for the formulation of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)H}$ is provided by a signal attributable to the hydride ligand at -15.05 ppm in the ^1H NMR spectrum (Figure 7), which

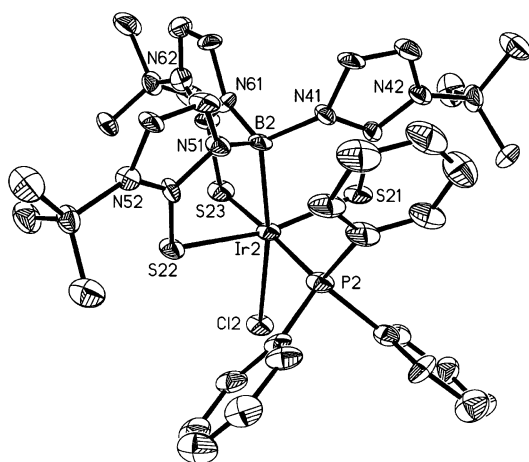


Figure 5. Molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Ir(PPh}_3\text{)Cl}$.

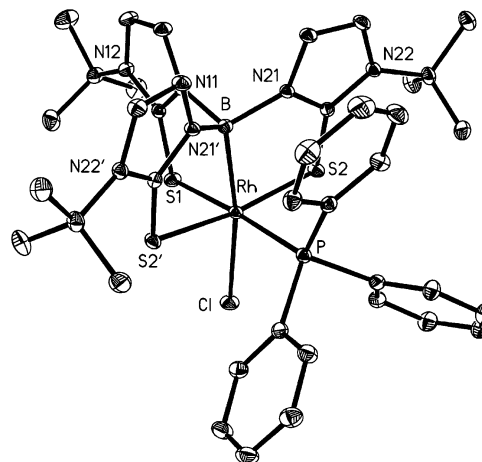


Figure 6. Molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)Cl}$.

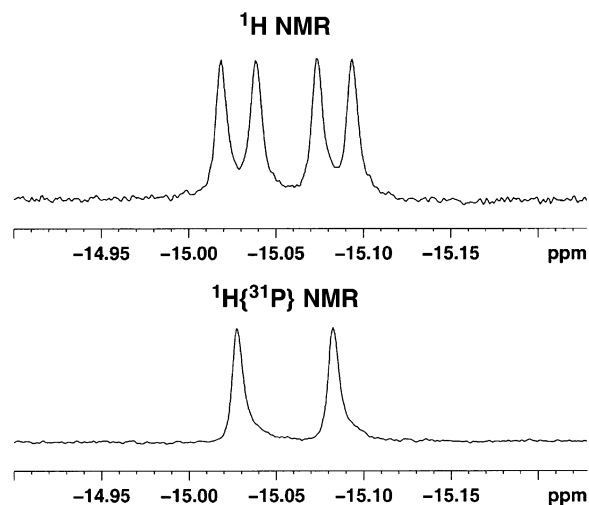


Figure 7. ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of the hydride signal of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)H}$ in C_6D_6 (the signal is observed at -16.2 in CD_3CN).

exhibits coupling to both ^{103}Rh ($^1J_{\text{Rh-H}} = 17$ Hz) and ^{31}P ($^2J_{\text{P-H}} = 6$ Hz), with the latter value being consistent with a *cis* disposition of hydride and PPh_3 ligands.¹⁸ Further support for the identification of $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)H}$ as the intermediate is provided by the fact that the same hydride signal in the ^1H NMR spectrum is also observed when $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)Cl}$ is treated with LiBH_4 .

3. Nature of the Metal–Boron Bonding in $[\kappa^3\text{-B,S,S-B(mim}^{\text{R}}\text{)}_3]\text{Ir(CO)(PPh}_3\text{)H}$ and $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{M(PPh}_3\text{)Cl}$ ($\text{M} = \text{Rh, Ir}$). The most important feature of the molecular structures of $[\kappa^3\text{-B,S,S-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Ir(CO)(PPh}_3\text{)H}$, $[\kappa^3\text{-B,S,S-B(mim}^{\text{Ph}}\text{)}_3]\text{Ir(CO)(PPh}_3\text{)H}$, $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Ir(PPh}_3\text{)Cl}$, and $[\kappa^4\text{-B(mim}^{\text{Bu}^t}\text{)}_3]\text{Rh(PPh}_3\text{)Cl}$, together with the aforementioned metallaboratrane compounds,^{4,6,9–14} pertains to the presence of a $\text{M}\rightarrow\text{BR}_3$ *dative* covalent bond (also referred to as coordinate covalent bond or donor–acceptor bond).¹⁹ While

(17) A similar observation has been made pertaining to the conversion of $[\kappa^4\text{-B(mim}^{\text{Me}}\text{)}_3]\text{Rh(PPh}_3\text{)H}$ to $[\kappa^4\text{-B(mim}^{\text{Me}}\text{)}_3]\text{Rh(PPh}_3\text{)Cl}$. See ref 11b.

(18) For representative values of *cis* and *trans* $^2J_{\text{P-H}}$ coupling constants, see: (a) Okazaki, M.; Ohshitanai, S.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **2002**, 2061–2068. (b) Paneque, M.; Sirol, S.; Trujillo, M.; Gutiérrez-Puebla, E.; Monge, M. A.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 218–221. (c) Circu, V.; Fernandes, M. A.; Carlton, L. *Polyhedron* **2003**, *22*, 3293–3298.

(19) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.

dative bonding is a common feature of transition metals, the metal is normally the electron pair *acceptor*, rather than the *donor*. There are, nevertheless, notable exceptions in which a metal center serves as an electron pair donor, which include situations in which (i) there is a $M\cdots H-X$ hydrogen bond^{20,21} and (ii) a metal–ligand bond is supplemented by back-bonding (e.g., carbonyl, olefin, and boryl compounds).²²

With respect to the dative covalent nature of the $M\rightarrow B$ bond, the Ir–B bond lengths in $[\kappa^3-B,S,S-B(mim^{Bu})_3]Ir(CO)-(PPh_3)H$ [2.179(4) Å], $[\kappa^3-B,S,S-B(mim^{Ph})_3]Ir(CO)(PPh_3)H$ [2.186(3) Å], and $[\kappa^4-B(mim^{Bu})_3]Ir(PPh_3)Cl$ [2.15(2) and 2.18(2) Å for two crystallographically independent molecules] are comparable to that of $[\kappa^3-B,S,S-B(mim^{Me})_2(H)]-Ir(CO)(PPh_3)H$, [2.21 Å].¹³ Furthermore, although these bond lengths are longer than those of the Ir–B normal covalent bonds in iridium–boryl complexes such as $Ir(PMe_3)_3(9-BBN)H_2$ (2.09 Å),²³ $Ir(PPh_3)_2(CO)(Cl)(Bcat)H$ (2.05 Å),^{16a} and $Ir(PMe_3)_2(CO)(B_5H_8)Br_2$ (2.07 Å),^{24,25} it is evident that the difference is sufficiently small that the Ir→B dative covalent interaction must be considered to be significant. Likewise, the Rh–B bond length in $[\kappa^4-B(mim^{Bu})_3]Rh(PPh_3)Cl$ [2.095(3) Å] is comparable to the Rh–B bond lengths in $[\kappa^4-B(mim^{Me})_3]Rh(PPh_3)Cl$ [2.13 Å]¹¹ and rhodium–boryl compounds, such as $RhHCl(PPr^i_3)_2(Bcat)$ [1.97 Å],²⁶ $Rh(PMe_3)_4(Bcat)$ [2.05 Å],²⁷ and $Rh(PMe_3)_3Cl_2(Bcat)$ [2.10 Å].²⁸

