Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 3523



A study of $M-X-BR_3$ (M = Pt, Pd or Rh; X = Cl or I) interactions in square planar ambiphilic ligand complexes: structural, spectroscopic, electrochemical and computational comparisons with borane-free analogues[†]

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Received 20th October 2011, Accepted 23rd December 2011 DOI: 10.1039/c2dt11991a

Reaction of $[PtCl_2(COD)]$ and $[PtI_2(COD)]$ with 2,7-di-*tert*-butyl-5-diphenylboryl-4-diphenylphosphino-9,9-dimethylthioxanthene (TXPB) afforded square planar $[PtCl_2(TXPB)]$ (**1B**) and $[PtI_2(TXPB)]$ (**4B**), both of which were crystallographically characterized. Single-crystal X-ray quality crystals were also obtained for $[PdCl_2(TXPB)]$ (**2B**; Emslie *et al.*, *Organometallics*, 2008, **27**, 5317) as **2B**·2CH₂Cl₂ and solvent-free **2B**. Both the chloro and iodo TXPB complexes exhibit metal–halide–borane bridging interactions similar to those in previously reported [RhCl(CO)(TXPB)] (**3B**) and [RhI(CO)(TXPB)] (**5B**) (Emslie *et al.*, *Organometallics*, 2006, **25**, 583 and *Inorg. Chem.*, 2010, **49**, 4060). To facilitate a more detailed analysis of M–X–BR₃ (X = Cl and I) interactions, a borane-free analogue of the TXPB ligand, 2,7-di-*tert*-butyl-4-diphenylphosphino-9,9-dimethylthioxanthene (TXPH), was prepared. Reaction with $[PtX_2(COD)]$ (X = Cl or I), $[PdCl_2(COD)]$ and 0.5 $[{RhCl(CO)_2}_2]$ provided square planar $[PtCl_2(TXPH)]$ (**1H**), $[PdCl_2(TXPH)]$ (**2H**), [RhCl(CO)(TXPH)] (**3H**) and $[PtI_2(TXPH)]$ (**4H**). M–Cl– BR₃ and M–I–BR₃ bonding in **1B–5B** was then probed through the use of structural comparisons, IR and NMR spectroscopy, cyclic voltammetry, and DFT calculations (Slater-type orbitals, Mayer bond orders, Hirshfeld charges, fragment analysis, SCF deformation density isosurfaces, and energy decomposition analysis).

Introduction

Ambiphilic ligands are defined as those containing a Lewis acidic group in addition to one or more conventional donors capable of σ -donation to the metal (*e.g.* a phosphine or an amine). These ligands may be generated *in situ* on a metal, as is typically the case for tris(*N*-alkylimazolyl)boranes, or they may be isolated prior to metal coordination. The transition metal chemistry of group 13 Lewis acid-containing ambiphilic ligands has seen a surge of activity over the past decade, much of it directed towards the isolation and study of unusual metal–Lewis acid bonds where the Lewis acid is considered a zero-electron donor Z-type ligand.¹ However, studies focused on the development of cooperative reactivity involving a pendant group 13

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Lewis acid have also been reported. These include: (1) pendant borane facilitated delivery of multiple hydride equivalents to a carbonyl ligand in $[\text{Re}(\text{CO})_4 \{\text{PPh}_2(\text{CH}_2)_2 B(\text{C}_8 \text{H}_{14})\}_2]^+$ (I in Fig. 1), followed by spontaneous alkyl migration to form a C-C bond,² (2) rate enhancements for the dehydrogenative coupling of PhSiH₃ by [(Me-Ind)NiMe(PPh₃)] in the presence of Me₂P-CH₂AlMe₂; the proposed intermediate in this reactivity is [(Me-Ind)NiMe(PMe₂CH₂AlMe₂)] (II in Fig. 1),³ (3) propene and methane formation upon reaction of [Cp*RhMe2(PMe2-CH₂AlMe₂)] with ethylene at 50 °C; [Cp*Rh⁺Me(C₂H₄)(PMe₂-CH₂AlMe₃⁻)] (III in Fig. 1) was identified as an intermediate in this reaction,⁴ (4) reaction of $Na[H_2B(mt)_2]$ (mt = *N*-methylimazolyl) with [RhCl(CS)(PPh₃)₂] to form [LRhH(PPh₃)] [IV in Fig. 1; $L = {H(mt)_2B}(Ph_3P)C=S$, presumably via the intermediates [{ κ^3 -H₂B(mt)₂}Rh(CS)(PPh₃)] (V in Fig. 1) and [{ κ^3 -HB(mt)₂}RhH(CS)(PPh₃)],⁵ (5) reaction of $[{\kappa^4-B(mt^{Bu})_3}]$ NiCl] (**VI** in Fig. 1; $mt^{Bu} = N$ -tert-butylimazolyl)) with I₂ or CHBr₃ to form [{ κ^3 -ClB(mt^{*i*Bu})₃}NiX] (VII in Fig. 1; X = I or Br), and with XeF₂ to produce $[{\kappa^3-FB(mt'^{Bu})_3}NiCl],^6$ and (6) reaction of [Pd(TXPB)] (VIII in Fig. 1; TXPB = 2,7-di-tertbutyl-5-diphenylboryl-4-diphenylphosphino-9,9-dimethylthioxanthene) with dibenzylidene-acetone (dba) to afford [Pd(dba) (TXPB)] (IX in Fig. 1); a zwitterionic palladium(II) η^3 -boratoxyallyl complex.⁷

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[†]Electronic supplementary information (ESI) available: Calculated structures for **1B–5B**, **1H–5H**, TXPB and [TXPB–I][–], and X-Ray crystallographic data. CCDC 849792–849797. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11991a



Fig. 1 Selected reactants, proposed intermediates and products from reactions involving a pendant group 13 Lewis acid (the group 13 element is highlighted).

Previous research in the Emslie group has focused on late transition metal complexes of the phosphine-thioether-borane ambiphilic ligand, TXPB, and a range of complexes containing direct metal-borane or metal-ligand-borane interactions have been prepared, including compounds VIII and IX in Fig. 1.7-9 The current work probes the nature of halide ligand coordination by a pendant borane; in particular the extent to which the strength of metal-halide-borane (M-X-BR₃) interactions vary between chloro and iodo complexes, and the effect that borane coordination has on the metal-halide bond. Our interest in these features is twofold: (1) for late transition metal catalysis involving halide ligands, it is possible to envisage modified reaction cycles involving halide coordination or abstraction by a pendant borane. However, to allow rational progress in this direction, a more detailed understanding of metal-halide-borane interactions is desirable. (2) The potential exists for a pendant borane to effect pre-coordination or cooperative activation of organic substrates. However, due to the ubiquitous nature of chloro, bromo and iodo ligands throughout much of transition metal chemistry, it is desirable to determine the extent to which coordination of halide co-ligands is likely to take place, potentially sequestering the pendant borane.

A previous publication reported the synthesis and structural characterization of [RhX(CO)(TXPB)] (X = F, Cl, Br and I) complexes, revealing short B–X distances in the chloro and bromo complexes, a long B–I interaction in the iodo complex, and halide abstraction by the borane in the fluoro complex.⁸ This trend is in keeping with the soft nature of rhodium(I), the classification of organoboranes as moderately hard Lewis acids, and the decrease in halide hardness as group 17 is descended.¹⁰ Herein we provide a more detailed analysis of M–X–BR₃ (M = Pt, Pd or Rh; X = Cl or I) bonding in [MX₂(TXPB)] and [MX(CO) (TXPB)] complexes through the use of crystallographic, spectroscopic, electrochemical and computational comparisons with borane-free TXPH ligand analogues (TXPH = 2,7-di-*tert*-butyl-4-diphenylphosphino-9,9-dimethylthioxanthene).

Results and discussion

Platinum dichloro and diiodo complexes of TXPB

Reaction of $[PtCl_2(COD)]$ with 2,7-di–*tert*-butyl-5-diphenylboryl-4-diphenylphosphino-9,9-dimethylthioxanthene $(TXPB)^7$ afforded colourless $[PtCl_2(TXPB)]$ (**1B**) in moderate yield (Scheme 1). The ³¹P NMR signal at 32.5 ppm (${}^{1}J_{P,Pt} = 3836$ Hz) demonstrates platinum–phosphine coordination and the ¹¹B NMR signal at 3 ppm is characteristic of 4-coordinate boron. These data are consistent with square planar platinum ligated by the phosphine and thioether groups of TXPB and two chloride anions, with one chloride forming a strong bridging interaction to the borane unit of TXPB. Analogous M–Cl–B bridging interactions have been observed in [RhCl(CO)(TXPB)] (**3B**) and $[{PdCl(TXPB)}_2].⁹$

X-ray quality crystals of $1B\cdot 2CH_2Cl_2$ were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution at -30 °C (Table 1, Fig. 2). Crystals of the previously reported **2B** were also obtained from CH_2Cl_2 /hexanes or toluene/hexanes at -30 °C; the resulting crystals, $2B\cdot 2CH_2Cl_2$ and solvent-free **2B**, differ in the orientation of the Pd–Cl bond with respect to the bend of the ligand backbone (Table 1, Fig. 2; *vide infra*).

