Palladium complexes with Pd→B dative bonds: Analysis of the bonding in the palladaboratrane compound [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$)†

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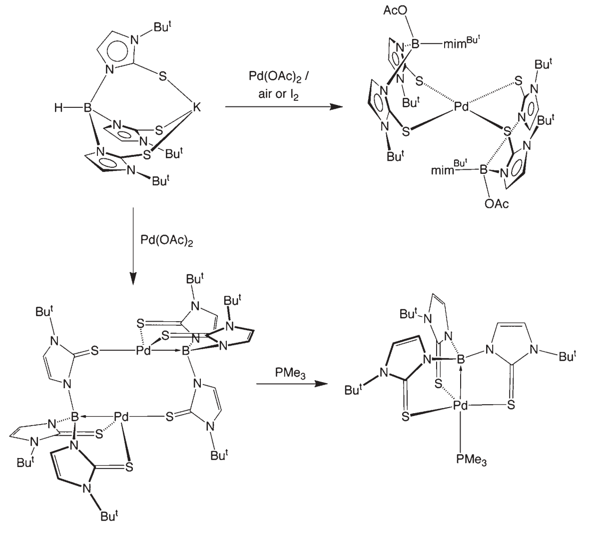
Received (in Berkeley, CA, USA) 14th August 2006, Accepted 15th September 2006
First published as an Advance Article on the web 12th October 2006
DOI: 10.1039/b611654j

The dinuclear complex {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$, which features a Pd→B dative bond, may be obtained by the reaction of [Tm$^{\mathrm{Bu^t}}$]K with Pd(OAc)$_2$; treatment of {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ with PMe$_3$ affords the mononuclear boratrane derivative [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$), for which a molecular orbital analysis indicates that the palladium center possesses a d^8 configuration.

Tris(2-mercapto-1-R-imidazolyl)hydroborato ligands ([HB(mim^R)$_3$] = [Tm^R]),[1] are emerging as a popular class of ligands with diverse applications. A particularly recent development is concerned with reactions that involve cleavage of the B–H bond to yield compounds in which the [B(mim^R)$_3$] fragment is attached to the metal *via* a metal-to-ligand M→B dative bond.[2] The first example of this transformation was reported in 1999 with Hill *et al.*'s synthesis of [κ^4-B(mim^{Me})$_3$]Ru(CO)(PPh$_3$),[3] and is noteworthy because it provided structural characterization of a transition metal compound with a metal-to-ligand M→B dative bond.[4,5] In addition to ruthenium, a variety of {M[B(mim^R)$_3$]} complexes have subsequently been obtained for other transition metals, including Fe, Os, Co, Rh, Ir and Pt.[6,7] Palladium, however, is a transition metal for which a {M[B(mim^R)$_3$]} derivative with a Pd→B dative bond has yet to be isolated and structurally characterized. Compounds that feature Pd→B dative bonds, therefore, represent interesting synthetic targets. Two such complexes, namely mononuclear [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) and dinuclear {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$, are reported here. In addition, [κ^2-AcOB(mim$^{\mathrm{Bu^t}}$)$_3$]$_2$Pd, a complex that contains a novel tris(2-mercaptoimidazolyl)borate ligand that features acetate substitution on boron, is also described.

Access to a complex that contains a Pd→B dative bond is readily achieved by the reaction of [Tm$^{\mathrm{Bu^t}}$]K with Pd(OAc)$_2$. Thus, as illustrated in Scheme 1, treatment of [Tm$^{\mathrm{Bu^t}}$]K with Pd(OAc)$_2$ under an inert atmosphere yields {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$, which has been structurally characterized by X-ray diffraction (Fig. 1),[8] thereby providing definitive evidence for the existence of the Pd→B bond.[9] Also of note, the bridging [B(mim$^{\mathrm{Bu^t}}$)$_3$] ligand adopts a κ^3-S$_2$B coordination mode to one metal and a κ^1-S coordination mode to the other. While complexes with tris(2-mercapto-1-R-imidazolyl)borane ligands are common,[3,6,7b,d] the coordination motif observed for {[μ-κ,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ represents a new bonding mode for this class of ligand.[10]