In view of the fact that BR_3 (R = H, halogen, alkyl, aryl) derivatives are well-known Lewis acids and that electron rich metal centers are basic,²⁹ it is perhaps surprising that complexes with $M\rightarrow BR_3$ interactions have not been structurally characterized for simple monodentate boranes.³⁰ Indeed,

investigations pertaining to the reactivity of transition metal compounds with BR_3 derivatives were initiated in the 1960s,^{29a} but the results of many of these early investigations have been called into question because of the lack of structural verification.³¹ For example, the first transition metal complex proposed to have a $M\rightarrow B$ bond was $Cp_2WH_2(BF_3)$, obtained via treatment of Cp_2WH_2 with BF_3 ,³² but the product of this reaction has subsequently been shown to be $[Cp_2WH_3][BF_4]$.^{31,33} It is, therefore, evident that the ability to isolate complexes such as $[\kappa^3-B,S,S-B(mim^{Bu})_3]Ir(CO)-(PPh_3)H$, $[\kappa^3-B,S,S-B(mim^{Ph})_3]Ir(CO)(PPh_3)H$, $[\kappa^4-B(mim^{Bu})_3]Ir(PPh_3)Cl$, and $[\kappa^4-B(mim^{Bu})_3]Rh(PPh_3)Cl$ which feature $M\rightarrow B$ dative bonds is a consequence of the chelating nature of the $[B(mim^R)_3]$ borane ligand.

Of particular interest, therefore, is the nature of the bonding in $\{[B(mim^R)_3]M\}$ complexes and the electronic impact that the borane ligand exerts on a metal center. In this regard, two important factors pertaining to the coordination of any ligand to a metal center are the effects that it has on (i) the electron count and (ii) the d^n configuration, both of which play an important role in evaluating the stability and reactivity of a molecule.

With respect to the electron count of the metal center, the $M\rightarrow B$ dative bond contributes no electrons since the boron atom serves the role of an electron *acceptor*. As such, the number of electrons contributed by the $[B(mim^R)_3]$ ligand to the electron count of a metal center depends only on the number of sulfur atoms coordinated, i.e., it is a 6-electron donor if coordinated through three sulfur atoms and a 4-electron donor if coordinated through two sulfur atoms. Thus, $[\kappa^3-B,S,S-B(mim^{Bu})_3]Ir(CO)(PPh_3)H$, $[\kappa^3-B,S,S-B(mim^{Ph})_3]Ir-$

- (20) For lead references, see: (a) Brammer, L. *Dalton* **2003**, 3145–3157. (b) Martin, A. J. *J. Chem. Educ.* **1999**, 76, 578–583. (c) Crabtree, R. H.; Eisenstein, O.; Sini, G.; Peris, E. *J. Organomet. Chem.* **1998**, 567, 7–11. (d) Shubina, E. S.; Belkova, N. V.; Epstein, L. M. *J. Organomet. Chem.* **1997**, 536, 17–29. (e) Brammer, L.; Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J. *Acta Crystallogr., Sect. B: Struct. Commun.* **1995**, 51, 632–640. (f) Brammer, L. In *Implications of Molecular and Materials Structure for New Technologies*; Howard, J. A. K., Ed.; Kluwer Academic Publishers: Netherlands 1999; pp 197–210. (g) Mareque Rivas, J. C.; Brammer, L. *Coord. Chem. Rev.* **1999**, 183, 43–80. (h) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, 16, 1846–1856. (i) Epshtein, L. M.; Shubina, E. S. *Organomet. Chem. U.S.S.R.* **1992**, 5, 31–38.
- (21) A simple illustration of an intramolecular $Mo\cdots H-O$ hydrogen bond is provided by $[\eta^6-C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$. See: Hascall, T.; Baik, M.-H.; Bridgewater, B. M.; Shin, J. H.; Churchill, D. G.; Friesner, R. A.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **2002**, 2644–2645.
- (22) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, 100, 717–774.
- (23) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, 112, 9399–9400.
- (24) Churchill, M. R.; Hackbarth, J. J. *Inorg. Chem.* **1975**, 14, 2047–2051.
- (25) For reviews that feature metal–boryl complexes, see: (a) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G.; Wright, L. J. *Chem. Rev.* **1998**, 98, 2685–2722. (b) Aldrige, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, 248, 535–559.
- (26) (a) Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, 22, 4557–4568. (b) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304–305.
- (27) Dai, C.; Stringer, G.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Inorg. Chem.* **1997**, 36, 272–273.
- (28) Souza, F. E. S.; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W. *Inorg. Chim. Acta* **2005**, 358, 1501–1509.

- (29) (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, 3, 231–238. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 927–949. (c) Angelici, R. J. *Acc. Chem. Res.* **1995**, 28, 51–60. (d) Pearson, R. G.; Ford, P. C. *Comm. Inorg. Chem.* **1982**, 1, 279–291. (e) Kotz, J. C.; Pedrotty, D. G. *Organomet. Chem. Rev., Sect. A* **1969**, 4, 479–547. (f) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991; pp 309–359.
- (30) Although simple borane adducts of transition metals are unknown, other Lewis acids are known to form adducts, as illustrated by $CpCo(CO)_2[HgCl_2]$,^{a-c} $CpCo(PMe_3)_2[HgCl_2]$,^d $CpCo(PMe_3)_2[ZnCl_2-(PMe_3)]$,^d $CpRh(PMe_3)_2[AlR_3]$,^e $[H_2C(C_5H_4)_2]Rh(CO)_2[HgX_2]$ (X = Cl, Br, I),^f $Cp^*Ir(CO)_2[MCl_2]$ (M = Zn, Cd, Hg),^g $Cp_2MoH_2[ZnBr_2-(DMF)]$,^h $CpM(CO)(NO)(PPh_3)[HgCl_2]$ (M = Mo, W),ⁱ $\{[\eta^6-C_6H_5-Me_3]Mo(CO)_3[HgCl_2]_2\}_2^{j,k}$ and $[CpFe(CO)_2(AlPh_3)]^-$. (a) Nowell, I. N.; Russell, D. R. *Chem. Commun.* **1967**, 817. (b) Cook, D. J.; Daws, J. L.; Kemmitt, R. D. W. *J. Chem. Soc. (A)* **1967**, 1547–1551. (c) Nowell, I. N.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2393–2395. (d) Dey, K.; Werner, H. *J. Organomet. Chem.* **1977**, 137, C28–C30. (e) Mayer, J. M.; Calabrese, J. C. *Organometallics* **1984**, 3, 1292–1298. (f) Cox, M. G.; Manning, A. R.; McCabe, A. J. *Organomet. Chem.* **1990**, 384, 217–221. (g) Einstein, F. W. B.; Yan, X.; Zhang, X.; Sutton, D. *J. Organomet. Chem.* **1992**, 439, 221–230. (h) Crotty, D. E.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, 16, 2346–2350. (i) Ginzburg, A. G.; Aleksandrov, G. G.; Struchkov, Yu. T.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1980**, 199, 229–242. (j) Ciplis, A. M.; Geue, R. J.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1976**, 35–37. (k) Edgar, K.; Johnson, B. F. G.; Lewis, J.; Wild, S. B. *J. Chem. Soc. A* **1968**, 2851–2855. (l) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, 18, 1097–1105.
- (31) (a) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, 37, 1786–1801. (b) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, 223, 1–51.
- (32) (a) Shriver, D. F. *J. Am. Chem. Soc.* **1963**, 85, 3509–3510. (b) Johnson, M. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1966**, 88, 301–304.
- (33) Braunschweig, H.; Wagner, T. Z. *Naturforsch.* **1996**, B51, 1618–1620.