In **1B**·2CH₂Cl₂, as well as **2B** and **2B**·2CH₂Cl₂, the M–Cl(1) bond is considerably longer than M–Cl(2) (Table 2), which can be rationalized as a consequence of the chloro ligand–borane interaction and/or the greater *trans* influence of PAr₃ *vs*. SAr₂ (*vide infra*).¹¹ In all chloro complexes in Table 1, the B–Cl(1)



Scheme 1 Preparation of [PtCl₂(TXPB)] (1B).

Structure	$1B{\cdot}2CH_2Cl_2$	2B	$\mathbf{2B} \cdot \mathbf{2CH}_2 \mathbf{Cl}_2$	4B ·1.31CH ₂ Cl ₂	$\mathbf{2H} \cdot \mathbf{2CH}_2 \mathbf{Cl}_2$	$\mathbf{4H} \cdot 1.5 \mathrm{CH}_2 \mathrm{Cl}_2$
Formula Formula wt T [K] Cryst. syst. Space group a [Å] b [Å] c [Å] a α [°] β [°] γ [°] Volume [Å ³]	$\begin{array}{c} C_{49}H_{52}BCl_6PPtS\\ 1122.54\\ 173(2)\\ Orthorhombic\\ Pna2(1)\\ 21.373(2)\\ 8.9593(9)\\ 25.330(3)\\ 90\\ 90\\ 90\\ 4850.4(8) \end{array}$	$\begin{array}{c} C_{47}H_{48}BCl_2PPdS\\ 863.99\\ 173(2)\\ Monoclinic\\ P2(1)/c\\ 11.2575(5)\\ 27.0326(13)\\ 13.7991(7)\\ 90\\ 97.258(3)\\ 90\\ 4165.7(3) \end{array}$	C ₄₉ H ₅₂ BCl ₆ PPdS 1033.85 173(2) Orthorhombic <i>Pna2</i> (1) 21.3801(14) 8.9678(6) 25.2512(17) 90 90 90 4841.5(6)	$\begin{array}{c} C_{48.31}H_{50.62}BCl_{2.62}I_2PPtS\\ 1246.93\\ 173(2)\\ Orthorhombic\\ Pna2(1)\\ 22.18(2)\\ 9.043(8)\\ 24.75(2)\\ 90\\ 90\\ 90\\ 90\\ 4964(8) \end{array}$	$\begin{array}{c} C_{37}H_{43}Cl_6PPdS\\ 869.84\\ 173(2)\\ Triclinic\\ P\bar{l}\\ 12.1463(18)\\ 12.547(2)\\ 13.883(2)\\ 76.402(10)\\ 74.583(10)\\ 81.960(10)\\ 1975.7(5) \end{array}$	$\begin{array}{c} C_{36.5}H_{42}Cl_{3}I_{2}PPtS\\ 1098.97\\ 173(2)\\ Triclinic\\ P\bar{I}\\ 12.451(2)\\ 12.803(2)\\ 13.852(2)\\ 75.815(2)\\ 74.648(2)\\ 80.524(4)\\ 2052.7(6) \end{array}$
Z Crystal size [mm ³] No. of reflns	4 0.24 × 0.18 × 0.01 27 401	4 0.17 × 0.12 × 0.02 25 320	4 0.32 × 0.28 × 0.12 72 714	$4 \\ 0.25 \times 0.13 \times 0.03 \\ 34768$	2 0.30 × 0.30 × 0.15 13 584	2 0.06 × 0.05 × 0.03 17 425
collected No. of indep. reflns	6568	5445	14 333	9159	6736	9987
θ range for collection [°] Completeness	2.07–26.48 99.3	1.49–22.50 100.0	1.61–30.67 99.5	1.65–26.36 99.8	1.56–24.75 99.4	2.02–28.35 97.3
Absorption correction	Numerical	Semi-empirical from equivalents	Numerical	Semi-empirical from equivalents	Semi-empirical from equivalents	Numerical
GOF on F^2 Final R_1 $[I > 2\sigma(I)]$ [%]	1.011 4.51	1.218 9.61	1.031 4.21	1.021 6.52	1.044 8.77	0.868 6.73

 Table 1
 Crystallographic data collection and refinement parameters for TXPB complexes 1B, 2B, and 4B, and TXPH complexes 2H and 4H

bond distances (1.98-2.15 Å) are only 0.04-0.22 Å longer than B-Cl in the chloroborate anions $[CPh_3][ClB(C_6F_5)_3]$ (1.928(2) Å)^{12} and $[\{ClPhB(\eta^{5}\text{-}C_{5}H_{4})_{2}\}ZrCl_{2}]^{-}$ (1.937(5) Å), 13 and boron is strongly pyramidalized [$\Sigma(C-B-C) = 337-342^{\circ}$]. These data, in keeping with the ¹¹B NMR chemical shifts (Table 2), are indicative of strong B-Cl interactions. Similar B-Cl distances and boron pyramidalizations have also been reported for borane functionalized $[(\eta^3 - allyl)Pd(\mu - Cl) \{PiPr_2(C_6H_4)BCy_2 - o\}]$ (B-Cl = 2.16 Å; $\Sigma(C-B-C) = 349^{\circ}$,¹⁴ [(Ph₃P)PdCl(μ -Cl){P*i*Pr₂(C₆H₄) BCy₂-o] (B-Cl = 2.11 Å; Σ (C-B-C) = 343°),¹⁵ [(η^2 : η^2 -nbd)Rh $(\mu-Cl) \{PiPr_2(C_6H_4)BCy_2-o\}\}$ (B-Cl = 2.12 Å; $\Sigma(C-B-C)$ = 343°),¹⁵ [(*p*-cymene)RuCl(μ -Cl)(NC₅H₄(CH₂BCy₂)-*o*}] (B-Cl = 2.11 Å; Σ (C–B–C) = 347°),¹⁶ [(κ^3 -Tp)OsCl(μ -Cl){NPh (BPh₂)}] (B-Cl = 2.11 Å; Σ (C-B-C) = 347°),¹⁷ [(η^{5} -Ind)TiCl $(\mu-Cl) \{C_5H_4B(C_6F_5)_2\} | (B-Cl = 2.01 \text{ Å}; \Sigma(C-B-C) = 342^\circ),^{18}$ and a B-Cl distance of 1.93 Å was calculated for the un-M-Cl-B bridge [(IMes)₂HPt(µ-Cl) supported in $\{BC_5H_4(SiMe_3)\}].^{19}$

In **1B**·2CH₂Cl₂ and **2B**·2CH₂Cl₂, the M–Cl–B bridge is directed towards the outside of the fold of the ligand backbone, resulting in a C(9)···S–M angle of 160–161° and an acute M–Cl–B angle of 95–96°. By contrast, in solvent-free **2B** and **3B**·hexane, the M–Cl–B bridge is directed into the fold of the ligand backbone, leading to a more acute C(9)···S–M angle of 146°, but allowing for an expanded M–Cl–B angle of 105–108° (Table 2). Observation of both possible M–Cl–B bridge orientations in the crystals of complex **2B** obtained under different conditions highlights the absence of a strong thermodynamic preference for one particular orientation in the chloro complexes. Furthermore, static structures are not preserved in solution; fluxional behaviour is observed for all of the chloro and iodo complexes in Table 1, resulting in equivalent CMe_2 groups at room temperature or slightly above.

Reaction of [PtI₂(COD)] with TXPB gave bright yellow [PtI₂(TXPB)] (**4B**) in 73% isolated yield (Scheme 2). The ¹¹B NMR signal at 50 ppm is indicative of a weaker PtX···B interaction than in related chloro TXPB complexes (*cf.* 69 ppm for the free TXPB ligand⁷ and 3–13 ppm for **1B–3B**). An analogous situation was observed for previously prepared [RhI(CO) (TXPB)] (**5B**; ¹¹B NMR δ 56 ppm).⁸

Single-crystal X-ray quality crystals of 4B·1.31CH₂Cl₂ were grown from CH₂Cl₂/hexanes at -30 °C. The solid state structure of **4B** (Tables 1–2, Fig. 2) revealed approximate square planarity at platinum $[P-Pt-I(1) = 175.0(1)^{\circ}$ and $S-Pt-I(2) = 171.8(1)^{\circ}]$ and an M-X-BR3 bridging interaction directed towards the outside of the fold of the ligand backbone; an analogous arrangement was observed in the platinum chloro analogue 1B. The B...I distance²⁰ in **4B** is 2.75(2) Å. Structurally characterized iodoborates (BR₃I⁻) are not available for comparison, but this distance is approximately 0.5 Å longer than the B-I bond in crystallographically characterized iodoboranes (cf. 2.15-2.17 Å in 1,3,5-triiodo-1,3,5-triborocyclohexane,²¹ and 2.22-2.25 Å in Me₃PBI₃).²² The boron atom in **4B** is also pyramidalized to a much lesser extent $[\Sigma(C-B-C) = 353(3)^{\circ}]$ than in **1B**, **2B** or **3B** $[\Sigma(C-B-C) = 337-342^{\circ}]$. For comparison, the B–I distance in the rhodium iodo complex 5B is 3.125(7) Å and the sum of the C-B-C angles is 357(1)°.8 The Pt-I(1) bond (trans to PAr₃; 2.637(2) Å) in 4B is significantly longer than Pt-I(2) (trans to SAr_2 ; 2.590(2) Å), presumably as a consequence of the iodo ligand-borane interaction and/or the greater trans influence of PAr₃ vs. SAr₂;¹¹ the latter effect is expected to dominate given the long B-I distance in 4B.



