Metallaboratranes: Tris(methimazolyl)borane Complexes of Rhodium(I)

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The syntheses and reactivity of the first rhodaboratranes, [RhX(PPh$_3$){B(mt)$_3$}] (X = Cl, H) and [Rh(η^4-C$_8$H$_{12}$){B(mt)$_3$}]Cl, are described in detail together with preliminary investigations of the mechanistic processes involved. The subsequent exploitation and circumvention of the lability of [RhCl(PPh$_3$){B(mt)$_3$}] in the synthesis of a range of isonitrile, [Rh(CNR)(PPh$_3$){B(mt)$_3$}]Cl (R = ^{t}Bu, C$_6$H$_3$Me$_2$-2,6, C$_6$H$_2$Me$_3$-2,4,6), phosphine, [Rh(PMe$_3$)$_n$(PPh$_3$)$_{2-n}${B(mt)$_3$}]Cl (n = 0, 1, 2), and dialkyldithiocarbamate, [Rh(S$_2$NEt$_2$){B(mt)$_3$}]Cl, complexes is described, along with the attempted synthesis of [Rh(CN^{t}Bu)$_2${B(mt)$_3$}]Cl from [Rh(η^4-C$_8$H$_{12}$){B(mt)$_3$}]Cl. Single-crystal X-ray structure determinations of [Rh(L)(L′){B(mt)$_3$}]Cl (L = CN^{t}Bu, CN(C$_6$H$_3$Me$_2$-2,6), L′ = PPh$_3$; L = L′ = PMe$_3$) are reported.

Introduction

The report of the hydrotris(methimazolyl)borate ligand by Reglinski[1] heralded a new chapter in the study of poly(azolyl)-borate compounds, in the fields of both organometallic and coordination chemistry. The HB(mt)$_3$ ligand has been mooted as a "soft analogue" of Trofimenko's ubiquitous hydrotris-(pyrazolyl)borate HB(pz)$_3$,[2] an analogy borne out to some extent by its now established affinity for the low-valent metals of groups 6−12.[3,4] The exploration of this aspect of poly-(methimazolyl)borate coordination chemistry continues apace, driven in no small part by the apparent utility of this "tamed-thiolate" ligand as a model for sulfur donors in metalloenzymes.[4] In contrast, the pursuit of complexes in which the transition metal is in a high oxidation state has been largely neglected, presumably due to a perceived incompatibility of the "soft" sulfur donor with "hard", high-valent metals, although this avenue is now being addressed by studies on the metals of groups 5 (Nb^V, Ta^V)[5] and 10 (Pt^{IV}).[6]

In an organometallic context, significant developments pertaining to this versatile ligand have also begun to emerge. The larger eight-membered chelate rings adopted in HB(mt)$_3$ML$_n$ complexes (cf. six for HB(pz)$_3$ML$_n$) and the variable hybridization at sulfur (cf. triganol pyrazolyl nitrogen donors) impart additional flexibility to the coordinated ligand, thus availing a range of novel bonding scenarios and structural motifs. Significant among these is the κ^3-*H*,*S*,*S*′ binding mode[3m,p,7] incorporating a three-center two-electron (3c-2e) B−H−M linkage, which exhibits an apparent propensity, in some instances, to undergo B−H activation. Such a process is

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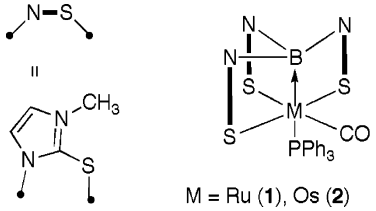
Chart 1. Metallaboratranes



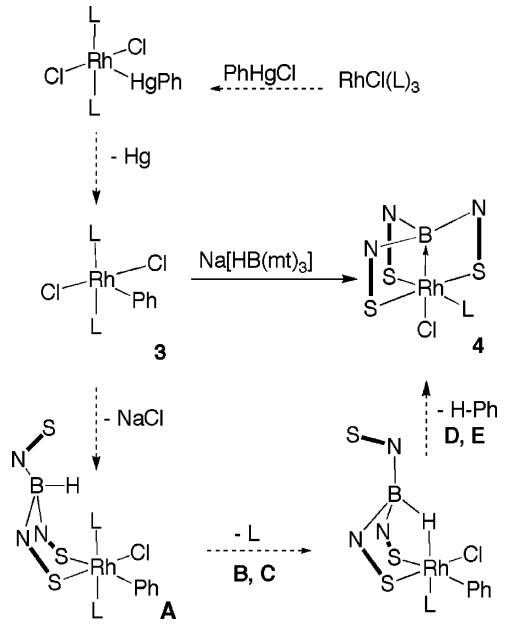
M = Ru (**1**), Os (**2**)