(CO)(PPh₃)H, [κ^4 -B(mim^{Bu})₃]Ir(PPh₃)Cl, and [κ^4 -B(mim^{Bu})₃]Rh(PPh₃)Cl possess 18-electron configurations.

The dⁿ configuration, i.e., the number of transition metal d electrons that are *not* involved in the formation of the metal–ligand bonds,³⁴ is an important quantity since it indicates whether a metal center possesses sufficient electrons for further reactivity, such as an oxidative addition reaction which requires a d^{≥2} configuration; furthermore, the dⁿ configuration plays an important role in determining the magnetic properties and electronic spectroscopy of a molecule. In a molecular orbital sense, the dⁿ configuration refers to the number of electrons that occupy nonbonding metal and metal–ligand antibonding orbitals with d character.^{34–37} Since coordination of a [B(mim^R)₃] ligand requires two electrons from the metal center to provide the M→B dative bond, it is evident that coordination to a dⁿ metal center results in a molecule that necessarily possesses a d^{n–2} center. On this basis, each of the complexes [κ^3 -B,S,S-B(mim^{Bu})₃]Ir(CO)(PPh₃)H, [κ^3 -B,S,S-B(mim^{Ph})₃]Ir(CO)(PPh₃)H, [κ^4 -B(mim^{Bu})₃]Ir(PPh₃)Cl, and [κ^4 -B(mim^{Bu})₃]Rh(PPh₃)Cl are described as octahedral 18-electron d⁶ molecules. However, this assignment is not in accord with the d⁸ configuration that has been assigned to the related rhodium compound, [κ^4 -B(mim^{Me})₃]Rh(PPh₃)Cl.¹¹

The origin of this discrepancy is a consequence of following the often assumed relationship between dⁿ configuration and oxidation number:³⁸

$$n = \text{number of valence electrons in neutral atom} - \text{oxidation number} \quad (1)$$

While this relationship provides the correct dⁿ values in many cases, it fails in situations where the oxidation number is not coincidentally the same as the valence (i.e., the number of electrons that an atom uses in bonding).³⁹ For example, common situations that result in departures of oxidation number from the valence are (i) the molecule possesses a metal–metal bond and (ii) the closed-shell charge associated with a ligand does not accurately reflect the bonding situation. As an illustration of the influence of a metal–metal bond, the molybdenum atoms in Cp(CO)₃Mo–Mo(CO)₃Cp possess an oxidation number of +1 because, by definition, homonuclear element–element bonds do not contribute to oxidation number. Despite the assignment of a

+1 oxidation number (which is most uncommon for molybdenum),⁴⁰ the molybdenum centers of Cp(CO)₃Mo–Mo(CO)₃Cp are divalent because each molybdenum must use one of its electrons in forming the Mo–Mo bond; as such, the molybdenum centers possess a d⁴ configuration, rather than the d⁵ configuration that would be implied by the +1 oxidation number (eq 1).

An illustration of the impact of an inappropriate ligand charge on the dⁿ configuration is provided by the cycloheptatrienyl ligand which is generally considered to be a closed-shell cation, (C₇H₇)⁺, for the purpose of oxidation number assignments.^{41–43} On this basis, molecules such as CpTi(η⁷-C₇H₇)⁴⁴ and a series of (η⁷-C₇H₇)TiL₂X complexes⁴⁵ are classified as Ti(0) with a d⁴ configuration.⁴² However, a large body of theoretical studies indicates that the assignment of a +1 charge to the cycloheptatrienyl ligand in such complexes is misleading because the metal is required to contribute *three* electrons to the M–(η⁷-C₇H₇) interaction.^{45–47} The titanium centers in CpTi(η⁷-C₇H₇) and (η⁷-C₇H₇)TiL₂X, therefore, adopt a d⁰ configuration, which is a much more reasonable assignment for titanium compounds than is a d⁴ configuration.

The dⁿ configuration is, therefore, more appropriately determined by the expression:³⁵

$$n = \text{number of valence electrons in neutral atom} - \text{valence} \quad (2)$$

The discrepancy with the assignment of the dⁿ configuration

(34) Jean, Y. *Molecular Orbitals of Transition Metal Complexes*; Oxford University Press: New York 2005; pp 12, 31.

(35) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127–148.

(36) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 299, 301.

(37) In this regard, it is pertinent to note that π and δ back-bonding interactions are not traditionally considered to change the dⁿ configuration, presumably because these are not the sole component of the metal–ligand bond. In the case of a M–BR₃ bond, however, the “back-bonding” interaction is of σ symmetry and is the *only* component. Thus, it is essential to consider this interaction in evaluating the dⁿ configuration.

(38) (a) *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York 1994; Vol. 2, p 961. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005; p 43. (c) Mingos, D. M. P. *Essential Trends in Inorganic Chemistry*; Oxford University Press: New York, 1998; p 299.

(39) (a) Sidgwick, N. V. *The Electronic Theory of Valency*; The Clarendon Press: Oxford, 1927. (b) Parkin, G. *J. Chem. Educ.* **2006**, in press.

(40) Examples of Mo(I) complexes include [(η⁶-C₆H₆)₂Mo]⁺, (dppe)₂Mo–(N₂)Cl, and CpMo(η⁶-C₆H₆). See: Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th Ed.; Wiley: New York, 1999; p 921.

(41) Elschenbroich, Ch.; Salzer, A. *Organometallics*; 2nd ed.; VCH: New York, 1992; p 358.

(42) For specific examples, see: (a) Andréa, R. R.; Terpstra, A.; Oskam, A.; Bruin, P.; Teuben, J. H. *J. Organomet. Chem.* **1986**, *307*, 307–317. (b) Gourier, D.; Samuel, E. *Inorg. Chem.* **1988**, *27*, 3018–3024. (c) Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **2004**, *248*, 273–278.