Fig. 2 Solid state structures of (a) $[PtCl_2(TXPB)] \cdot 2CH_2Cl_2$ (**1B** $\cdot 2CH_2Cl_2$), (b) $[PdCl_2(TXPB)] \cdot 2CH_2Cl_2$ (**2B** $\cdot 2CH_2Cl_2$), (c) $[PdCl_2(TXPB)]$ (**2B**), (d) the previously reported $[RhCl(CO)(TXPB)] \cdot hexane$ (**3B** $\cdot hexane$), (e) $[PtL_2(TXPB)] \cdot 1.31CH_2Cl_2$ (**4B** $\cdot 1.31CH_2Cl_2$), and (f) the previously reported $[RhI(CO)(TXPB)] \cdot hexane$ (**5B** $\cdot hexane$). Ellipsoids are at 50% probability. One CMe₃ group in **1B** $\cdot 2CH_2Cl_2$ and **2B** $\cdot 2CH_2Cl_2$ is disordered over two positions; only one orientation is shown. Hydrogen atoms and lattice solvent are omitted for clarity.

Complexes of a borane-free analogue of TXPB

To probe in more detail the factors responsible for differences in the M-X(1) and M-X(2) bond lengths in **1B**, **2B**, and **4B**, and the nature of $M-X-BR_3$ interactions, complexes of a borane-free analogue of TXPB, 2,7-di-*tert*-butyl-4-diphenylphosphino-9,9-dimethylthioxanthene (TXPH), were prepared.

The TXPH ligand was accessed by lithiation of 2,7-di-*tert*butyl-4-bromo-5-diphenylphosphino-9,9-dimethylthioxanthene $(TXPBr)^7$ followed by quenching with deoxygenated MeOH. Reaction of [PtCl₂(COD)], [PdCl₂(COD)], 0.5[{RhCl(CO)₂}₂] and [PtI₂(COD)] with TXPH then provided [PtCl₂(TXPH)] (**1H**), [PdCl₂(TXPH)] (**2H**), [RhCl(CO)(TXPH)] (**3H**) and [PtI₂(TXPH)] (**4H**), respectively (Scheme 3). As in complex **3B**, the CO ligand in **3H** is *cis* to the phosphine donor, based on a ${}^{2}J_{C,P}$ coupling of 16 Hz.²³ Sharp CO stretches at 2010 and 2001 cm⁻¹ were observed for **3B** and **3H** respectively in Nujol, indicative of decreased electron density at the metal centre in **3B**. However, a very broad carbonyl stretch at 2013 cm⁻¹ was observed for both complexes in CH₂Cl₂.

X-ray quality crystals of $2H \cdot 2CH_2Cl_2$ and $4H \cdot 1.5CH_2Cl_2$ were grown by slow diffusion of hexanes into CH_2Cl_2 solutions of each complex at -30 °C (Table 1, Fig. 3). Both complexes are square planar with M–P, M–S, M–X(1) and M–X(2) bond distances (Table 3) very close to those in the TXPB analogues (Table 2). These data highlight that in complexes **2B** and **4B** (and by extrapolation, **1B**), the greater *trans*-influence of PAr₃ *vs.* SAr₂ donors¹¹ is the major factor responsible for elongation of the M–X(1) bond relative to M–X(2). In both **2H**·2CH₂Cl₂ and **4H**·1.5CH₂Cl₂, C9···S–M angles of 158° were observed,

 Table 2
 Crystallographic, spectroscopic and electrochemical data for late transition metal TXPB chloro and iodo complexes^a

Complex 1B		2B		3B	4B	5B
Metal and co-ligands	PtCl ₂	PdCl ₂		RhCl(CO)	PtI ₂	RhI(CO)
³¹ P NMR [δ , ppm] ¹ $J_{P,Pt}$ or ¹ $J_{P,Rh}$ [Hz] ¹ $J_{C,Rh}$ ² $J_{C,P}$ for CO [Hz] ¹¹ B NMR [δ , ppm]	32.5 3836 $-$ 3	58.4 		63.8 161 77/18 12	$ 41.6 \\ 3517 \\ \overline{} \\ 50 $	67.2 167 74/14 56
$E_{\rm p}$ vs. SCE (CH ₂ Cl ₂ , 200 mV s ⁻¹)	$E_{\rm pc} = -1.55$	$E_{\rm pc} = -0.81$		$E_{\rm pa} = 0.97$	$E_{\rm pc} = -1.43$	$E_{\rm pa} = 0.79$
$v(CO)(CH_2Cl_2/Nujol) [cm^{-1}]$	—	_		2013/2010	—	2002/2004
X-ray crystal structure reference Lattice solvent in crystal M-X(1) [Å] M-X(2) or M-CO [Å] M-P [Å] M-S [Å] B-X(1) [Å] M-X(1)-B [°] $\Sigma(C-B-C) [°]$ S-C(12)-C(5)-B ^b [°] C(9)S-M [°] M-(PCCSplane) ^c [Å] B-(CCCplane) ^d [Å] Ligand bend ^e [°]	This work $2 \text{ CH}_2\text{Cl}_2$ 2.391(2) 2.321(2) 2.213(2) 2.243(2) 2.14(1) 95.9(3) 342(2) 20(2) 160 0.54 0.46 51	This work $2 CH_2Cl_2$ 2.396(1) 2.313(1) 2.226(1) 2.256(1) 2.101(4) 94.6(1) 340(1) 19.6(4) 161 0.57 0.42 51	This work None 2.352(3) 2.290(3) 2.219(3) 2.320(3) 1.98(1) 107.7(4) 337(1) -5(2) 146 1.05 0.45 47	8 Hexane 2.381(2) 1.82(1) 2.205(2) 2.379(2) 2.00(1) 104.6(3) 340(1) -13(1) 146 1.02 0.43 43	This work $1.31 \text{ CH}_2\text{Cl}_2$ 2.637(2) 2.290(2) 2.222(5) 2.246(5) 2.75(2) 82.7(5) 352(2) 26(3) 163 0.45 0.26 53	8 Hexane 2.664(1) 1.855(7) 2.224(1) 2.300(1) 3.125(7) 74.0(1) 357(1) 17(1) 165 0.14 0.16 53

^{*a*} In the X-ray crystal structures of **1B–5B**, atoms C(1)–C(13) of the xanthene ligand backbone are numbered as shown in Scheme 1. ^{*b*} Positive S–C (12)–C(5)–B torsion angles indicate that boron is oriented up into the fold of the thioxanthene backbone. ^{*c*} PCCS plane = P–C4–C11–S. ^{*d*} CCC plane = C5–C36–C42. ^{*e*} Ligand bend = the angle between the two aromatic rings in the thioxanthene backbone of the ligand [*i.e.* the angle between the C (1)/C(2)/C(3)/C(4)/C(10)/C(11) and C(5)/C(6)/C(7)/C(8)/C(12)/C(13) planes].



Scheme 2 Preparation of [PtI₂(TXPB)] (4B).

and the M–X(1) bond is directed towards the outside of the fold of the ligand backbone, leading to C9...S–M angles in the 157–165° range. This M–X(1) bond orientation is analogous to that in **1B**·2CH₂Cl₂, **2B**·2CH₂Cl₂, **4B**·1.31CH₂Cl₂, and **5B**·hexane, but not **2B** or **3B**·hexane.

Electrochemistry of chloro and iodo complexes

All TXPB complexes and their TXPH analogues were investigated by cyclic voltammetry (CV) in CH₂Cl₂ (platinum disk electrode, [NBu₄][PF₆] base electrolyte, FeCp*₂ calibrant; Tables 2 and 3). Palladium and platinum complexes exhibited an irreversible reduction peak while rhodium complexes **3B** and **5B** gave rise to an irreversible oxidation peak. At a scan rate of 200 mV s⁻¹, the E_{pc} values for **4B** and **4H** are equal within error. By contrast, the E_{pc} values for the Pd and Pt chloro TXPB complexes are less negative, by 80–300 mV, than those for TXPH analogues, suggesting decreased electron density at the metal centre in chloro TXPB complexes. However, these differences should be viewed with some caution given the sensitivity



Scheme 3 Preparation and complexation of the TXPH ligand.

of irreversible peak potentials to parameters such as uncompensated resistance, diffusion coefficients and test complex concentration ($E_{1/2}$ values are insensitive to these parameters).²⁴ More reversible redox behaviour was not observed in a CV of **2H** in CH₂Cl₂ at -78 °C using [NBu₄][B(C₆F₅)₄] as the base electrolyte.

DFT calculations

To further investigate the strength and consequences of halide ligand-borane coordination, DFT calculations (ADF, all-electron, TZ2P, ZORA, VWN, PW91) were carried out on **1B–5B** (for



Fig. 3 Solid state structures for: (a) $[PdCl_2(TXPH)] \cdot 2CH_2Cl_2$ (2H·2CH₂Cl₂) and (b) $[Ptl_2(TXPB)] \cdot 1.5CH_2Cl_2$ (4H·1.5CH₂Cl₂) with ellipsoids at 50% probability. Both CMe₃ groups in 2H·2CH₂Cl₂ and one CMe₃ group in 2B·2CH₂Cl₂ are disordered over two positions; only one orientation is shown. Hydrogen atoms and lattice solvent are omitted for clarity.

