

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

Keliang Pang, Stephanie M. Quan and Gerard Parkin*

Received (in Berkeley, CA, USA) 14th August 2006, Accepted 15th September 2006

First published as an Advance Article on the web 12th October 2006

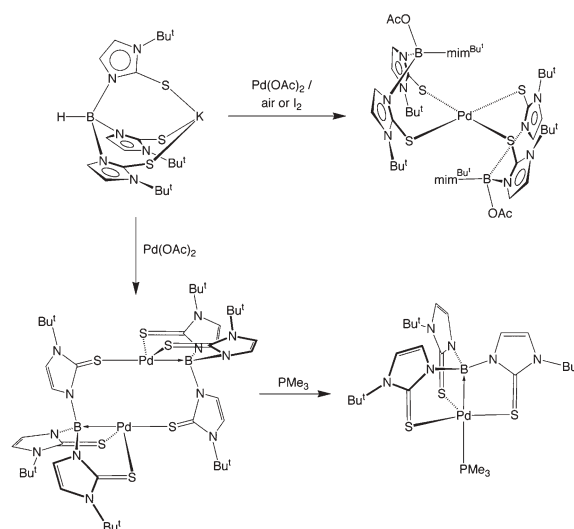
DOI: 10.1039/b611654j

The dinuclear complex $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$, which features a Pd→B dative bond, may be obtained by the reaction of $[\text{Tm}^{\text{Bu}^t}]\text{K}$ with Pd(OAc)_2 ; treatment of $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ with PMe_3 affords the mononuclear boratrane derivative $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3\text{)}$, for which a molecular orbital analysis indicates that the palladium center possesses a d^8 configuration.

Tris(2-mercapto-1-R-imidazolyl)hydroborato ligands ($[\text{HB(mim}^{\text{R}})_3] = [\text{Tm}^{\text{R}}]$),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 $[\text{B(mim}^{\text{R}})_3]$ fragment is attached to the metal *via* a metal-to-ligand $\text{M} \rightarrow \text{B}$ dative bond.² The first example of this transformation was reported in 1999 with Hill *et al.*'s synthesis of $[\kappa^4\text{-B(mim}^{\text{Me}})_3]\text{Ru(CO)(PPh}_3\text{)}$,³ and is noteworthy because it provided structural characterization of a transition metal compound with a metal-to-ligand $\text{M} \rightarrow \text{B}$ dative bond.^{4,5} In addition to ruthenium, a variety of $\{\text{M}[\text{B(mim}^{\text{R}})_3]\}$ 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 $\{\text{M}[\text{B(mim}^{\text{R}})_3]\}$ 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 $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3\text{)}$ and dinuclear $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$, are reported here. In addition, $[\kappa^2\text{-AcOB(mim}^{\text{Bu}^t})_3]\text{Pd}$, 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 $[\text{Tm}^{\text{Bu}^t}]\text{K}$ with Pd(OAc)_2 . Thus, as illustrated in Scheme 1, treatment of $[\text{Tm}^{\text{Bu}^t}]\text{K}$ with Pd(OAc)_2 under an inert atmosphere yields $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$, 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 $[\text{B(mim}^{\text{Bu}^t})_3]$ ligand adopts a $\kappa^3\text{-S}_2\text{B}$ coordination mode to one metal and a $\kappa^1\text{-S}$ 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 $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ represents a new bonding mode for this class of ligand.¹⁰

$\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ is fluxional on the NMR timescale at room temperature, but a spectrum that exhibits three chemically



Scheme 1

inequivalent mim^{Bu^t} groups may be observed upon cooling to 228 K. The $\kappa^1\text{-S}$ bridging interaction in $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$ is readily cleaved upon addition of PMe_3 to give the mononuclear palladaboratrane derivative $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3\text{)}$, as illustrated in Scheme 1. The molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd(PMe}_3\text{)}$ has been determined by X-ray diffraction (Fig. 2),⁸ thereby demonstrating that the palladium has a trigonal bipyramidal geometry, in which the $[\text{B(mim}^{\text{Bu}^t})_3]$ ligand coordinates in a $\kappa^4\text{-S}_3\text{B}$ manner with the boratrane motif.

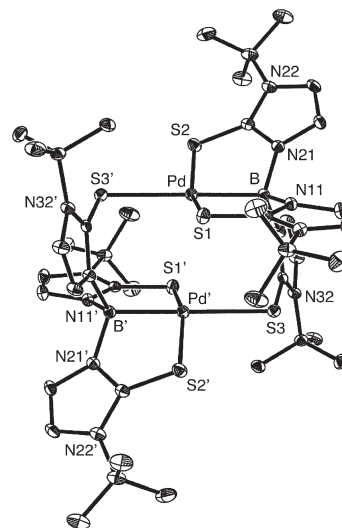


Fig. 1 Molecular structure of $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^t})_3]\text{Pd}\}_2$.