Scheme 1

{[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ is fluxional on the NMR timescale at room temperature, but a spectrum that exhibits three chemically inequivalent mim$^{\mathrm{Bu^t}}$ groups may be observed upon cooling to 228 K. The κ^1-S bridging interaction in {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ is readily cleaved upon addition of PMe$_3$ to give the mononuclear palladaboratrane derivative [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$), as illustrated in Scheme 1. The molecular structure of [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) has been determined by X-ray diffraction (Fig. 2),[8] thereby demonstrating that the palladium has a trigonal bipyramidal geometry, in which the [B(mim$^{\mathrm{Bu^t}}$)$_3$] ligand coordinates in a κ^4-S$_3$B manner with the boratrane motif.

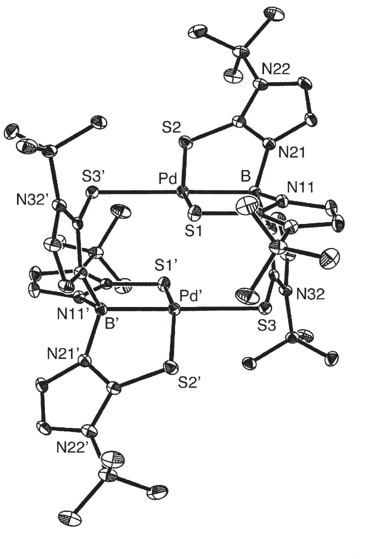


Fig. 1 Molecular structure of {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$.

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† Electronic supplementary information (ESI) available: Experimental details and crystallographic data. See DOI: 10.1039/b611654j

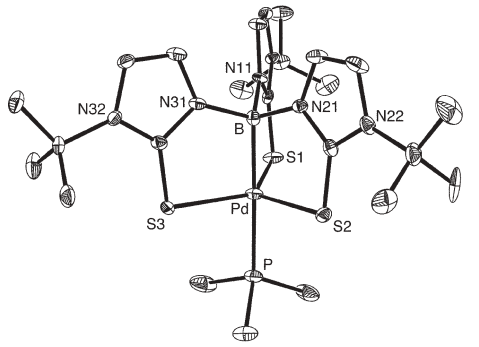

Fig. 2 Molecular structure of [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$).

The most important aspect of both {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ and [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) is concerned with the nature of the Pd→B interaction, because metals are normally the electron pair *acceptor* component of a dative bond rather than the electron pair *donor*. Decisive evidence that the Pd→B interactions in {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ and [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) are significant is provided by the fact that the Pd–B bond lengths are close to the shortest values listed in the Cambridge Structural Database.[11] For example, the Pd–B bond lengths of {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ (2.073(4) Å) and [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) (2.050(8) Å) are comparable to those in the boryl compounds Pd(dmpe){B-1,2-(NMe)$_2$CH$_2$CH$_2$}(SnMe$_3$) (2.077(6) Å)[12] and Pd(PMe$_3$)$_2${B-1,2-(NMe)$_2$CH$_2$CH$_2$}Cl (2.006(9) Å and 2.037(9) Å).[13,14] Further evidence in support of a Pd–B interaction is provided by the observation of a distinctive $^2J_{\mathrm{P-B}}$ coupling constant of 116 Hz in both the ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra.

Since the Pd→B interactions are significant, an important issue to consider is the impact of the coordination of boron to the metal center, specifically with respect to the change in d^n configuration. In this regard, the closely related compound [κ^4-B(mim$^{\mathrm{Me}}$)$_3$]Pt(PPh$_3$) has been described as the first five-coordinate zerovalent d^{10} platinum compound, thereby suggesting that the coordination of boron to the platinum has no impact on the valence state or d^n configuration of the metal center.[15] On the other hand, a molecular orbital analysis of [κ^4-B(mim$^{\mathrm{H}}$)$_3$]Ir(PH$_3$)Cl indicates that the complex is appropriately described as possessing an octahedral d^6 iridium center, thereby indicating that coordination of the boron to a metal center reduces the d^n configuration to d^{n-2}.[6c] Adopting the former view of a M→B interaction, the palladium complex [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) would be described as possessing a zerovalent d^{10} Pd center, while the latter view would characterize the molecule as possessing a divalent d^8 Pd center.