 Table 3
 Spectroscopic, crystallographic and electrochemical data for TXPH complexes

Complex	1H	2H	3H RhCl	4H	
Metal and co-ligands	PtCl ₂	PdCl ₂	(CO)	PtI ₂	
³¹ P NMR [δ , ppm] ¹ $J_{C,Rh}/^2 J_{C,P}$ for CO	38.6	61.4	69.5 78/16	43.6	
${}^{I}J_{P,Pt}$ or ${}^{I}J_{P,Rh}$ [Hz]	3458		148	3251	
$ \begin{array}{c} E_{\rm p} \ vs. \ {\rm SCE} \ ({\rm CH}_2{\rm Cl}_2, \\ 200 \ {\rm mV \ s}^{-1}) \end{array} $	$E_{\rm pc} = -1.63$	$E_{\rm pc} = -1.11$	Ill defined	$E_{\rm pc} = -1.45$	
$v(CO)(CH_2Cl_2/Nujol)$	_	_	2013/ 2001	_	
Lattice solvent in	—	$2CH_2Cl_2$		$1.5 \mathrm{CH}_2 \mathrm{Cl}_2$	
M–X(1) [Å] M–X(2) or M–CO		2.369(3) 2.308(3)		2.658(1) 2.607(1)	
M–P [Å] M–S [Å] C(9)···S–M [°]		2.216(3) 2.260(3) 158		2.232(3) 2.258(3) 158	
Ligand bend ^{<i>u</i>} [°]		48		49	

^{*a*} Ligand bend = the angle between the two aromatic rings in the thioxanthene backbone of the ligand [*i.e.* the angle between the C(1)/C (2)/C(3)/C(4)/C(10)/C(11) and C(5)/C(6)/C(7)/C(8)/C(12)/C(13) planes]. In the X-ray crystal structures of **2H** and **4H**, atoms C(1)–C(13) of the xanthene ligand backbone are numbered as shown in Scheme 3.

complex **2B**, the geometry in **2B**·2CH₂Cl₂ was used as the starting point for geometry optimization), **1H–4H**, and [RhI(CO) (TXPH)] (**5H**). The geometry optimized structures for crystallographically characterized **1B–5B**, **2H** and **4H** match closely with experimental values (Table 4). For example, calculated M–P, M–S, M–X bond lengths lie within 0.05 Å (2%) of the experimental values, and the calculations satisfactorily reproduced the bond angles at the metal (<1.5% deviation for TXPB complexes and <3.5% deviation for TXPH complexes). M–X–B bond angles were also reproduced to within 6% of crystallographic values, and calculated B–X bond distances in the TXPB complexes differed from crystallographically determined values by 1.5–3% in **1B–3B** and **5B** and 5% in **4B**. The larger difference between calculated and crystallographic bond lengths in **4B** may be a consequence of a particularly shallow potential energy surface associated with changes in the B–X bond length in iodo complexes.

At least one molecular orbital involved in B–X(1) bonding was observed for all TXPB complexes (Fig. 4), and selected Mayer bond orders²⁵ and Hirshfeld charges²⁶ are listed in Table 5. The B–X(1) Mayer bond orders are 0.626, 0.654, 0.639, 0.585 and 0.337 in **1B**, **2B**, **3B**, **4B** and **5B** (the B–I(1) Mayer bond order is 0.509 for the TZ2P geometry optimized structure of **4B** with the B–X(1) bond constrained to the crystallographically determined bond distance). These data are indicative of greater covalency in B–Cl bonds relative to B–I bonds, despite the higher electronegativity of chlorine. However, they do not provide direct insight into the strength of B–Cl *vs.* B–I bonding.

Now comparing TXPB complexes with their TXPH analogues, the differences in M–P, M–S and M–X(2) Mayer bond orders are never more than 4%. By contrast, the M–X(1) Mayer bond orders for **1B–5B** are 19, 27, 20, 10 and 8% lower than the corresponding bond orders for **1H–5H**, indicating that the M–X (1) bonds in all five TXPB complexes are weakened as a result of borane complexation; to a greater extent in chloro complexes **1B–3B**. Calculated M–X(1) bond distances are also elongated (by 0.049, 0.070 and 0.030 Å) in chloro TXPB complexes **1B–3B**, relative to their TXPH analogues. By contrast, the M–X(1) bonds in **4B** and **5B** lie within 0.01 Å of the M–X(1) distances in their TXPH analogues.

Borane coordination in TXPB complexes also results in less negative Hirshfeld charges on X(1), relative to TXPH complexes; Hirshfeld charges on X(1) lie in the -0.01 to -0.14 range for **1B–5B**, compared with -0.27 to -0.37 in **1H–5H**. These changes as a result of boron–halide coordination are accompanied by a slight reduction in the positive charge on boron; Hirshfeld charges on boron are 0.02-0.04 in **1B–4B** and 0.08 in **5B**, compared with 0.12 in the free TXPB ligand (for comparison, the Hirshfeld charges on boron and iodine are 0.01 and -0.25 in the [TXPB–I][–] anion calculated at the same level of theory; B–I = 2.456 Å; Σ (C–B–C) = 339.1°; B–I Mayer bond order = 0.793).

All TXPB and TXPH complexes were further investigated through a fragment approach that considered the interaction of an uncharged MX_2 (M = Pt or Pd) or RhX(CO) fragment with a neutral TXPB or TXPH ligand (fragments were generated from

Compound	1B	1H	2B	2H	3B	3H	4B	4H	5B	5H
MXY	PtCl ₂	PtCl ₂	PdCl ₂	PdCl ₂	RhCl(CO)	(CO)	PtI ₂	PtI ₂	RhI(CO)	(CO)
M-P	2.222	2.224	2.233	2.239	2.225	2.229	2.243	2.243	2.241	2.236
M–S	[2.248] [2.243(2)]	2.257	[2.226(1)] 2.258 [2.256(1)]	2.286 [2.260(3)]	[2.203(2)] 2.394 [2.379(2)]	2.379	[2.222(5)] 2.276 [2.246(5)]	[2.252(3)] 2.279 [2.258(3)]	[2.320] [2.300(1)]	2.383
M-X(1)	2.414 [2.391(2)]	2.365	2.428 [2.396(1)]	2.358 [2.369(3)]	[2.399 [2.381(2)]	2.369	2.689 [2.637(2)]	2.690 [2.658(1)]	2.699 [2.664(1)]	2.690
М-Ү	2.324 [2.321(2)]	2.323	2.319 [2.313(1)]	2.320 [2.308(3)]	1.841 [1.82(1)]	1.841	2.643 [2.590(2)]	2.640	1.845 [1.855(7)]	1.839
B-X(1)	2.107 [2.14(1)]		2.065 [2.101(4)]		2.040	—	2.614 [2.75(2)]		3.043 [3.125(7)]	
P-M-X(1)	173.9 [174.8(1)]	177.5	171.9 [173.35(3)]	176.8 [171.1(1)]	170.6 [172.6(1)]	175.9	174.4 [175.0(1)]	173.3 [169.3(1)]	170.5 [169.58(4)]	173.2
S-M-Y	172.5 [173.4(1)]	178.1	173.2 [171.80(3)]	175.6 [175.7(1)]	169.2 [171.3(3)]	172.5	172.2 [171.8(1)]	179.8 [178.3(1)]	166.1 [163.8(2)]	174.1
M-X(1)-B	98.3 [95.9(3)]		98.6 [94.6(1)]		105.0 [104.6(3)]		87.7 [82.7(5)]		78.0 [74.0(1)]	—
Σ(С-В-С)	340.8 [342(2)]		338.9 [340(1)]	—	339.0 [340(1)]	_	346.6 [352(2)]		353.9 [357(1)]	_
^{<i>a</i>} For complex 2B , crystallographic values are from 2B \cdot 2CH ₂ Cl ₂ .										

Table 4 Calculated bond lengths (Å) and angles (°) for complexes **1B–5B** and **1H–5H** [Y = X(2) or CO]. Where available, crystallographic values⁴ are shown in square brackets²⁷

(a) (b) (b) (c) (c)

Fig. 4 Slater-type molecular orbitals involved in B–X(1) bonding in chloro complex 1B and iodo complex 4B: (a) HOMO–13 in 1B, (b) HOMO–17 in 1B, (c) HOMO–28 in 1B, (d) HOMO–21 in 4B. Iso-surfaces are set to 0.03.

the TZ2P geometry optimized structures of each complex). For each TXPB complex and TXPH analogue, the Hirshfeld charge on the TXPB fragment is less positive than the Hirshfeld charge on the TXPH fragment by 0.06–0.15 electrons, consistent with donation of electron density from X(1) to boron. Regions in which electron density is depleted or increased upon combination of each MX₂ or MX(CO) fragment with TXPB or TXPH are illustrated in the SCF deformation density (SCF electron density for the molecule minus the sum of the SCF electron density for the two fragments) isosurfaces in Fig. 5. These isosurfaces clearly show electron donation from the halide to the borane in both the chloro and iodo TXPB complexes.