implicated en route to the group 8 metallaboratrane complexes $[M(CO)(PPh_3)\{\kappa^4\text{-}B(mt)_3\}]$ (*M*→*B*, Chart 1, mt = methimazolyl, M = Ru **1**,[7a] Os **2**[8]), which comprise a dative metal→boron linkage, housed within a cage structure. Significantly, these were the first unequivocally authenticated examples of transition-metal 2c-2e borane complexes, the existence of metal→boron dative bonding, though long postulated,[9,10] having fallen into question with the discovery that early examples had been incorrectly formulated.[11,12]

The structures of **1** and **2** are based upon tricyclo[3.3.3.0] cages, in which the transannular *M*→*B* bond is subtended by three methimazolyl buttresses. It has thus far been our interpretation of the bonding in these complexes that the buttresses impose a monovacant octahedral geometry at the d^8 metal center, precluding relaxation of the $d^8\text{-}ML_5$ fragment to more conventional trigonal-bipyramidal or, via ligand dissociation, square planar $d^8\text{-}ML_4$ structures. A "lone-pair" of electrons is thus housed in a metal-based orbital of σ symmetry (sp^3d^2 type), which is necessarily oriented toward, and accommodated by, the Lewis acidic bridgehead boron(III) atom. One can thus envisage that the propensity for attaining the metallaboratrane motif is intrinsically linked not only to the d electron count—since only for a minimum d^8 configuration would such an orbital be occupied—but also to the relative basicity of this metal lone-pair. This basicity will in turn be a function of metal oxidation state, overall charge, and the ancillary ligand set. Our exploration of the first two of these influences has led to metallaboratranes from groups 9 (Rh^I, Ir^I)[13,14] and 10 (Pt^0, Pt^{II})[15]—including both neutral and cationic examples—thereby illustrating a degree of generality for the metallaboratrane motif with respect to d^8 and d^{10} metals, with apparently limited dependence upon oxidation state and charge. However, the influence exerted by ancillary ligands is a somewhat more complex issue that we are only now beginning to explore.

These three factors are inextricably linked and might be expected to influence both the propensity to attain a metallaboratrane motif and subsequently its relative stability and/or reactivity. A full understanding of each, and the inherent character of the metallaboratrane cage, thus calls for a systematic investigation. Herein, we describe the first such study, with the report of the synthesis of a family of rhodium-based metallaboratranes. Further, we discuss the factors involved in their formation and their inherent reactivity and outline the early indications in relation to the mutual influences between the metallaboratrane fragment and ancillary ligands. Aspects of this work have formed the basis of a preliminary communication.[13]

Scheme 1. Formation of the Rhodaboratrane 4 (L = PPh_3)



Results and Discussion

The group 8 metallaboratranes **1** and **2** (Chart 1) were originally obtained from the reaction between the hydrotris(methimazolyl)borate salt $Na[HB(mt)_3]$ and the organometallic complexes $[MRCl(CO)(PPh_3)_{2,3}]$ (M = Ru, Os; R = aryl, vinyl, hydrido), wherein the σ-organyl or hydride ligands ultimately serve as hydrogen acceptors.[7a,8] The synthesis of a rhodaboratrane, isoelectronic with **1** and **2**, thus required a rhodium(III) σ-organyl, to which end the complex $[Rh(C_6H_5)Cl_2(PPh_3)_2]$ (**3**) appeared ideally suited. Since the preparation of **3** has previously been achieved only via a multistep procedure, via the curious fragmentation of an $SbPh_3$ ligand to afford the σ-phenyl function,[16] we sought a more convenient route. This was achieved by treating Wilkinson's catalyst with 1 equiv of phenylmercuric chloride in thf under reflux for 2−3 h. After separation from the deposited elemental mercury and extraction into dichloromethane, complex **3** was precipitated from the concentrated solution by the addition of excess ethanol and so obtained in high yields (60−80%) in analytically pure form. Although not investigated, this approach offers the advantage that, in principle, numerous σ-organyls might be obtained from readily available Ar−HgCl reagents, precluding the need to prepare the corresponding stibines, the analogous cleavage of which is by no means guaranteed to proceed.