Department of Chemistry, Columbia University in the City of New York, New York 10027, USA. E-mail: parkin@columbia.edu

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

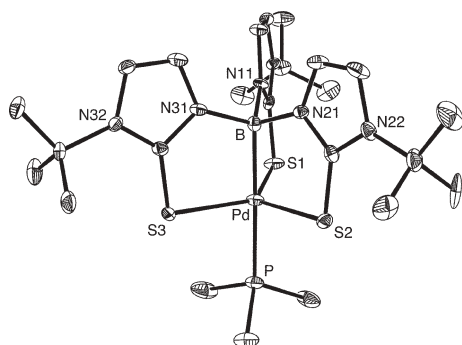


Fig. 2 Molecular structure of $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$.

The most important aspect of both $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd}\}_2$ and $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ 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 $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd}\}_2$ and $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ 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 $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd}\}_2$ (2.073(4) Å) and $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ (2.050(8) Å) are comparable to those in the boryl compounds $\text{Pd(dmpe)}\{\text{B-1,2-(NMe}_2\text{CH}_2\text{CH}_2\text{)}_2\text{(SnMe}_3\text{)}\}$ (2.077(6) Å)¹² and $\text{Pd(PMe}_3\text{)}_2\{\text{B-1,2-(NMe}_2\text{CH}_2\text{CH}_2\text{)}_2\text{Cl}\}$ (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 $^2J_{\text{P-B}}$ coupling constant of 116 Hz in both the $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ 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 $[\kappa^4\text{-B(mim}^{\text{Me}})_3]\text{Pt(PPh}_3\text{)}$ 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 $[\kappa^4\text{-B(mim}^{\text{H}})_3]\text{Ir(PH}_3\text{)Cl}$ 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 $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ 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 $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$, 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 $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ 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}

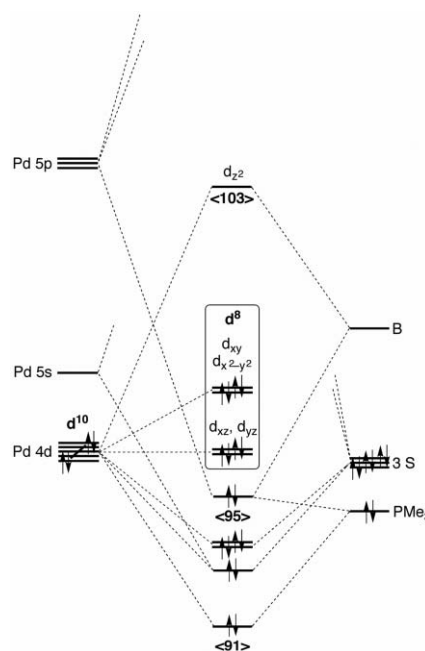


Fig. 3 Molecular orbital diagram for $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$ with idealized C_{3v} symmetry, focusing on σ -interactions.

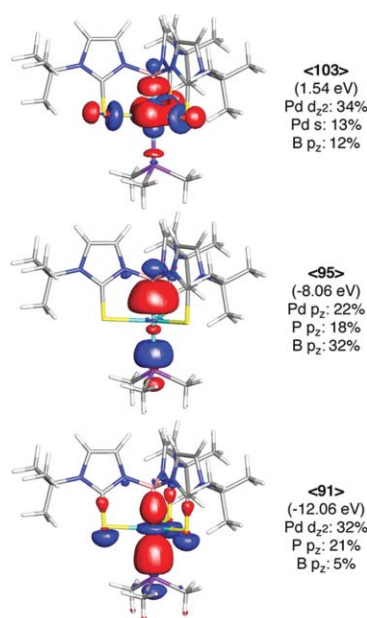


Fig. 4 The molecular orbitals involved in the B–Pd–P interaction for $[\kappa^4\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd(PMe}_3\text{)}$.

By analogy, $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}^i})_3]\text{Pd}\}_2$ 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

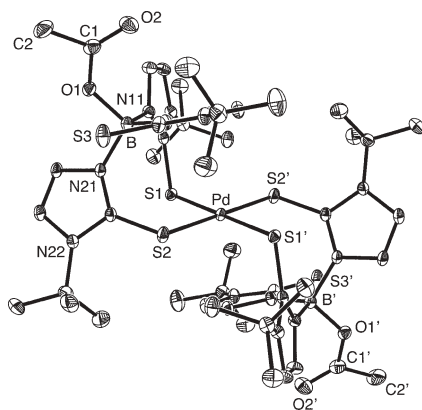


Fig. 5 Molecular structure of $[\kappa^2\text{-AcOB(mim}^{\text{Bu}})_3]_2\text{Pd}$ (triclinic form).