Particularly valuable insight into the bonding situation in TXPB complexes was gained through energy decomposition

analysis of **1B–5B** and **1H–5H** (Table 5, Fig. 6), which partitions the total interaction energy (ΔE_{int}) between two prepared fragments into three major components: (1) orbital mixing (ΔE_{orb}), which includes electron pair bonding, charge-transfer, donor–acceptor interactions, and intrafragment polarization, (2) the electrostatic interaction energy (ΔE_{elec}), which is typically dominated by nucleus–electron attractions, and (3) Pauli repulsion (ΔE_{Pauli}) which arises from destabilizing interfragment interactions between electrons with the same spin.

The orbital mixing contribution is substantially more negative in TXPB complexes relative to their TXPH analogues; by 274-322 kJ mol⁻¹ in **1B-3B**, 163 kJ mol⁻¹ in **4B**, and 102 kJ mol^{-1} in **5B**. These data support the presence of a strong covalent contribution to B-Cl(1) bonding, and a weaker but still significant covalent contribution to B-I(1) bonding. In TXPB complexes, the electrostatic contribution to bonding is also more negative than that in TXPH analogues, and this difference is markedly more pronounced in chloro complexes than iodo complexes; ΔE_{elec} (TXPB_complex)– ΔE_{elec} (TXPH_complex) is -192 to -233 kJ mol^{-1} in **1B–3B**, compared with -101 and -85 kJ mol^{-1} in **4B** and **5B**. These data are commensurate with the greater electronegativity of chlorine vs. iodine, and the shorter B-X distances in chloro vs. iodo complexes. In contrast to the orbital mixing and electrostatic terms, the Pauli repulsion term is more positive in TXPB complexes relative to TXPH analogues; by approx. 400 kJ mol⁻¹ in **1B–3B** and approx. 200 kJ mol⁻¹ in 4B and 5B. The larger Pauli repulsion term in chloro vs. iodo TXPB complexes presumably arises due to closer approach of the borane and the chloro ligand.

Overall, the total interaction energy (ΔE_{int}) for combination of an MX₂ or MX(CO) fragment with a TXPB or TXPH fragment is more positive in TXPB complexes than in TXPH analogues, and this difference is more pronounced in chloro complexes than iodo complexes; ΔE_{int} (TXPB_complex)– ΔE_{int} (TXPH_complex) is -80 to -110 kJ mol⁻¹ in **1B-3B**, compared with -30 and

Compound MXY	1B PtCl ₂	1H PtCl ₂	2B PdCl ₂	2H PdCl ₂	3B RhCl(CO)	3H RhCl(CO)	4B PtI ₂	4H PtI ₂	5B RhI(CO)	5H RhI(CO)
	1.211 1.040 0.645 <i>19%</i> 0.849 0.626	1.212 1.023 0.766 0.839	1.098 0.922 0.569 27% 0.794 0.654	1.068 0.884 0.723 0.777	1.1774 0.7447 0.6047 20% 1.3126 0.6387	1.152 0.7695 0.7234 1.289	1.170 0.983 0.729 <i>10%</i> 0.904 0.5850	1.165 0.980 0.804 0.905	1.1609 0.8590 0.6889 8% 1.2875 0.3368	1.1293 0.7660 0.7466 1.2611
M Hirshfeld X(1) Hirshfeld $\Delta[X(1) Hirsh]^b$ X(2) Hirshfeld B Hirshfeld	0.1330 -0.0497 0.2606 -0.2529 0.0347	0.103 -0.3103 -0.2629	0.3238 -0.0825 <i>0.2846</i> -0.3118 0.0230	0.2960 -0.3671 -0.3099	0.0410 -0.0319 0.2885 	0.0080 -0.3204	0.0668 -0.0114 <i>0.2546</i> -0.1931 0.0430	0.0394 -0.2660 -0.2027	0.0180 -0.1448 0.1262 0.0847	-0.0221 -0.2710
MXY Hirshfeld L Hirshfeld $\Delta[L Hirsh]^c$	-0.2076 0.2077 -0.1462	-0.3537 0.3539	-0.2107 0.2112 -0.1427	-0.3537 0.3539	-0.0449 0.0449 -0.1207	-0.1652 0.1656	-0.2412 0.2418 -0.1533	-0.3949 0.3951	-0.1231 0.1238 -0.0600	-0.1832 0.1838
$\Delta E_{\rm int} \\ \Delta (\Delta E_{\rm int}) \\ \Delta E_{\rm orb} \\ \Delta (\Delta E_{\rm orb})$	-573 -80 -1030 -274	-493 -756	-491 -108 -905 -322	-383 -583	-477 -110 -810 -294	-367 -516	-455 -30 -880 -163	-425 -718	-368 -19 -605 -102	-348 -503
ΔE_{elec} $\Delta (\Delta E_{elec})$ ΔE_{Pauli} $\Delta (\Delta E_{Pauli})$	-1344 -192 1801 387	-1152 1414	-1102 -233 1516 448	-869 1068	-982 -198 1315 382	-784 933	-1258 -101 1684 234	-1157 1450	-877 -85 1115 168	-792 947

Table 5 Mayer bond orders (MBO), Hirshfeld charges, and energy decomposition analysis data for complexes **1B–5B** and **1H–5H**. Hirshfeld charges for MXY and L are from fragment analysis $[X = X(1), Y = X(2) \text{ or CO}, L = TXPB \text{ or } TXPH]^{27}$

 ΔE_x in kJ mol⁻¹. ΔE_{int} = total interaction energy; ΔE_{orb} = orbital mixing energy; ΔE_{elec} = electrostatic interaction energy; ΔE_{Pauli} = Pauli repulsion energy; $\Delta(\Delta E_x) = \Delta E_x$ (TXPB complex) – ΔE_x (TXPH analogue). ^{*a*} Δ [M–X(1)] = [(M–X(1) distance in TXPH complex/M–X(1) distance in TXPB analogue)*100] – 100. ^{*b*} Δ [X(1) Hirshfeld' for TXPB complex–'X(1) Hirshfeld' for TXPH analogue. ^{*c*} Δ [L Hirsh] = 'L Hirshfeld' for TXPB complex–'L Hirshfeld' for TXPH analogue.

-19 kJ mol⁻¹ in **4B** and **5B**. In chloro TXPB complexes, the larger contribution (relative to iodo TXPB complexes) from B-X bonding to the total interaction energy arises from significantly more negative orbital mixing and electrostatic terms, which are partially offset by a larger Pauli repulsion term. The presence of a significantly stronger B-X interaction in the chloro complexes relative to the iodo complexes is commensurate with the experimentally determined ¹¹B NMR chemical shifts, B-X distances, and C-B-C angles. The relative weakness of the B-I interactions in **4B** and **5B** is consistent with the poor match between a fairly hard borane Lewis acid and a soft iodide anion. Indeed, [NBu₄] [BI₄] is reported to be extremely labile,²⁸ [NEt₄][BI₄] is proposed to ionize to $[NEt_4]^+$, $[BI_2(NCMe)_2]^+$ and I^- (2 equiv.) upon dissolution in acetonitrile,²⁹ in the reaction of BPh₃ with [NEt₄]I in CH₂Cl₂, the equilibrium lies towards the reactants rather than the iodoborate salt, and $[Co(C_5H_4B^iPr_2I)]$ $(C_5H_4B^iPr_2)$] is substantially dissociated to $[Co(C_5H_4B^iPr_2)_2]$ I in reported, as has [C₇H₇][PhBI₃].³⁴

Conclusions

The chloro TXPB complexes **1B**, **2B** and **3B** exhibit strong $M-Cl(1)-BR_3$ bridging interactions, resulting in B-Cl(1) distances that are only 0.04–0.22 Å longer than those reported for chloroborate complexes, significant pyramidalization at boron, and approx. 60 ppm shifts in the ¹¹B NMR signal to lower

frequency than free TXPB. By contrast, TXPB iodo complexes 4B and 5B display B-I(1) distances that are roughly 0.5 Å longer than those reported for iodoboranes, only slight pyramidalization at boron, and ¹¹B NMR signals that are shifted 10-20 ppm to lower frequency than free TXPB. Structural, spectroscopic and/or computational comparison of TXPB complexes 1B-5B with TXPH complexes 1H-5H allowed for more detailed analysis of the M-X(1)-BR3 interactions in TXPB complexes. Crystallographically and computationally determined M-X(1) and M-X(2) bond lengths revealed that the differing transinfluence of PAr₃ and SAr₂ donors plays a major role in the elongation of M-X(1) bonds relative to M-X(2) bonds. However, in all the TXPB complexes, borane-coordination does result in reduced M-X(1) Mayer bond orders and smaller Hirshfeld charges on X(1) relative to the TXPH analogues. Energy decomposition analysis using MX₂ or MX(CO) and TXPB or TXPH fragments revealed a larger contribution from B-X bonding to the total interaction energy in chloro TXPB complexes, relative to iodo TXPB complexes; ΔE_{int} (TXPB complex)- ΔE_{int} (TXPH_complex) is -80 to -110 kJ mol⁻¹ in **1B**-**3B** vs. -30 and -19 kJ mol⁻¹ in **4B** and **5B**. The larger contribution in chloro complexes arises from significantly more negative orbital mixing and electrostatic terms, which are partially offset by a larger Pauli repulsion term. The presence of a significantly stronger B-X interaction in the chloro complexes relative to the iodo complexes is consistent with the trends in B-X Mayer bond order, ¹¹B NMR chemical shift, irreversible peak potentials from cyclic voltammetry, B-X distance, and C-B-C angle.