The reaction between complex **3** and $Na[HB(mt)_3]$ proceeds readily in dichloromethane solution, at ambient temperature, to afford after 1 h the anticipated rhodaboratrane complex $[RhCl(PPh_3)\{B(mt)_3\}]$ (**4**, Scheme 1), which precipitates from filtered and concentrated dichloromethane solutions upon the addition of diethyl ether. Samples so obtained are, however, frequently contaminated by free triphenylphosphine, displaced from **3** during the reaction, which proved remarkably difficult to remove. However, we have found that if the reaction is performed in a 1:10 mixture of ethanol/dichloromethane, although oxidation of the free phosphine becomes prevalent under aerobic conditions, the isolated purity of **4** is significantly

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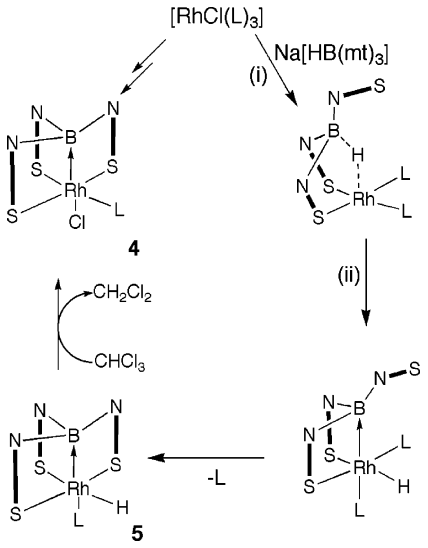
enhanced, with Ph_3PO proving more convenient to remove via fractional crystallization.

As noted in a preliminary communication,[13] the identity of **4** has been unequivocally established from analytical, spectroscopic, and crystallographic data. Most immediately indicative of the metallaboratrane structural motif is the presence in the ^1H NMR spectrum of resonances associated with two unique methimazolyl environments, i.e., two NCH_3 resonances and two imidazolyl-derived $NCH_A{=}CH_BN$ AB systems, which arise due to the conformationally locked geometry imposed upon octahedral coordination to the metal center. The retention of one PPh_3 ligand is apparent from integration of the aromatic proton resonances in the ^1H NMR spectrum and the observation in the $^{31}P\{^1H\}$ NMR spectrum of a single resonance (δ_P 28.8) exhibiting doublet multiplicity (^{103}Rh, $I = 1/2$, 100%, J_{RhP} 125.9 Hz). That the ^{31}P NMR resonance is relatively sharp (hhw 8 Hz) implies that the phosphine ligand lies *cis* to the metal−boron linkage, since a *trans* disposition routinely effects significant broadening of the resonance due to an enhanced interaction with the boron quadrupole. In the present case, this precludes direct spectroscopic verification of the Rh−B interaction, since the breadth of the $^{11}B\{^1H\}$ NMR resonance (hhw 50 Hz) prohibits resolution of $^{103}Rh-^{11}B$ spin−spin coupling, while the paucity of metallaboratranes renders the chemical shift (δ_B 1.7) uninformative in this respect, other than being suggestive of four-coordinate boron. Notwithstanding, the Rh−B linkage can be inferred from the absence in the infrared spectrum of any absorption bands characteristic of either terminal (B−H) or bridging (B−H−Rh) borohydride functionalities, evidence for which is similarly absent from the ^1H NMR spectrum.

It is interesting to note that while the synthesis of **4** has only been reliably achieved via the outlined procedure, we have encountered small amounts during attempts to prepare the hydrotris(methimazolyl)borate complex $[Rh(PPh_3)_2\{HB(mt)_3\}]$ via the reaction between Wilkinson's catalyst and $Na[HB(mt)_3]$. While the product mixture was essentially intractable, crystals of **4**, identified both from X-ray diffraction and microanalytical data, were observed to form in modest quantities from NMR samples. Although initially a perplexing occurrence, our subsequent demonstrations[14,15] that the $HB(mt)_3$ ligand can undergo B−H activation even in the absence of a hydrogen acceptor co-ligand—that is, insertion of the metal into the B−H linkage to afford a dative $M \rightarrow B$ interaction and metal hydride—do allow us to speculate as to the origin of **4** in this instance. We suspect that the reaction between Wilkinson's catalyst and $Na[HB(mt)_3]$ (Scheme 2) affords initially a complex of the type $[Rh(PPh_3)_2\{\kappa^3\text{-}S,S',H\text{-}HB(mt)_3\}]$ (i), which is unstable toward activation of the bridging B−H linkage (ii), thus generating $[RhH(PPh_3)\{B(mt)_3\}]$ (**5**), which is isoelectronic with $[PtH(PPh_3)\{B(mt)_3\}]^+$.[15] Hydride−chloride exchange, behavior typical of hydrido complexes in chlorinated solvents, can then afford **4**, though whether this occurs via a classical radical process or is induced by adventitious HCl is unclear.