(43) In addition to the monocation, the cycloheptatrienyl ligand has also been considered to be an anion, [C₇H₇][–], for oxidation number assignments,^{a,b} but since the monoanion is not closed-shell, it is not particularly appropriate for the determination of oxidation numbers. The trianion [C₇H₇]^{3–} is a closed-shell species and has also been proposed for the assignment of oxidation numbers.^c However, the oxidation number should be determined by assigning the charge which is associated with the ligand in its *most stable* uncoordinated form,^d and on this basis, the trianion [C₇H₇]^{3–} should not be used for oxidation number assignments (although it is appropriate for the assignment of valence). (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 26. (b) Reference 38b, p 150. (c) Janiak, C. Klapötke, T. M.; Hans-Jürgen Meyer, H. J.; Reidel, E. *Moderne Anorganische Chemie*; Gruyter: Berlin, 2003. (d) Reference 41, p 309.

(44) (a) van Oven H. O.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1970**, *23*, 159–163. (b) Zeinstra, J. D.; de Boer, J. L. *J. Organomet. Chem.* **1973**, *54*, 207–211.

(45) Davies, C. E.; Gardiner, I. M.; Green, J. C.; Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 669–683.

(46) (a) Menconi, G.; Kaltsoyannis, N. *Organometallics* **2005**, *24*, 1189–1197. (b) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1995**, 3727–3730. (c) Green, J. C.; Green, M. L. H.; Kaltsoyannis, N.; Mountford, P.; Scott, P.; Simpson, S. J. *Organometallics* **1992**, *11*, 3353–3361. (d) Green, J. C.; Kaltsoyannis, N.; Sze, K. H.; MacDonald, M. J. *Am. Chem. Soc.* **1994**, *116*, 1994–2004. (e) Tamm, M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Schmid, R. *Organometallics* **2005**, *24*, 3163–3171.

(47) Green, M. L. H.; Ng, D. K. P. *Chem. Rev.* **1995**, *95*, 439–473.

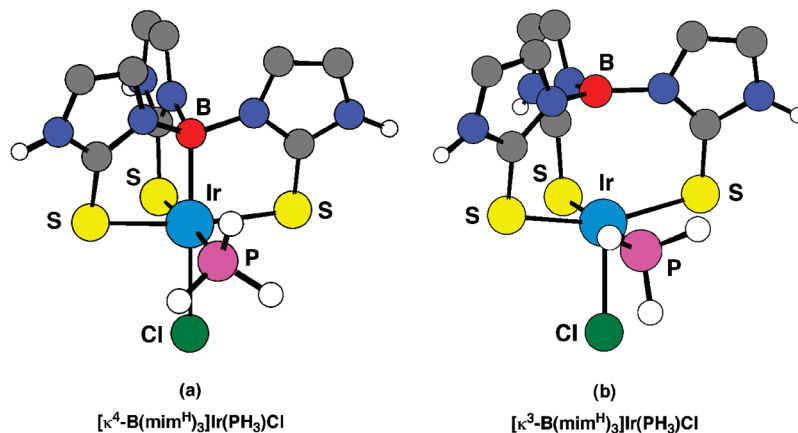


Figure 8. Geometry-optimized structures of $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$ and $[\kappa^3\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$, with the latter constrained to having a planar geometry and a $\text{B}\cdots\text{Ir}$ separation of 3.0 Å.

for $\{\text{[B(mim}^{\text{R}})_3]\text{M}\}$ derivatives is, therefore, a result of the fact that, although the $\text{[B(mim}^{\text{R}})_3]$ ligand may be considered to be neutral in its closed-shell form,^{48,49} coordination of the boron to a metal requires the metal to provide two electrons and thereby reduces the d^n configuration by two units.

To address the nature of the bonding in more detail, and thereby establish that the use of the valence provides a better method of evaluating the electronic nature of a molecule, we have performed DFT calculations on the simplified counterpart $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$. The geometry-optimized structure of $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$ is illustrated in Figure 8a, and a simplified molecular orbital diagram based on Fenske–Hall calculations is presented in Figure 9. The most important aspect of the calculation is that it clearly indicates that the metal center has a d^6 configuration and *not* a d^8 configuration. Specifically, with respect to the metal-based

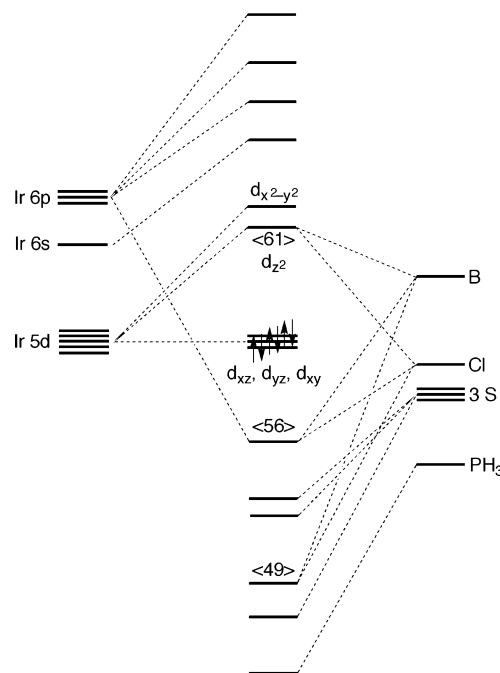


Figure 9. Qualitative molecular orbital diagram for $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$.

d orbitals, there are only 6 electrons housed in formally nonbonding orbitals, i.e., the d_{xy} , d_{xz} , and d_{yz} orbitals of the “ t_{2g} ” set in octahedral symmetry.⁵⁰ All other electrons involved in the $\text{[B(mim}^{\text{H}})_3]\text{—Ir}$ interaction are located in bonding orbitals. The molecular orbital analysis, therefore, clearly indicates that the d^n configuration predicted by consideration of the valence (eq 2) is more appropriate than that derived by consideration of the oxidation number (eq 1). In support of the proposed d^6 configuration for $[\kappa^3\text{-B,S,S-B(mim}^{\text{Bu}^t})_3]\text{Ir(CO)(PPh}_3\text{)H}$, $\nu(\text{CO})$ (1989 cm^{-1}) is distinctly greater than those of monovalent d^8 iridium complexes such as $\text{Ir(PR}_3)_2(\text{CO)Cl}$ ($1929\text{—}1961\text{ cm}^{-1}$),⁵¹ an observation that is consistent with reduced back-bonding for the higher-valent complex. For further comparison, $\nu(\text{CO})$ for $[\kappa^3\text{-B,S,S-$

(48) The term “closed shell” refers to molecules for which all occupied orbitals are fully occupied, i.e., there are no unpaired electrons and there are no partially occupied degenerate orbitals. It is important to note that a closed-shell configuration does *not* require an inert gas configuration. Thus, the neutral $\text{B(im}^{\text{R}})_3$ molecule is a closed-shell molecule. See, for example: (a) Kutzelnigg, W.; Smith, V. H., Jr. *Int. J. Quantum Chem.* **1968**, *2*, 531–552. (b) Daudel, R.; Kozmutza, C.; Goddard, J. D.; Csizmadia, I. G. *J. Mol. Struct.* **1978**, *50*, 363–369.