Fig. 5 SCF deformation density isosurfaces from fragment analysis of (a) chloro complex **1B** and (b) iodo complex **4B**. Blue represents increased electron density and red represents depleted electron density, relative to the constituent MX_2 and TXPB fragments (isosurfaces are set to 0.003).

Experimental section

General details

An argon-filled MBraun UNIIab glove box equipped with a -30 °C freezer was employed for the manipulation and storage of the TXPB ligand and its complexes, and reactions were performed on a double manifold high vacuum line using

standard techniques.³⁵ A Fisher Scientific Ultrasonic FS-30 bath was used to sonicate reaction mixtures where indicated. Residual oxygen and moisture was removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.

Anhydrous CH₂Cl₂ was purchased from Aldrich. Hexanes and toluene were initially dried and distilled at atmospheric pressure from CaH₂ and Na, respectively. Unless otherwise noted, all proteo solvents were stored over an appropriate drying agent (toluene, benzene = Na/Ph₂CO; hexanes = Na/Ph₂CO/tetraglyme; CH₂Cl₂ = CaH₂) and introduced to reactions *via* vacuum transfer with condensation at -78 °C. The deuterated solvents CD₂Cl₂ and C₆D₅Br (ACP Chemicals) were dried over CaH₂. [PdCl₂(COD)], [PtCl₂(COD)] and [Ptl₂(COD)] were purchased from Strem Chemicals. [{RhCl(CO)₂}₂] and 'BuLi (1.7 M in pentane) were purchased from Sigma-Aldrich. Prior to use, 'BuLi solutions were titrated with *N*-benzylbenzamide (Aldrich) at -45 °C.³⁶ The compounds TXPBr and TXPB were prepared as previously described.⁷

NMR spectroscopy (¹H, ¹³C{¹H}, DEPT-135, DEPTq, COSY, HSQC, HMBC) was performed on Bruker DRX-500 and AV-600 spectrometers. All ¹H NMR and ¹³C NMR spectra were referenced relative to SiMe₄ through a resonance of the employed deuterated solvent or proteo impurity of the solvent; CD_2Cl_2 (5.32 ppm), C_6D_5Br (δ 7.30, 7.02, 6.94 ppm) for ¹H NMR, and CD_2Cl_2 (54.0 ppm), C_6D_5Br (δ 130.9, 129.3, 126.1, 122.3 ppm) for ¹³C NMR. Herein, numbered proton and carbon atoms refer to the positions of the xanthene backbone in the TXPB or TXPH ligands (see Schemes 1 and 3).

Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyser and IR spectra were recorded on a Bio-Rad FTS-40 FTIR instrument. Cyclic voltammetry (CV) studies were carried out using a PAR (Princeton Applied Research) model 283 potentiostat (using PAR PowerCV software) in conjunction with a three-electrode cell under an argon atmosphere. The auxiliary electrode was a platinum wire, the pseudo-reference electrode a silver wire, and the working electrode a platinum disc (1.6 mm diameter, Bioanalytical Systems). Solutions were 1×10^{-3} M in test compound and 0.1 M in [NⁿBu₄][PF₆] as the supporting electrolyte in CH₂Cl₂. In all



Fig. 6 Graphs of (a) ΔE_{int} , (b) ΔE_{orb} , (c) ΔE_{elec} , and (d) ΔE_{Pauli} from energy decomposition analysis of complexes **1B–5B** and **1H–5H** using MX₂, MX(CO), TXPB and TXPH fragments in conformations corresponding to those in each complex. Double headed arrows are provided for graphical comparison of the magnitude of ΔE_x (TXPB_complex)– ΔE_x (TXPH_complex) (x = int, orb, elec or Pauli) between chloro and iodo complexes.

experiments, potentials were calibrated by addition of [FeCp*₂]; the $E_{1/2}$ value for [FeCp*₂]^{0/+1} is -0.07 V vs. the SCE.³⁷

Single-crystal X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on either: (a) a P4 diffractometer with a Bruker Mo rotating-anode generator and a SMART1K CCD area detector, or (b) a SMART APEX II diffractometer with a 3 kW sealed tube Mo generator, both in the McMaster Analytical X-Ray (MAX) Diffraction Facility. In all cases, non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated in ideal positions and then updated with each cycle of refinement. The following groups were rotationally or positionally disordered over two positions: (a) one of the *tert*-butyl substituents in 1B·2CH₂Cl₂, (b) both molecules of CH₂Cl₂ in **1B**·2CH₂Cl₂, (c) one of the *tert*butyl substituents in $2B \cdot 2CH_2Cl_2$, (d) both molecules of CH_2Cl_2 in $2B \cdot 2CH_2Cl_2$, (e) both of the *tert*-butyl substituents in 2H·2CH₂Cl₂, (f) one of the *tert*-butyl substituents in **4H** \cdot 1.5CH₂Cl₂, and (g) one molecule of CH₂Cl₂ in 4H·1.5CH₂Cl₂; the other half molecule of CH₂Cl₂ was SQUEEZED from this lattice due to unresolvable disorder.³⁸

In all cases, disorder was modelled allowing occupancy and positional parameters to refine freely. All tert-butyl methyl groups in cases (a), (c), (e) and (f) above were restrained to have equivalent thermal parameters, and were refined anisotropically. The quaternary carbon-methyl carbon bond distances within the disordered *tert*-butyl substituents in **1B**·2CH₂Cl₂, **2B**·2CH₂Cl₂, 2H·2CH₂Cl₂, and 4H·1.5CH₂Cl₂ were restrained to approximately 1.54 Å. In addition, the C_{methyl}-C-C_{methyl} bond angles in the disordered tert-butyl substituent in 1B·2CH2Cl2 were restrained to approximately 109.5°. For cases (a), (c), and (f), the disorder found within each of the modelled tert-butyl substituents was equal to 0.59(1), 0.637(5), and 0.41(1), respectively. For case (e), the disorder found within the tert-butyl substituents was 0.46(3) (C16-C19) and 0.14(1) (C20-C23). The carbonchlorine bond distances in molecules of CH2Cl2 found in 1B·2CH₂Cl₂, 2B·2CH₂Cl₂, 4B·1.31CH₂Cl₂ and 4H·1.5CH₂Cl₂ were restrained to approximately 1.77 Å. For cases (b), (d) and (g), CH_2Cl_2 carbon and chlorine atoms were restrained to have equivalent thermal parameters, respectively. For case (b), CH₂Cl₂ carbon and chlorine atoms were refined using the ISOR command; unrestrained anisotropic refinement of the CH2Cl2 molecules resulted in unstable refinement of the carbon atoms. The disorder for each molecule of CH_2Cl_2 in case (b) is 0.56(2) (C48, Cl3, Cl4) and 0.60(3) (C49, Cl5, Cl6). For case (d), the CH₂Cl₂ carbon and chlorine atoms were refined anisotropically, and the disorder for each molecule of CH₂Cl₂ is 0.46(6) (C48, Cl3, Cl4) and 0.43(1) (C49, Cl5, Cl6). For case (g), one molecule of CH_2Cl_2 [disorder = 0.39(1)] was refined using the ISOR command because unrestrained anisotropic refinement resulted in unstable refinement for the carbon atom. Both molecules of CH_2Cl_2 in **4B**·1.31 CH_2Cl_2 were refined with partial occupancy [0.60(1) for C48, Cl1, Cl2; 0.70(1) for C49, Cl3, Cl4]. Positional disorder throughout 4B·1.31CH₂Cl₂ and 4H·1.5CH₂Cl₂ was resolved by applying similar constraints to the thermal parameters.

[PtCl₂(TXPB)]·hexane (1B)

A solution of [PtCl₂(COD)] (52 mg, 1.39×10^{-4} mol) and TXPB (100 mg, 1.46×10^{-4} mol) in CH₂Cl₂ (10 mL) was

stirred at room temperature for 1 h. The resulting solution was evaporated to dryness in vacuo leaving an oily orange solid to which hexanes (15 mL) was added. After sonication for 30 min, the mixture was filtered to collect a peach solid, which was washed with hexanes (\times 1) and dried *in vacuo*. Yield = 78 mg (59%). ¹H NMR (CD₂Cl₂): δ 7.83 (s, 1H, CH¹), 7.77 (m, 1H, Ph), 7.63-7.59 (broad m, 1H, Ph), 7.60 (m, 1H, CH⁸), 7.57-7.48 (m, 3H, Ph), 7.38-7.12 (m, 15 H, Ph), 7.25 (d, J 11 Hz, 1H, CH^3), 7.13 (s, CH^6), 2.17, 1.55 (broad s, 2 × 3H, CMe_2), 1.25 (s, 9H, C²CMe₃), 1.17 (s, 9H, C⁷CMe₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 155.05 (s, C²CMe₃), 151.58, 149.43 (broad s, $C^5 \& ipso-BPh_2$), 151.01 (s, C^7CMe_3), 150.50 (s, C^{12}), 145.84 (d, *J* 12 Hz, C^{10}), 140.96 (s, C^{13}), 137.86 (s, C^{11}), 135.9, 135.2, 134.6, 134.1, 133.0, 132.9, 129.7, 129.2, 127.5, 127.4, 127.4, 126.7 (s, $12 \times Ph$), 133.97 (s, CH^6), 131.65 (d, J 66 Hz, C^4), 129.20 (s, CH³), 127.11 (s, CH¹), 121.17 (s, CH⁸), 43.03 (s, CMe_2), 35.64 (s, C² CMe_3), 35.28 (s, C⁷ CMe_3), 31.42 (s, 2 × CMe₃), 28.36, 26.19 (s, 2 × CMe₂). ³¹P{¹H} (CD₂Cl₂): δ + 32.48 (s, ${}^{1}J_{P,195Pt}$ 3836 Hz). ${}^{11}B$ (CD₂Cl₂): δ 3 (broad s). Anal. calcd for C₅₃H₆₂PSBCl₂Pt: C, 61.27; H, 6.01. Found: C, 61.33; H, 5.47%.