In order to verify this postulate, we sought to prepare and isolate the putative complex **5**. This goal was approached by the reaction between $[RhCl(\eta^4\text{-}C_8H_{12})(PPh_3)]$ and 1 equiv of $Na[HB(mt)_3]$ in dichloromethane, which is complete after 4 h. The complex **5** is a moderately air-stable yellow solid, identified on the basis of spectroscopic data (Table 1, Experimental Section), which reflect the characteristic signatures of a metallaboratrane, in addition to confirming the presence of the hydride and phosphine ligands. The acquisition of microanalytical data for **5** was, however, confounded by its slow, solid-state, decomposition over the course of several hours, even when

Scheme 2. Proposed Formation of the Rhodaboratrane 4 from Wilkinson's Catalyst (L = PPh_3)



stored under an inert atmosphere. Surprisingly, subsequent preparations of this material, while universally successful, have failed to allow for its isolation with complete exclusion of intractable contaminants, the removal of which is precluded by the intolerance of **5** toward conventional purification methods. However, the identity of **5** is further supported by the observation of the parent ion (*m*/*z* 716.1) and characteristic fragments in the ESI+ mass spectrum. The solution behavior of **5** in chlorinated solvents was also convincingly observed during prolonged NMR acquisitions. Over several hours, the ^1H NMR signals associated with **5** were replaced, inter alia, with resonances characteristic of the chloro-rhodaboratrane complex **4**. The complex nature of this product mixture and the trace amounts of DCl presumably present in commercial deuterochloroform are both consistent with the low yields of **4** that have been obtained in this way and, while inconclusive, do support our suggested mechanism. Moreover, we have subsequently observed a further example of B−H activation at a rhodium(I) center that is apparently followed by hydride/chloride exchange, in our reported, high-yield, synthesis of the rhodaboratrane salt $[Rh(\eta^4\text{-}C_8H_{12})\{B(mt)_3\}]Cl$ (**6·Cl**),[17] from $[RhCl(\eta^4\text{-}C_8H_{12})]_2$.

A trait common to each of the rhodaboratranes **4**−**6**$^+$ is their propensity to decompose in solution, yielding largely intractable mixtures. This is least pronounced in the case of the salt **6·Cl**, which survives for up to one week, depending upon the solvent used, while both **4** and **5** become completely intractable within a matter of hours. The processes involved in this remain unclear, although it is apparent that the lability of the ancillary ligands—rather than of the boratrane fragment—is of primary significance, the progressive loss of the phosphine from both **4** and **5** being readily observed by ^{31}P NMR spectroscopy. Where spectroscopic samples are prepared without the rigorous exclusion of air and moisture, free triphenylphosphine is rarely observed. Rather, triphenylphosphine oxide is the predominant, often exclusive, phosphorus-containing species. This would seem to imply that the $[Rh\{B(mt)_3\}]^+$ cation is an effective catalyst for the oxidation of PPh_3, given the typical reluctance of this process. Indeed, catalytic oxidation by late transition metals has been widely observed, and its kinetics thoroughly explored.[18]

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Table 1. Phosphorus-31 and Hydrogen-1 NMR Data for Rhodaboratrane Complexes[a]