(49) It is pertinent to comment on the charge assigned to a BR_3 ligand for the purpose of oxidation number assignments. Specifically, boron has a Pauling electronegativity (2.0) that is intermediate between the values for many transition metals, e.g., Co (1.8) and Rh (2.2),^a and thus, the charge assigned to a BR_3 ligand (0 or -2) could, in principle, vary for two otherwise closely related compounds. For this reason, it is pertinent to consider other factors to establish which charge should be assigned to a BR_3 ligand. Two different criteria that are used to determine the charge are (i) the charge assigned to the ligand should be such that the donor atom has an octet configuration^b and (ii) the charge assigned to the ligand should correspond to the ligand in its *stable* closed-shell configuration,^c a criterion that is in keeping with the notion that the oxidation number of an atom was originally derived by removing the ligand in the form that it is *commonly encountered* in an uncoordinated state (e.g., Cl^- , NH_3 , and OH_2). The former criterion would assign a charge of -2 to the ligand, whereas the latter would assign a charge of zero. Of these, a charge of zero is preferred for oxidation number assignments because neutral BR_3 derivatives are ubiquitous, whereas the dianion $[\text{BR}_3]^{2-}$ is an unusual example of a compound with boron in the $+1$ oxidation state and is unknown. For this reason, the $\text{[B(mim}^{\text{R}})_3]$ ligand has been assigned a charge of zero in the assignment of oxidation numbers (for example, see ref 14). (a) Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 93. (b) Reference 34, p 13. (c) Reference 43d.

(50) Using Green’s “Covalent Bond Classification”, the complexes are classified as trivalent ML_3X_3 . See ref 35.

(51) Shin, J. H.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Inorg. Chem.* **2001**, *40*, 5626–5635.

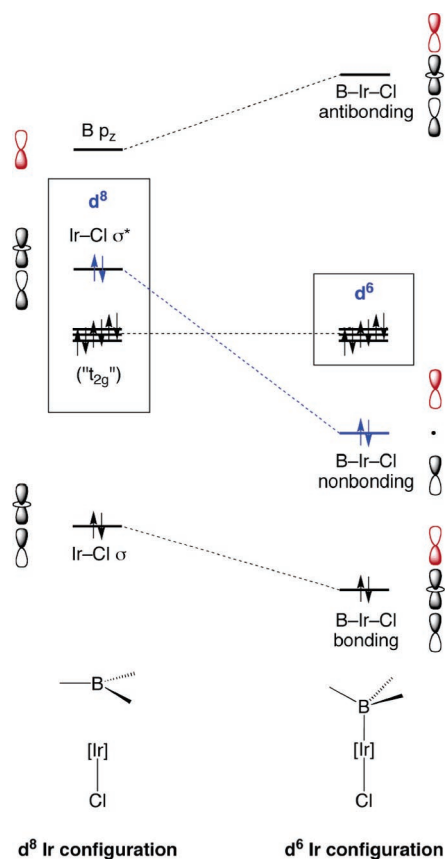


Figure 10. Orbital correlation diagram for coordination of a BR_3 moiety to Ir in a position that is trans to a Cl ligand.

$B(\text{mim}^{\text{Bu}})_3\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}$ is in the range observed for trivalent $\text{Ir}(\text{PR}_3)_2(\text{CO})(\text{X})(\text{Bcat})\text{H}$ derivatives ($1984\text{--}2118\text{ cm}^{-1}$).¹⁶

It is instructive to consider in more detail how coordination of the boron to the d^8 iridium center causes the iridium to adopt a d^6 configuration. For this purpose, it is useful to consider the molecular orbital diagram of a hypothetical $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$ species in which the boron does not coordinate to the iridium center (Figure 8b). Examination of Figure 10 illustrates that the HOMO of such a species possesses d_z^2 character and is the σ -antibonding component of the Ir–Cl bond (the $d_{x^2-y^2}$ orbital is responsible for binding the PH_3 and three sulfur ligands and is at higher energy); coupled with the six electrons that occupy the d_{xz} , d_{yz} , and d_{xy} orbitals, the iridium is assigned a d^8 configuration.

Upon approaching the iridium center, the empty boron p_z orbital interacts with the iridium d_z^2 -derived HOMO. However, since the d_z^2 orbital also interacts with the Cl p_z orbital, a classic 3-center-4-electron interaction ensues, thereby resulting in bonding, nonbonding, and antibonding B–Ir–Cl orbitals (Figure 11). The outcome of this interaction is, therefore, the transfer of a pair of electrons from a metal-based d_z^2 orbital to a ligand-based orbital.⁵² As a result, the “ d_z^2 ” B–Ir–Cl σ -antibonding orbital of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$ is unoccupied and the iridium center possesses a d^6 configuration.

(52) While this ligand-based orbital is nonbonding with respect to d_z^2 , it is stabilized by interaction with the metal p_z orbital and thus may be regarded as a metal–ligand bonding orbital.

An illustration of the manner in which the orbitals involved in the 3-center-4-electron interaction transform upon approach of the boron is provided by comparison of the molecular orbitals of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$ with those of the geometry-optimized structure of $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]$ in which the $[\text{B}(\text{mim}^{\text{H}})_3]$ fragment is constrained to having a planar geometry at boron with an $\text{Ir}\cdots\text{B}$ distance of 3 \AA (Figure 8). The Ir–Cl σ -bonding interaction in $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]$ is largely composed of overlap between the Ir d_z^2 and Cl p_z orbital, as illustrated by MO (52) in Figure 11,⁵³ while MO (60) corresponds largely to the Ir–Cl σ -antibonding orbital. However, it is evident that boron p_z character is already mixing into this orbital and that the Ir–B interaction is starting to be developed at an $\text{Ir}\cdots\text{B}$ separation of 3.0 \AA ; as a consequence, MO (61) does not correspond to a pure boron p_z orbital but has a significant amount of Ir d_z^2 character. Despite this mixing, the structure does, nevertheless, provide a useful means to indicate how the orbitals transform upon coordination of the boron. Comparison with the three corresponding orbitals of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$ indicates that the most dramatic change is observed for the Ir–Cl σ -bonding orbital (52) of $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]$, which takes on substantial Ir–B bonding character in MO (49) of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$. A distinct change is also observed for the Ir–Cl σ -antibonding MO (60) of $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]$, which becomes the B–Cl ligand-based MO (56) of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$, with significant Cl p_z character and negligible iridium d_z^2 character. Finally, the LUMO (61) of $[\kappa^3\text{-S,S,S-B}(\text{mim}^{\text{H}})_3]$, which has largely boron p_z character, becomes LUMO (61) of $[\kappa^4\text{-B}(\text{mim}^{\text{H}})_3]\text{Ir}(\text{PH}_3)\text{Cl}$ with mainly iridium d_z^2 character.

The essential feature of a general M–B bonding interaction is illustrated by the simplified molecular orbital diagram shown in Figure 12, which reduces the discussion to the situation for a 2-center interaction. Thus, the interaction between a filled metal-based orbital and the empty orbital on boron results in a filled M–B bonding orbital and an unoccupied M–B antibonding orbital. Since the M–B bonding orbital is occupied by a pair of electrons that were originally on the metal, a metal center that originally possessed a d^n configuration becomes d^{n-2} upon coordination to boron.