[PtI₂(TXPB)] (4B)

A solution of [PdI₂(COD)] (37 mg, 6.64×10^{-4} mol) and TXPB (55 mg, 8.01×10^{-5} mol) in CH₂Cl₂ (10 mL) was stirred at room temperature for 30 min. The resulting solution was evaporated to drvness in vacuo leaving an orange solid to which hexanes (10 mL) was added. After sonication, the mixture was filtered to collect an orange solid, which was washed with hexanes and dried in vacuo. Yield = 55 mg (73%). ¹H NMR (CD_2Cl_2) : δ 7.84 (s, 1H, CH^1), 7.78 (d, J 2 Hz, 1H, CH^8), 7.54-7.45 (m, 6H, p-PPh2 & m-PPh2), 7.43-7.36 (m, 8H, o- PPh_2 and BPh_2), 7.25 (dd, J = 9, 2 Hz, 1H, CH^3), 7.05–6.97 (m, 6H, BPh₂), 6.98 (d, J 2 Hz, CH⁶), 2.03 (broad s, 6H, CMe₂), 1.25 (s, 9H, C^2CMe_3), 1.16 (s, 9H, C^7CMe_3). ¹³C{¹H} NMR (CD_2Cl_2) : δ 154.98 (s, C^2CMe_3), 150.26 (s, C^7CMe_3), 146.92 (broad s, C⁵), 146.35 (d, J 12 Hz, C¹⁰), 145.99 (broad s, ipso-BPh₂), 143.36 (s, C¹³), 139.71 (d, J 22 Hz, C¹¹), 138.70 (s, BPh₂), 134.95 (d, J 11 Hz, m-PPh₂), 134.00 (CH⁶), 132.30 (d, J 61 Hz, ipso-PPh₂), 132.23 (s, p-PPh₂), 129.64 (s, C¹²), 129.09 (s, BPh₂), 129.01 (s, CH³), 128.77 (d, J 12 Hz, m-PPh₂), 127.41 (s, BPh₂), 126.88 (s, CH¹), 123.41 (s, CH⁸), 44.01 (s, CMe₂), 35.58 (s, C^2CMe_3), 35.27 (s, C^7CMe_3), 31.48 (s, C^2CMe_3), 31.40 (s, C^7CMe_3), 27.01 (s, CMe_2). ³¹P{¹H} (CD₂Cl₂): δ 41.61 $({}^{1}J_{P,195Pt} 3517 \text{ Hz})$. ${}^{11}B$ (CD₂Cl₂): δ 50 ppm (broad s). Anal. calcd for C₄₇H₄₈PSBI₂Pt: C, 49.72; H, 4.26. Found: C, 49.43; H, 4.51%.

TXPH ligand

A 1.81 M solution of *tert*-butyl lithium in pentane (1.8 mL, 3.32 mmol) was added to a solution of TXPBr (1.00 g, 1.66 mmol) in toluene (60 mL) at -78 °C, and the mixture was allowed to warm to room temperature over 12 h. The resulting yellow solution was cooled to -78 °C and N₂-saturated MeOH (0.2 mL, 4.9 mmol) was added dropwise. After stirring for 10 min at -78 °C and 20 min at room temperature, the mixture

was evaporated to dryness in vacuo. Hexanes (30 mL) was then added, and the mixture was sonicated before filtration to collect a white solid, which was washed with hexanes $(\times 1)$ and evaporated to dryness in vacuo. Yield 765 mg (88%). ¹H NMR (CD_2Cl_2) : δ 7.55 (m, 2H, CH^1 & CH^8), 7.38–7.35 (m, 6H, o– PPh₂ and p-PPh₂), 7.31 (app. t d, J 7, 2 Hz, 4H, m-PPh₂), 7.29 (d, J 8 Hz, 1H, CH⁵), 7.19 (dd, J 8, 2 Hz, 1H, CH⁶), 6.72 (dd, J 4, 2 Hz, 1H, CH^3), 1.72 (s, 6H, CMe₂), 1.27 (d, ${}^{2}J_{H,P}$ 8 Hz, 9H, PMe₃), 1.32 (s, 9H, $C^{7}CMe_{3}$), 1.12 (s, 9H, $C^{2}CMe_{3}$). ¹³C{¹H} NMR (CD₂Cl₂): δ 150.38 (s, C^7 CMe₃), 149.49 (s, C^2 CMe₃), 143.03 (s. C¹⁰), 142.82 (s, C¹³), 137.21 (d, J 11 Hz, ipso-PPh₂), 135.99 (d, J 28 Hz, C^{11}), 135.24 (d, J 9 Hz, C^4), 134.52 (d, J 20 Hz, m-PPh₂), 130.34 (d, J 9 Hz, C¹²), 129.4–129.0 (s, p-PPh₂ & d, o-PPh₂), 128.74 (s, CH³), 127.52 (s, C⁵), 123.69 (s, CH⁶), 122.76 (s, CH^1), 121.97 (s, CH^8), 41.50 (s, CMe_2), 35.27 (s, 2 × CMe_3), 31.74 (s, C⁷C Me_3), 31.45 (s, C²C Me_3), 25.32 (s, C Me_2). ${}^{31}P{}^{1}H{}$ (CD₂Cl₂): $\delta - 8.26$ (s). Anal. calcd for C₃₅H₃₉PS: C, 80.42; H, 7.52. Found: C, 80.18; H, 7.50%.

[PtCl₂(TXPH)] (1H)

A solution of [PtCl₂(COD)] (72 mg, 1.91×10^{-4} mol) and TXPH (100 mg, 1.91×10^{-4} mol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 1 h. The resulting yellow solution was evaporated to dryness in vacuo leaving a yellow solid to which benzene (15 mL) was added. After sonication, the mixture was filtered to give a pale yellow solid which was washed with benzene and dried *in vacuo*. Yield = 70 mg (43%). ¹H NMR (CD_2Cl_2) : δ 8.78 (d, J 8 Hz, 1H, CH⁵), 7.88 (dd, J 12, 8 Hz, 2H, o-PPh₂ A), 7.80 (s, 1H, CH¹), 7.67 (dd, J 13, 8 Hz, 2H, o-PPh₂ B), 7.64 (s, 1H, CH⁸), 7.63 (t, J 8 Hz, 1H, p-PPh₂ A), 7.56 (app. t, J 6 Hz, 2H, m-PPh₂ A), 7.50 (t, J 7 Hz, 1H, p-PPh₂ B), 7.43 (d, J 10 Hz, 1H, CH⁶), 7.40 (d, J 9 Hz, 1H, CH³), 2.13, 1.74 (s, $2 \times 3H$, CMe₂), 1.35, 1.26 (s, $2 \times 9H$, CMe₃). ¹³C{¹H} NMR $(CD_2Cl_2): \delta$ 155.45 (d, J 7 Hz, C²CMe₃), 152.78 (s, C⁷CMe₃), 146.53 (d, J 12 Hz, C¹⁰), 143.35 (s, C¹³), 139.09 (d, J 20 Hz, C¹¹), 134.55 (d, J 12 Hz, o-PPh₂ B), 134.43 (d, J 11 Hz, o-PPh₂ A), 132.79 (s, *p*-P*Ph*₂ A & B), 131.69 (d, *J* 65 Hz, *C*⁴ or *ipso*-PPh₂), 130.22 (s, CH⁵), 129.49 (d, J 12 Hz, m-PPh₂ A), 129.30 (d, J 12 Hz, m-PPh₂ B), 128.55 (s, CH³), 127.59 (s, CH¹), 125.86 (s, C¹²), 125.00 (s, CH⁶), 123.15 (s, CH⁸), 43.71 (s, CMe_2), 35.68 (s, C^2CMe_3), 35.55 (s, C^7CMe_3), 31.58 (s, $C^{7}CMe_{3}$), 31.45 (s, $C^{2}CMe_{3}$), 26.56, 26.05 (s, 2 × CMe_{2}). ³¹P {¹H} (CD₂Cl₂): δ + 38.60 (s, ¹J_{P195Pt} 3458 Hz). Anal. calcd for C₃₅H₃₉PS: C, 53.30; H, 4.98. Found: C, 53.05; H, 5.27%.