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

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

In summary, $[\kappa^4\text{-B(mim}^{\text{Bu}})_3]\text{Pd(PMe}_3)$ and $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}})_3]\text{Pd}\}_2$ have been shown by X-ray diffraction to possess Pd→B bonds. Calculations indicate that the palladium center in $[\kappa^4\text{-B(mim}^{\text{Bu}})_3]\text{Pd(PMe}_3)$ 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, $[\kappa^2\text{-AcOB(mim}^{\text{Bu}})_3]_2\text{Pd}$, which contains an interesting boron-functionalized $[\text{AcOTm}^{\text{Bu}}]$ ligand, has been isolated.

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

Notes and references

- For example, derivatives with $\text{R} = \text{Me},^a\text{-c Ph},^d \text{Mes},^d \text{Cum},^e \text{Bu}^e, \text{CH}_2\text{Ph},^f$ and $p\text{-Tol}^f$ 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.

- Dative M→B interactions can also be represented as M^+-B^- . Despite their different appearance, however, these representations correspond to exactly the same bonding situation. See, for example: G. Parkin, *Organometallics*, 2006, **25**, 4744.
- (a) A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759; (b) M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 4446.
- Early examples of compounds proposed to possess M→B interactions have been questioned. See, for example: (a) H. Braunschweig, *Angew. Chem., Int. Ed.*, 1998, **37**, 1786; (b) H. Braunschweig and M. Colling, *Coord. Chem. Rev.*, 2001, **223**, 1.
- 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.
- (a) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2006, **25**, 289 and references therein; (b) D. J. Mihalcik, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2004, 1626; (c) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny and G. Parkin, *Inorg. Chem.*, 2006, **45**, 2588; (d) J. S. Figueroa, J. G. Melnick and G. Parkin, *Inorg. Chem.*, 2006, **45**, 7056.
- For other types of complexes with M→B bonds, see ref. 5 and: (a) K. S. Cook, W. E. Piers, T. K. Woo and R. McDonald, *Organometallics*, 2001, **20**, 3927; (b) K. S. Cook, W. E. Piers and S. J. Rettig, *Organometallics*, 1999, **18**, 1575; (c) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2005, **24**, 1062; (d) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, *Angew. Chem., Int. Ed.*, 2006, **45**, 1611; (e) R. J. Blagg, J. P. H. Charmant, N. G. Connelly, M. F. Haddow and A. G. Orpen, *Chem. Commun.*, 2006, 2350; (f) H. Braunschweig, K. Radacki, D. Rais and G. R. Whittell, *Angew. Chem., Int. Ed.*, 2005, **44**, 1192; (g) S. A. Westcott, T. B. Marder, R. T. Baker, R. L. Harlow, J. C. Calabrese, K. C. Lam and Z. Lin, *Polyhedron*, 2004, **23**, 2665; (h) D. Curtis, M. J. G. Lesley, N. C. Norman, A. G. Orpen and J. Starbuck, *J. Chem. Soc., Dalton Trans.*, 1999, 1687; (i) H. Braunschweig, C. Kollann and D. Rais, *Angew. Chem., Int. Ed.*, 2006, **45**, 5254.
- 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.
- The mechanism of $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}})_3]\text{Pd}\}_2$ formation and the ultimate fate of the B–H hydrogen is unknown.
- A binuclear rhodium complex derivative that exhibits a bridging $[\text{B(mim}^{\text{Me}})_3]$ ligand has been reported, but the bridging mode is very different to that in $\{[\mu\text{-}\kappa^1, \kappa^3\text{-B(mim}^{\text{Bu}})_3]\text{Pd}\}_2$. See: I. R. Crossley, A. F. Hill, E. R. Humphrey and A. C. Willis, *Organometallics*, 2005, **24**, 4083.
- Pd–B bond lengths for compounds listed in the Cambridge Structural Database (CSD) span the range 2.006–2.686 Å, with a mean value of 2.259 Å (CSD version 5.27).
- S. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada and M. Tanaka, *Organometallics*, 1996, **15**, 5450–5452.
- S. Onozawa and M. Tanaka, *Organometallics*, 2001, **20**, 2956.
- For a further example, see: H. Braunschweig, K. Radacki, D. Rais and G. R. Whittell, *Angew. Chem., Int. Ed.*, 2005, **44**, 1192.
- I. R. Crossley and A. F. Hill, *Organometallics*, 2004, **23**, 5656.
- B–Pd–S3' = 178.4(1)° and S1–Pd–S2 = 154.7(1)°.
- 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.
- Y. Jean, *Molecular Orbitals of Transition Metal Complexes*, Oxford University Press, New York, 2005, pp. 66.
- 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.
- For an example of the transfer of an acetate ligand to boron, see: K. Fujita, S. Hikichi, M. Akita and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, 2000, 117.