The transition from a d^n to d^{n-2} configuration upon coordination of a BR_3 fragment bears a close analogy to the change resulting from the interaction of a metal center with another Lewis acid, namely H^+ . Thus, it is widely recognized that protonation of a d^n metal center results in the formation of a metal hydride in which the metal center has a d^{n-2} configuration.^{35,54} As with the formation of a $\text{M}\rightarrow\text{BR}_3$ bond, protonation of a d^n metal center results in a d^{n-2} configuration because the metal–hydride bond requires a pair of electrons and the only source of these electrons is the metal center. The use of oxidation numbers to determine the value of d^n ,

(53) In addition to MO (52), MO (53) also has Ir–Cl σ -bonding character. MO (52) and MO (53) differ due to interaction of the Ir–Cl σ -bonding orbital with an in-phase and out-of-phase combination of sulfur p orbitals in the $[\text{IrS}_3\text{P}]$ equatorial plane.

(54) For examples of the interaction of H^+ with d^8 metal centers, see: Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406–413.

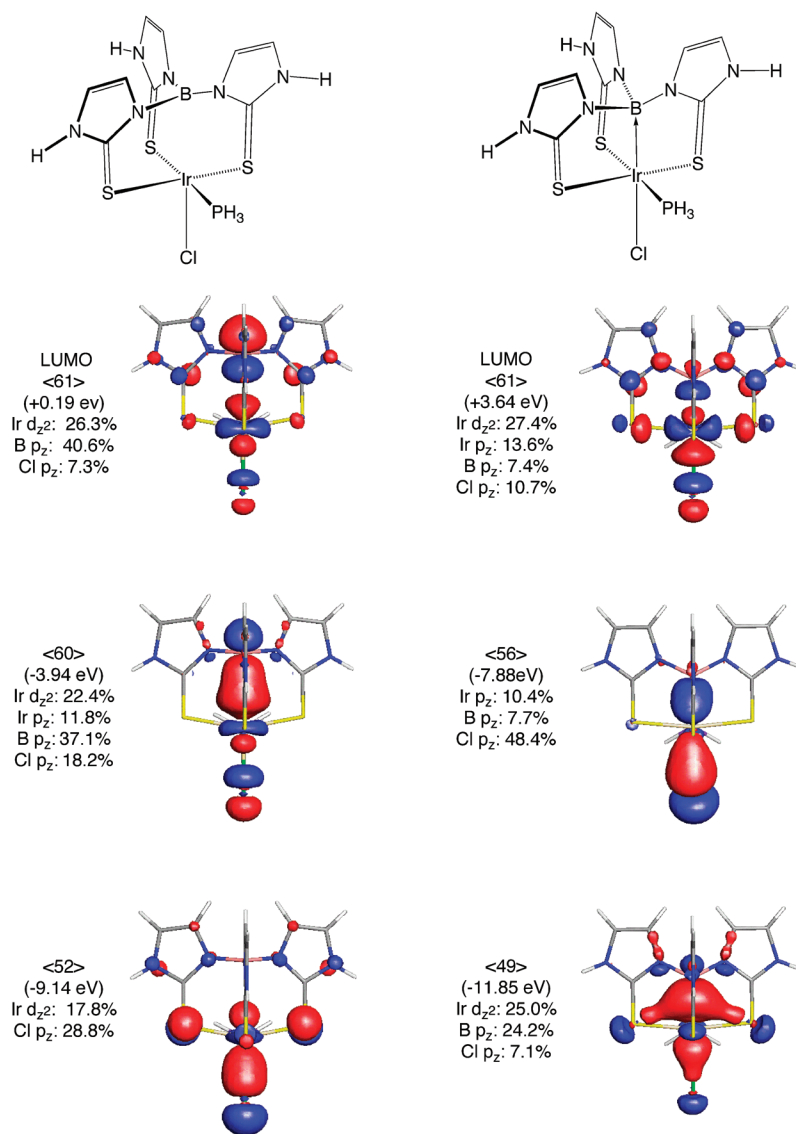


Figure 11. Molecular orbitals corresponding to the 3-center-4-electron interactions in $[\kappa^3\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$ (left) and $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$ (right).

therefore, fails when there exists a metal-to-ligand $\text{M}\rightarrow\text{Z}$ dative bond. As such, the failure to predict the correct d^n configuration provides a further illustration of how oxidation numbers may give a misleading description of the bonding situation in molecules.

In view of the above analysis of the $\text{M}\rightarrow\text{BR}_3$ interaction, it is evident that the proposed d^n configuration in other $\{[\text{B(mim}^{\text{R}})_3]\text{M}\}$ derivatives should be re-evaluated. For example, $[\kappa^4\text{-B(mim}^{\text{Me}})_3]\text{Pt(PPh}_3\text{)}$, which has been described as the first five-coordinate zerovalent d^{10} platinum complex,¹⁴ is more appropriately described as possessing a divalent d^8 Pt center.

Finally, it has been noted that the term “oxidative addition” is not appropriate for the reaction of a metal center, M, with a B–H bond of a $[\text{R}_3\text{B–H}]^-$ derivative because the oxidation number of M does not change in forming the product $[\text{M(BR}_3\text{)H}]^-$.¹³ However, while it is certainly true that there is no change in oxidation number of the metal if BR_3 is viewed as a neutral ligand, the reaction of a metal center with a B–H bond of $[\text{R}_3\text{B–H}]^-$ does result in an increase

in valence and a corresponding decrease in the d^n count of the metal. In essence, therefore, the reaction is “oxidative” in nature on the basis that the metal must use two of its electrons to achieve the cleavage.

Conclusions

In summary, a series of iridium and rhodium complexes that feature $\text{M}\rightarrow\text{B}$ dative bonds, namely $[\kappa^3\text{-B,S,S-B(mim}^{\text{R}})_3]\text{-Ir(CO)(PPh}_3\text{)H}$ ($\text{R} = \text{Bu}^t, \text{Ph}$) and $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{M(PPh}_3\text{)Cl}$ ($\text{M} = \text{Rh, Ir}$), has been synthesized and structurally characterized by X-ray diffraction. Details of the $\text{M}\rightarrow\text{B}$ interaction in these complexes have been elucidated by molecular orbital analyses which indicate that the iridium centers possess d^6 configurations. The d^6 configuration is in accord with the value predicted by using a method that employs the valence to determine d^n but is not in accord with the d^8 configuration that is predicted by using the oxidation number. Thus, even though $\text{B(mim}^{\text{R}})_3$ may be regarded as a neutral closed-shell ligand, coordination to a d^n transition metal via the boron results in the formation of