[PdCl₂(TXPH)]·0.5C₆H₆ (2H·0.5C₆H₆)

A solution of [PdCl₂(COD)] (52 mg, 1.82×10^{-4} mol) and TXPH (100 mg, 1.91×10^{-4} mol) in CH₂Cl₂ (10 mL) was stirred at room temperature for 1 h. The resulting orange solution was evaporated to dryness *in vacuo* leaving a bright yellow solid to which benzene (10 mL) was added. After sonication, the mixture was filtered to give a pale yellow solid, which was washed with benzene and dried *in vacuo*. Yield = 98 mg (77%). ¹H NMR (C₆D₅Br, 60 °C): δ 9.38 (d, J 7 Hz, 1H, CH⁵), 7.74 (broad s, 5H, CH¹ & *o*-PPh₂), 7.53 (s, 1H, CH⁸), 7.29 (s, 1H, CH³), 7.14 (m, 3H, CH⁶ & *p*-PPh₂), 7.04 (broad s, *m*-PPh₂),

1.69 (s, 6H, CMe_2), 1.18 (s, 9H, C^7CMe_3), 1.08 (s, 9H, C^2CMe_3). ${}^{13}C{}^{1}H$ NMR (C_6D_5Br , 60 °C): δ 154.29 (s, C^2CMe_3), 152.82 (s, C^7CMe_3), 146.46 (d, J 12 Hz, C^{10}), 142.11 (s, C^{13}), 137 (C^{11}), 133.85 (d, J 11 Hz, o-PP h_2), 131.89 (s, p-PP h_2), 130.82 (s, CH^5), 128.5 ($CH^3 \& m$ -PP h_2), 126.40 (s, CH^1), 125.23 (s, C^{12}), 124.69 (s, CH^6), 122.06 (s, CH^8), 42.63 (s, CMe_2), 34.88 (s, C^2CMe_3), 34.70 (s, C^7CMe_3), 31.04 (s, C^7CMe_3), 30.85 (s, C^2CMe_3), 26.60 (s, CMe_2). ${}^{31}P{}^{1}H{}$ (CD_2Cl_2): δ + 61.42 (s). Anal. calcd for $C_{38}H_{42}PSCl_2Pd$: C, 62.77; H, 5.82. Found: C, 63.11; H, 5.67%.

[RhCl(CO)(TXPH)] (3H)

A mixture of [{Rh(μ -Cl)(CO)₂}₂] (35 mg, 9.00 × 10⁻⁵ mol) and TXPH (100 mg, 1.91×10^{-4} mol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 1 h. At this temperature, CO was evolved, and the mixture was then warmed to room temperature and stirred for 1 h. The resulting orange solution was evaporated to dryness in vacuo to give an orange solid to which hexanes (15 mL) was added. After sonication, the mixture was filtered to give a mustard yellow solid which was washed with hexanes and dried *in vacuo*. Yield = 98 mg (79%). ¹H NMR (CD₂Cl₂): δ 8.85 $(d, J 8 Hz, 1H, CH^5)$, 7.79 (s, 1H, CH^1), 7.67 (dd, J 12, 8 Hz, 4H, o-PPh₂), 7.62 (s, 1H, CH⁸), 7.50 (t, J 7 Hz, 2H, p-PPh₂), 7.44 (app. t, J 8 Hz, 4H, m-PPh₂), 7.40 (d, J 9 Hz, 1H, CH³), 7.35 (d, J 8 Hz, 1H, CH⁶), 1.86 (s, 6H, CMe₂), 1.33, 1.24 (s, 2 × 9H, CMe₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 185.99 (dd, ¹J_{C,Rh} 78, $^{2}J_{C,P}$ 16 Hz, RhCO), 153.58 (s, $C^{2}CMe_{3}$), 152.77 (s, $C^{7}CMe_{3}$), 146.11 (d, J 13 Hz, C¹⁰), 143.24 (s, C¹³), 136.85 (d, J 27 Hz, C¹¹), 134–133 (C⁴ & ipso-PPh₂), 133.57 (d, J 12 Hz, o-PPh₂), 131.70 (s, *p*-PP*h*₂), 129.67 (s, *C*⁵), 129.39 (d, *J* 11 Hz, *m*-PP*h*₂), 128.33 (s, CH³), 127.33 (s, C¹²), 126.36 (s, CH¹), 124.70 (s, CH⁶), 122.75 (s, CH⁸), 42.86 (s, CMe₂), 35.65 (s, C²CMe₃), 35.48 (s, C^7CMe_3), 31.62 (s, C^7CMe_3), 31.49 (s, C^2CMe_3), 25.91 (s, CMe₂). ³¹P{¹H} (CD₂Cl₂): δ + 69.52 (d, ¹J_{PRh} 148 Hz). Anal. calcd for C₃₆H₃₉OPSClRh: C, 62.75; H, 5.70. Found: C, 62.70; H, 5.99%.

[PtI₂(TXPH)]·0.5 toluene (4H·0.5 toluene)

A solution of [PtI₂(COD)] (128 mg, 2.30×10^{-4} mol) and TXPH (120 mg, 2.30×10^{-4} mol) in CH₂Cl₂ (10 mL) was stirred at room temperature for 1 h and then evaporated to drvness in vacuo. The residue was then sonicated in toluene (5 mL), and filtered to collect a pale yellow powder. Yield = 141 mg (60%). ¹H NMR (CD₂Cl₂): δ 8.66 (d, J 8 Hz, 1H, CH⁵), 7.86, 7.70 (v. broad s, 2×2 H, *o*-P*Ph*₂), 7.75 (s, 1H, C*H*¹), 7.61 (s, 1H, CH^8), 7.59, 7.47 (v. broad s, 2 × 1H, p-PPh₂), 7.49 (v. broad s, 4H, m-PPh₂), 7.39-7.33 (m, 2H, CH³ & CH⁶), 2.12, 1.81 (s, $2 \times 3H$, CMe_2), 1.34 (s, 9H, C^7CMe_3), 1.22 (s, 9H, $C^{2}CMe_{3}$). ¹³C{¹H} NMR (CD₂Cl₂): δ 155.50 (s, $C^{2}CMe_{3}$), 153.43 (s, C^7CMe_3), 146.2 (s, C^{10}), 143.58 (s, C^{13}), 139.77 (d, J 23 Hz, C¹¹), 134.91 (d, J 11 Hz, o-PPh₂), 133.13 (d, J 60 Hz, C⁴ or ipso-PPh₂), 132.60 (s, p-PPh₂), 132.36 (s, CH⁵), 129.09 (d, J 12 Hz, m-PPh₂), 128.30 (s, CH³), 127.44 (s, CH¹), 126.01 (s, C¹²), 124.66 (s, CH⁶), 123.28 (s, CH⁸), 43.81 (s, CMe₂), 35.62 (s, C^2CMe_3), 35.54 (s, C^7CMe_3), 31.58 (s, C^7CMe_3), 31.46 (s, $C^{2}CMe_{3}$, 26.28 (s, 2 × CMe_{2}). ³¹P{¹H} (CD₂Cl₂): δ + 47.36 (s, ${}^{1}J_{P,195Pt}$ 3249 Hz). Anal. calcd for C_{38.5}H₄₃PSI₂Pt: C, 45.44; H, 4.26. Found: C, 45.45; H, 4.33%.

DFT calculations

All structures were fully optimized with the ADF DFT package (SCM, version 2010.02).³⁹ The adiabatic local density approximation (ALDA) was used for the exchange-correlation kernel⁴⁰ and the differentiated static LDA expression was used with Vosko-Wilk-Nusair (VWN) parameterization.41 All geometry optimizations were conducted using the zero-order regular approximation (ZORA)⁴² for relativistic effects, and were gradient corrected using the exchange and correlation functionals of Perdew and Wang (PW91).43 Geometry optimizations were initially conducted using a double- ζ basis set with one polarization function (DZP) and a medium core, followed by a triple- ζ all-electron basis set with two polarization functions (TZ2P). Crystallographically determined geometries were used as the starting point for calculations on 1B-5B, 2H and 4H (for 2B, the structure from 2B·2CH₂Cl₂ was used). Geometry optimized structures of 1B and 3B were used as the starting point for calculations on 1H and 3H (after replacement of the BPh₂ group in the TXPB complexes with a hydrogen atom).

Bonding was analysed in more detail using a fragment approach that considered the interaction of an uncharged MXY $[MXY = PtCl_2, PdCl_2, RhCl(CO), PtI_2 \text{ or } RhI(CO)]$ fragment with a neutral TXPB or TXPH ligand (fragments were generated from the TZ2P geometry optimized structures of each complex). Hirshfeld charges,²⁶ SCF deformation density isosurfaces and energy decomposition analyses⁴⁴ were employed to further probe the nature of metal-ligand and boron-halide bonding. Deformation density maps were computed by subtracting the sum of the SCF electron density for the two fragments (maintained at their optimized positions) from the SCF electron density for the complex. The resulting isosurfaces illustrate the electronic reorganization that occurs upon interaction between the two fragments to form the complex. Mayer bond orders^{25,45} were obtained using the ADF keyword EXTENDEDPOPAN. Visualization of the computational results was performed using the ADF-GUI (SCM) or Discovery Studio Visualizer (Accelrys).

Acknowledgements

D. J. H. E. thanks NSERC of Canada for a Discovery Grant, Canada Foundation for Innovation and Ontario Innovation Trust for New Opportunities Grants, and Ontario Centers of Excellence for an Early Researcher Award. B. E. C. thanks the Government of Ontario for an Ontario Graduate Scholarship and NSERC of Canada for a PGS-D award.

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