complex	δ_P (J_{RhP}) [hhw]	δ_H
[RhCl(PPh$_3$){B(mt)$_3$}] (**4**)	28.8 (125.9)	3.46 (s, 6H, NCH$_3$), 3.67 (s, 3H, NCH$_3$), 6.76, 7.65 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.82, 8.10 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 7.1−7.5 (m, 15 H, C$_6$H$_5$)
[RhH(PPh$_3$){B(mt)$_3$}] (**5**)	22.9 [220]	−16.5 (dd, 1H, $^1J_{RhH}$ 16.8, $^2J_{PH}$ 3.5, RhH), 3.36 (s, 6H, NCH$_3$), 3.46 (s, 3H, NCH$_3$); 6.43, 6.56 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.69, 6.92 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 7.24−7.37 (m, 9H, C$_6$H$_5$), 7.59−7.60 (m, 6H, C$_6$H$_5$)
[Rh(PPh$_3$)(CN^{t}Bu){B(mt)$_3$}]$^+$ (**8**$^+$)	9.8 [260]	0.9 (s, 9H, CCH$_3$), 3.44 (s, 6H, NCH$_3$), 3.45 (s, 3H, NCH$_3$), 6.68, 7.61 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.95, 8.83 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 7.35−7.58 (m, 15H, C$_6$H$_5$)
[Rh(PPh$_3$)(CNXyl){B(mt)$_3$}]$^+$ (**9a**$^+$)	33.0 [112]	2.27 (s, 6H, CCH$_3$-2,6), 2.88 (s, 6H, NCH$_3$), 3.48 (s, 3H, NCH$_3$), 6.70, 7.36 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.65, 8.34 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 7.07 (m, 1H, C$_6$H$_3$), 7.09 (m, 2H, C$_6$H$_3$), 7.20−7.40 (m, 15 H, C$_6$H$_5$)
[Rh(PPh$_3$)(CNXyl){B(mt)$_3$}]$^+$ (**9b**$^+$)	9.1 [270]	1.66 (s, 6H, CCH$_3$-2,6), 3.44 (s, 6H, NCH$_3$), 3.51 (s, 3H, NCH$_3$), 6.72, 7.64 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.93, 8.74 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 6.88 (m, 1H, C$_6$H$_3$), 6.90 (m, 2H, C$_6$H$_3$); 7.27−7.31 (m, 9H, C$_6$H$_5$), 7.52−7.60 (m, 6H, C$_6$H$_5$)
[Rh(PPh$_3$)(CNMes){B(mt)$_3$}]$^+$ (**10a**$^+$)	33.3 (113.2)	1.60 (s, 6H, CCH$_3$-2,6), 2.21 (s, 3H, CCH$_3$-4), 3.49 (s, 6H, NCH$_3$), 3.51 (s, 3H, NCH$_3$), 6.68, 8.81 (s × 2, 1H × 2, NCH═CH), 6.63, 8.41 (s × 2, 2H × 2, NCH═CH), 6.69 (s, 2H, C$_6$H$_2$), 7.23−7.41 (m, 15 H, C$_6$H$_5$)
[Rh(PPh$_3$)(CNMes){B(mt)$_3$}]$^+$ (**10b**$^+$)	9.2 [260]	1.60 (s, 6H, CCH$_3$-2,6), 2.21 (s, 3H, CCH$_3$−4), 3.42 (s, 6H, NCH$_3$), 3.50 (s, 3H, NCH$_3$); 6.71, 7.63 (2 × d, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.92, 8.71 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 6.69 (s, 2H, C$_6$H$_2$), 7.27−7.32 (m, 9H, C$_6$H$_5$), 7.51−7.60 (m, 6H, C$_6$H$_5$)
[Rh(PPh$_3$)$_2${B(mt)$_3$}]$^+$ (**11**$^+$)	30.9 (127.5), 11.1 [61][b]	2.73 (s, 6H, NCH$_3$), 3.16 (s, 3H, NCH$_3$), 6.64 (s, 2H, NCH═CH), 6.76 (s, 1H, NCH═CH), 7.46−7.78 (m, 36H, NCH═CH and C$_6$H$_5$).
[Rh(S$_2$CNEt$_2$){B(mt)$_3$}] (**12**)		1.18−1.34 (m, 6H, CCH$_3$), 3.48 (s, 6H, NCH$_3$), 3.49 (s, 3H, NCH$_3$), 6.43, 6.63 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.73, 6.91 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH).
[Rh(PMe$_3$)(PPh$_3$){B(mt)$_3$}]$^+$ (**13**$^+$)	30.8 [30] (121)[c] −39.7 [300]	1.17 (d, 9 H, $^2J_{PH}$ 5.3, PCH$_3$), 2,98 (s, 6H, NCH$_3$), 3.46 (s, 3H, NCH$_3$), 6.65, 7.35 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 6.59, 8.32 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH), 7.26−7.37 (m, 15 H, C$_6$H$_5$)
[Rh(PMe$_3$)$_2${B(mt)$_3$}]$^+$ (**14**$^+$)	0.2 (117.5)[d] −38.6 [300]	1.16 (d, 9H, $^2J_{PH}$ 9.6, PCH$_3$), 1.41 (d, 9H, $^2J_{PH}$ 5.5, PCH$_3$), 3,47 (s, 3H, NCH$_3$), 3.49 (s, 6H, NCH$_3$), 6.74, 7.23 (d × 2, 1H × 2, $^3J_{HH}$ 2, NCH═CH), 7.16, 8.41 (d × 2, 2H × 2, $^3J_{HH}$ 2 Hz, NCH═CH)