In order to evaluate which one of these conflicting views more appropriately describes the bonding in [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$), we performed a molecular orbital analysis, the results of which indicate that the palladium center is more accurately characterized by a d^8 configuration, with only four of the metal-based non-bonding and antibonding orbitals of d-character being occupied (Fig. 3 and Fig. 4). A d^{10} configuration would require occupation of the LUMO, which has d$_{z^2}$ character, and corresponds to the antibonding component of the interaction with the five ligand sigma orbitals. The molecular orbital analysis of [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) is, therefore, in accord with the notion that coordination of a BX$_3$ group to a metal reduces the d^n configuration to d^{n-2} because the metal is required to provide two electrons to form the M→B bond.[2,6c]

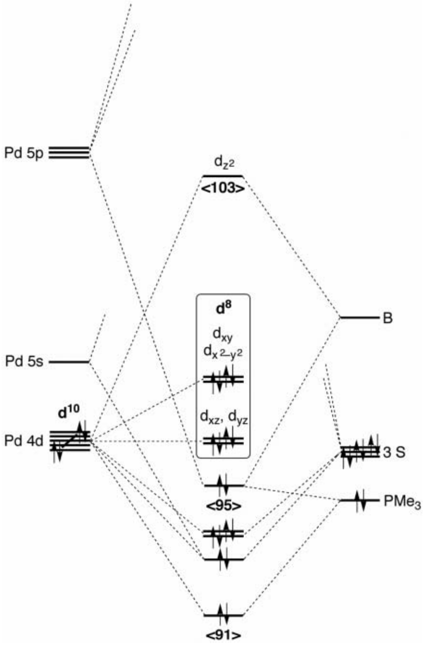

Fig. 3 Molecular orbital diagram for [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$) with idealized C_{3v} symmetry, focusing on σ-interactions.

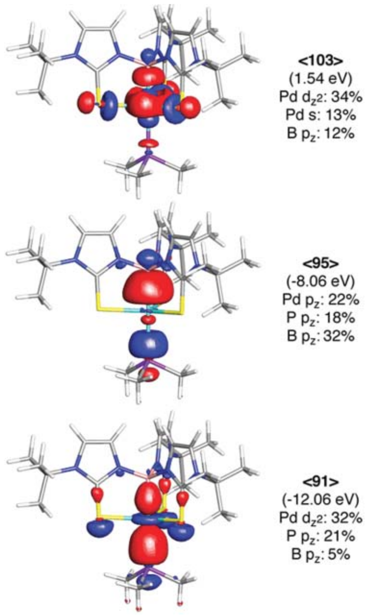

Fig. 4 The molecular orbitals involved in the B–Pd–P interaction for [κ^4-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd(PMe$_3$).

By analogy, {[μ-κ^1,κ^3-B(mim$^{\mathrm{Bu^t}}$)$_3$]Pd}$_2$ is also classified as possessing d^8 Pd centers. Evidence in support of this assignment is provided by the fact that the coordination geometry of palladium in this complex much more closely resembles a distorted square-planar geometry than a tetrahedral geometry (Fig. 1).[16,17] The significance of this observation is that the geometry adopted by four-coordinate palladium and platinum compounds is closely linked to their d^n configuration. Specifically, it is well known that d^{10} metal centers are characterized by a tetrahedral geometry, whereas d^8 metal centers are commonly characterized by a

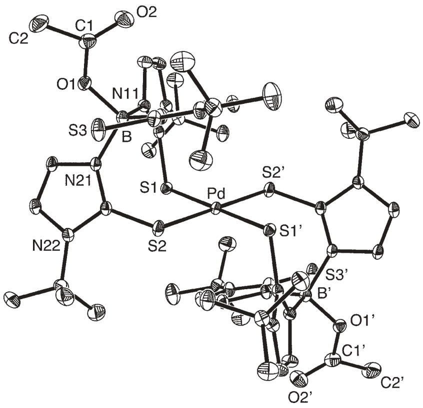

Fig. 5 Molecular structure of $[\kappa^2\text{-AcOB}(\text{mim}^{\text{Bu}^t})_3]_2\text{Pd}$ (triclinic form).

square-planar geometry, as illustrated by d^{10} $M(PR_3)_4$ and d^8 $M(PR_3)_2Cl_2$, respectively.[18,19] The distorted square-planar geometry for $\{[\mu\text{-}\kappa^1,\kappa^3\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ is, therefore, also in agreement with the notion of a d^8 configuration at Pd.