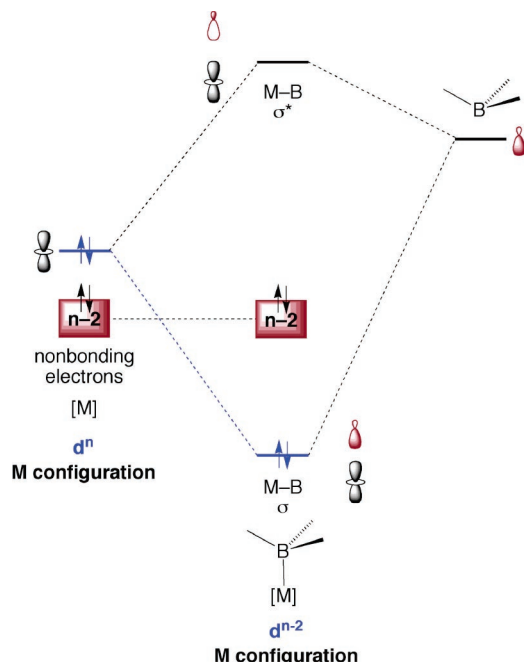


Figure 12. Generic molecular orbital diagram for coordination of a BR_3 moiety to a d^n transition metal center. The formation of the $M-B$ bond requires a pair of electrons that must be supplied by the metal center, and so the metal center in the adduct adopts a d^{n-2} configuration.

a complex in which the metal center possesses a d^{n-2} configuration because the metal must supply both electrons for the $M-B$ bond. As such, the present study emphasizes that the use of oxidation numbers to determine the d^n configuration fails when there is a metal-to-ligand $M \rightarrow Z$ dative bond.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques under a nitrogen or argon atmosphere. Solvents were purified and degassed by standard procedures. 1H and ^{13}C NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_5H and 1.94 for CD_2HCN). ^{31}P NMR spectra were referenced relative to 85% H_3PO_4 ($\delta = 0$) using $P(OMe)_3$ in C_6D_6 as an external reference ($\delta = 141.0$). Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometers and are reported in wavenumbers. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB) and a *m*-nitrobenzyl alcohol matrix. $(COD)RhCl(PPh_3)_5$ ⁵⁵ and $(COD)Ir(PPh_3)_3Cl$ ⁵⁶ were obtained by the literature methods.

Synthesis of $[\kappa^3-B,S,S,S-B(mim^{Bu^i})_3]Ir(CO)(PPh_3)H$. A mixture of $Ir(PPh_3)_2(CO)Cl$ (100 mg, 0.128 mmol) and $[Tm^{Bu^i}]K$ (132 mg, 0.256 mmol) was treated with benzene (5 mL) and stirred overnight at room temperature. Over this period, the yellow solution became colorless and a white deposit formed. The mixture was filtered, and the filtrate was concentrated to approximately half the initial volume. Pentane (5 mL) was added to induce precipitation, and

the volume of the sample was further reduced to deposit more material. The mixture was filtered, and the solid was washed with pentane (5 mL) and dried in vacuo giving $[\kappa^3-B,S,S,S-B(mim^{Bu^i})_3]Ir(CO)(PPh_3)H$ as a white powder (32 mg, 25%). Anal. Calcd for $C_{40}H_{49}BIrN_6OPS_3$: C, 50.0%; H, 5.1%; N, 8.8%. Found: C, 50.4%; H, 5.3%; N, 9.5%. IR Data (KBr pellet, cm^{-1}): 2963 (w), 2923 (m), 2853 (w), 2100 (w), 1989 (s), 1479 (w), 1435 (m), 1388 (s), 1342 (m), 1254 (w), 1188 (s), 1158 (s), 1094 (s), 1027 (m), 821 (w), 800 (w), 746 (w), 695 (s), 516 (m). 1H NMR data (C_6D_6 , ppm): -10.90 [s, Ir-H], 1.14 [s, 9H of Bu^i], 1.39 [s, 9H of Bu^i], 1.83 [s, 9H of Bu^i], 6.47 [m, 1H of imidazole ring], 6.64 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], 6.66 [m, 1H of imidazole ring], 6.67 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], 6.70 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], 6.73 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], 6.95 [m, 3H of PPh_3], 7.05 [m, 6H of PPh_3], 7.81 [m, 6H of PPh_3]. ^{31}P NMR (C_6D_6): 5.9 ppm [s]. Mass spectrum: $m/z = 959.7 \{M - 1\}^+$.

Synthesis of $[\kappa^3-B,S,S,S-B(mim^{Ph})_3]Ir(CO)(PPh_3)H$. A mixture of $Ir(PPh_3)_2(CO)Cl$ (19 mg, 0.024 mmol) and $[Tm^{Ph}]Li$ (17 mg, 0.031 mmol) was treated with benzene (2 mL) and occasionally shaken at room temperature over a period of 12 h. Over this period, the yellow solution became colorless and a pale brown deposit formed. The mixture was filtered, and pentane (0.5 mL) was added to induce precipitation. The volume of the sample was further reduced to deposit more material. The mixture was filtered, and the solid was dried in vacuo giving $[\kappa^3-B,S,S,S-B(mim^{Ph})_3]Ir(CO)(PPh_3)H$ as a white powder (5 mg, 20%). 1H NMR data (C_6D_6 , ppm): -10.8 [broad s, 1H of Ir-H], 6.46 [m, 1H of imidazole ring A], 6.56 [m, 1H of imidazole ring B], 6.61 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring C], $6.73-6.75$ [m, 3 aryl H and 1H of imidazole ring B], 6.77 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring A], 6.80 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring C], 6.89 [m, 6 aryl H], $6.90-7.15$ [m, 9 aryl H], $7.02-7.06$ [m, 2 aryl H], $7.25-7.28$ [m, 2 aryl H], $7.72-7.77$ [m, 6 aryl H], $7.81-7.84$ [m, 2 aryl H]. ^{31}P NMR data (C_6D_6 , ppm): 4.56 [s, PPh_3].

Synthesis of $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)Cl$. A mixture of $(COD)Rh(PPh_3)Cl$ (15 mg, 0.03 mmol) and $[Tm^{Bu^i}]K$ (15 mg, 0.03 mmol) was treated with benzene (3 mL) to give a solution which deposited yellow-orange crystals over a period of 3 days. The crystals were isolated by decanting the solution and extracted into MeCN (2 mL). The extract was allowed to stand at room temperature, thereby depositing $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)Cl$ as yellow-orange needles⁵⁷ which were isolated by decanting and dried in vacuo (15 mg, 58%). Anal. Calcd for $C_{39}H_{48}BClRhN_6PS_3$: C, 53.4%; H, 5.5%; N, 9.6%. Found: C, 52.4%; H, 5.2%; N, 9.2%. 1H NMR data (CD_3CN , ppm): 1.39 [s, 18H of 2 Bu^i], 1.66 [s, 9H of Bu^i], 6.31 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], 6.47 [br, 2H of imidazole ring], 6.86 [d, $J_{H-H} = 2$ Hz, 2H of imidazole ring], 6.94 [d, $J_{H-H} = 2$ Hz, 1H of imidazole ring], $7.17-7.80$ [m, 15 H of PPh_3]. ^{31}P NMR data (CD_3CN , ppm): 27.5 [d, $^1J_{Rh-P} = 121$ Hz, Rh- PPh_3]. Mass spectrum: $m/z = 876.3 \{M - 1\}^+$.