While the dimer $\{[\mu\text{-}\kappa^1,\kappa^3\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ is obtained from the reaction of $[\text{Tm}^{\text{Bu}^t}]\text{K}$ with Pd(OAc)_2 when performed in an inert atmosphere, the novel complex $[\kappa^2\text{-AcOB}(\text{mim}^{\text{Bu}^t})_3]_2\text{Pd}$ may be isolated if the reaction is performed in air or in the presence of I_2 (Scheme 1). The molecular structure of $[\kappa^2\text{-AcOB}(\text{mim}^{\text{Bu}^t})_3]_2\text{Pd}$ has been determined by X-ray diffraction (Fig. 5),[8] thereby demonstrating the formation of a unique tris(2-mercaptoimidazolyl) borate ligand which features an acetate substituent on boron. In this regard, related $[\text{XTm}^{\text{Bu}^t}]$ ligands have recently been obtained in an iron system *via* reactions of the ferraboratrane $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Fe(CO)}_2$ with, for example, $[\text{PhC(O)O}]_2$ and CHCl_3, to give $[\text{PhC(O)OTm}^{\text{Bu}^t}]\text{Fe}[\kappa^2\text{-OC(O)Ph}]$ and $[\text{ClTm}^{\text{Bu}^t}]\text{FeCl}$, respectively.[6d,20] On this basis, it is possible that a $\{[\text{B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd(OAc)}\}$ boratrane species plays a role in the formation of $[\kappa^2\text{-AcOB}(\text{mim}^{\text{Bu}^t})_3]_2\text{Pd}$ *via* a metal-centered B–O coupling step, but other mechanisms are certainly feasible.

In summary, $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3)$ and $\{[\mu\text{-}\kappa^1,\kappa^3\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ have been shown by X-ray diffraction to possess Pd→B bonds. Calculations indicate that the palladium center in $[\kappa^4\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3)$ has a d^8 (and not d^{10}) configuration, in accord with the concept that the palladium center must provide a pair of electrons to form the Pd→B bond.[2] Finally, $[\kappa^2\text{-AcOB}(\text{mim}^{\text{Bu}^t})_3]_2\text{Pd}$, which contains an interesting boron-functionalized $[\text{AcOTm}^{\text{Bu}^t}]$ ligand, has been isolated.

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

Notes and references

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

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5 Structurally characterized complexes with M→B bonds are, however, well known for the main group metals. See: A. H. Cowley, *Chem. Commun.*, 2004, 2369 and references therein.

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8 The molecular structures of all new compounds have been determined by X-ray diffraction. Thermal parameters for the structures illustrated are at the 20% probability level. CCDC 617723–617726. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b611654j.

9 The mechanism of $\{[\mu\text{-}\kappa^1,\kappa^3\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ formation and the ultimate fate of the B–H hydrogen is unknown.

10 A binuclear rhodium complex derivative that exhibits a bridging $[\text{B}(\text{mim}^{\text{Me}})_3]$ ligand has been reported, but the bridging mode is very different to that in $\{[\mu\text{-}\kappa^1,\kappa^3\text{-B}(\text{mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$. See: I. R. Crossley, A. F. Hill, E. R. Humphrey and A. C. Willis, *Organometallics*, 2005, **24**, 4083.

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17 Butterfly distortions have been observed for some other four-coordinate d^8 Pd complexes. See: (*a*) C. M. Frech, L. J. W. Shimon and D. Milstein, *Angew. Chem., Int. Ed.*, 2005, **44**, 1709; (*b*) O. Grossman, C. Azerraf and D. Gelman, *Organometallics*, 2006, **25**, 375; (*c*) J. Yin and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 6043.

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19 For a rare example of a tetrahedral d^8 Pd complex, see: J. S. L. Yeo, J. J. Vittal and T. S. A. Hor, *Chem. Commun.*, 1999, 1477.

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