Generation of $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)H$. The hydride complex $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)H$ may be observed via 1H NMR spectroscopy as an intermediate in the reaction of $(COD)Rh(PPh_3)Cl$ with $[Tm^{Bu^i}]K$. In addition, $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)H$ may be generated by treating $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)Cl$ with $LiBH_4$. A solution of $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)Cl$ (5 mg) in CD_3CN (0.7 mL) was treated with $LiBH_4$ (3 mg). The reaction was monitored by 1H NMR spectroscopy and demonstrated the formation of $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)H$.

(55) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735–4741.

(56) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395–403.

(57) Note that X-ray diffraction indicates that the needles obtained prior to desolvation are of composition $[\kappa^4-B(mim^{Bu^i})_3]Rh(PPh_3)Cl \cdot 2MeCN \cdot 2C_6H_6$; as such, it is important not to dry the crystals and remove all traces of benzene before crystallizing from acetonitrile.

Table 1. Crystal, Intensity Collection, and Refinement Data

	$[\kappa^3\text{-B,S,S-B(mim}^{\text{Bu}})_3\text{-Ir(CO)(PPh}_3\text{)H}]$	$[\kappa^3\text{-B,S,S-B(mim}^{\text{Ph}})_3\text{-Ir(CO)(PPh}_3\text{)H}]$	$[\kappa^4\text{-B(mim}^{\text{Bu}})_3\text{-Ir(PPh}_3\text{)Cl}]$	$[\kappa^4\text{-B(mim}^{\text{Bu}})_3\text{-Rh(PPh}_3\text{)Cl}]$
lattice	triclinic	triclinic	triclinic	monoclinic
formula	$\text{C}_{44}\text{H}_{55}\text{BN}_8\text{OPS}_3\text{Ir}$	$\text{C}_{48}\text{H}_{40}\text{BN}_7\text{OPS}_3\text{Ir}$	$\text{C}_{53}\text{H}_{76}\text{BClN}_6\text{O}_{3.5}\text{PS}_3\text{Ir}$	$\text{C}_{55}\text{H}_{66}\text{BClN}_8\text{PS}_3\text{Rh}$
fw	1042.12	1061.03	1218.81	1115.5
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$
$a/\text{\AA}$	11.247(1)	12.243(1)	14.527(4)	9.765(1)
$b/\text{\AA}$	14.301(1)	14.218(8)	17.832(5)	19.775(1)
$c/\text{\AA}$	16.423(1)	16.425(1)	24.242(7)	14.192(1)
$\alpha/^\circ$	99.379(1)	95.879(1)	89.748(6)	90
$\beta/^\circ$	97.000(1)	110.785(1)	78.524(4)	92.316(2)
$\gamma/^\circ$	103.366(1)	113.132(1)	85.921(5)	90
$V/\text{\AA}^3$	2500.4(2)	2358.9(2)	6138(3)	2738.4(3)
Z	2	2	4	2
temp (K)	243	243	243	243
radiation (λ , \AA)	0.71073	0.71073	0.71073	0.71073
ρ (calcd), g cm^{-3}	1.384	1.494	1.319	1.353
μ (Mo K α), mm^{-1}	2.867	3.040	2.39	0.549
θ max, deg	28.3	28.3	23.3	28.3
no. of data	10 918	15 998	17 189	19 261
no. of params	520	556	937	344
R1	0.0295	0.0227	0.0694	0.0343
wR2	0.0815	0.0633	0.144	0.0613
GOF	1.079	1.035	1.067	1.033

Rh(PPh₃)H after 24 h at room temperature. ¹H NMR data (CD₃CN, ppm): −16.2 [dd, $J_{\text{Rh-H}} = 17$ Hz, $J_{\text{P-H}} = 6$ Hz, Rh–H], 1.56 [s, 18H of 2 Bu^t], 1.68 [s, 9H of Bu^t], 6.70 [d, $J_{\text{H-H}} = 2$ Hz, 1H of imidazole ring], 7.02 [br, 1H of imidazole ring], 7.06 [br, 2H of imidazole ring], 7.21 [d, $J_{\text{H-H}} = 2$ Hz, 1H of imidazole ring], 7.32–7.38 and 7.55–7.61 [m, 15 H, PPh₃].

Synthesis of $[\kappa^4\text{-B(mim}^{\text{Bu}})_3\text{]Ir(PPh}_3\text{)Cl}$. A mixture of (COD)-IrCl(PPh₃) (34 mg, 0.06 mmol) and [Tm^{Bu}]K (30 mg, 0.06 mmol) was treated with benzene (1 mL) and allowed to stand at room temperature for 1 h. Acetonitrile (70 μL) was added to the solution and stirred, resulting in the deposition of small yellow-orange crystals after standing at room temperature for a period of 2 days. The crystals were isolated by filtration and extracted into THF (2 mL). The extract was allowed to stand at room temperature, thereby depositing $[\kappa^4\text{-B(mim}^{\text{Bu}})_3\text{]Ir(PPh}_3\text{)Cl}$ as large yellow-orange crystals, which were isolated by decanting and dried in vacuo (ca. 10 mg, 18%). ¹H NMR data (CD₃CN, ppm): 1.39 [s, 18H of 2 Bu^t], 1.66 [s, 9H of Bu^t], 6.30 [d, $J_{\text{H-H}} = 2$ Hz, 1H of imidazole ring], 6.46 [d, $J_{\text{H-H}} = 2$ Hz, 2H of imidazole ring], 6.95 [d, $J_{\text{H-H}} = 2$ Hz, 2H of imidazole ring], 6.99 [d, $J_{\text{H-H}} = 2$ Hz, 1H of imidazole ring], 7.12–7.39 [m, Rh–PPh₃]. Mass spectrum: $m/z = 966.5$ $\{M - 1\}^+$.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection, and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10).⁵⁸

Computational Details. All calculations were carried out using DFT as implemented in the Jaguar 5.0 and 6.0 suite of ab initio quantum chemistry programs.⁵⁹ Geometry optimizations were performed with the B3LYP functional and the 6-31G** (C, H, N, B, O, S, P) and LACVP (Rh, Ir) basis sets. Molecular orbital analyses were performed with the aid of JIMP,⁶⁰ which employs Fenske–Hall calculations⁶¹ and visualization using MOPLLOT.⁶²

Acknowledgment. We thank the National Science Foundation (CHE-03-50498) for support of this research.

Supporting Information Available: Cartesian coordinates for geometry optimized structures (5 pages); crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC051975T

- (58) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1981.
- (59) *Jaguar 6.0*; Schrödinger, Inc.: Portland, 2005.
- (60) Manson, J.; Webster, C. E.; Hall, M. B. *JIMP Development Version 1.1.5 (built for Windows PC and Redhat Linux 7.3)*; Department of Chemistry, Texas A&M University: College Station, TX, (<http://www.chem.tamu.edu/jimp/>), 2005.
- (61) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.
- (62) Lichtenberger, D. L. *MOPLLOT, Version 2.0*; Department of Chemistry, University of Arizona: Tucson, 1993.