[a] Measured in CDCl$_3$ at 25 °C, *J* and half-height-width [hhw] values given in Hz. [b] As PF$_6$ salt: $\delta_P = -143.1$ (sep., J_{PF} 712 Hz). [c] J_{PP} not resolved. [d] J_{PP} 21.5 Hz.

While the product mixtures have not been comprehensively characterized, it has been found that when chloroform solutions of **4**, **5**, or **6·Cl** are allowed to stand, the enigmatic bimetallic rhodaboratrane salt [Rh$_2${B(mt)$_3$}$_2${κ^2-*S*,*S*′-HB(mt)$_3$}]Cl (**7·Cl**, *Rh→B*, Chart 2) crystallizes from solution as the hexachloroform solvate. As we have reported recently,[17] this material is a trace component of decomposition mixtures, but can be prepared in isolable, albeit modest, yields from **6·Cl** and an excess of Na{HB(mt)$_3$]. With respect to the decomposition process, the stability of the "Rh{B(mt)$_3$}" fragment is clear, although one must question the origin of the terminal HB(mt)$_3$ ligand, since the presence of free [HB(mt)$_3$]$^-$ in admixture with any of **4** to **6** should be evident from their in situ NMR spectra. Since this is not the case, one must presume the in situ generation of ligated HB(mt)$_3$ from a boratrane and some hydrogen source. While we have not pursued this process, one can conjecture (Scheme 3) that when dissolved in deuterochloroform, which was not rigorously purified, a rhodaboratane such as **4** might be susceptible to hydrochlorination by trace HCl, thus affording [RhCl$_2${κ^2-HB(mt)$_3$}(PPh$_3$)], i.e., initial metal protonation followed by B−H elimination and coordination of the choride to the metal center. In the presence of the electrophilic [Rh{B(mt)$_3$}]$^+$ fragment (or its adducts, vide supra), chelation of the pendant methimazolyl donor would follow, thus initiating a bimolecular transfer of the HB(mt)$_3$ ligand. The neutral [Rh{κ^2-HB(mt)$_3$}{B(mt)$_3$}] complex so generated would then be susceptible to electrophilic attack by a further equivalent of [Rh{B(mt)$_3$}]$^+$, leading to the formation of **7·Cl**.

The isolation of complex **4** was of some significance to metallaboratrane chemistry, not least in providing an example of a metallaboratrane sustained at a metal center in a nonzero oxidation state.[15,3m] Moreover, the presence of both a labile ligand (PPh$_3$) and metal−halide linkage would seem to render it an ideal substrate for further derivatization. However, the instability of this compound, both in solution and the solid state, constitutes a significant obstacle in this respect. In addressing this problem, we sought to exploit the lability of the PPh$_3$ ligand, by treating samples of **4**, generated in situ, with an excess of a more potent σ-donor, in an attempt to trap the 16-electron "[RhCl{B(mt)$_3$}]$^+$" fragment as a less labile derivative. In the interests of obviating any difficulties associated with the presence of free phosphine, the initial ligands of choice were the isonitriles CNR (R = ^{t}Bu, C$_6$H$_3$Me$_2$-2,6 (Xyl), C$_6$H$_2$Me$_3$-2,4,6 (Mes)). Surprisingly, when samples of **4**, generated as described in dichloromethane, are stirred with excess of an isonitrile, the isolated products are not those arising from

(18) See for example: (a) Graham, B. W.; Laing, K. R.; O'Connor, C. J.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1237. (b) Graham, B. W.; Laing, K. R.; O'Connor, C. J.; Roper, W. R. *J. Chem. Soc., Chem. Commun*. **1970**, 1272, and references therein.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 8^+, 9^+, and 14^+ (two molecules in the asymmetric unit), with Estimated Standard Uncertainties (esd's) in Parentheses

Complex $\mathbf{8}^+$

Rh(1)−S(1)	2.368(2)	S(1)−Rh(1)−S(3)	92.58(7)
Rh(1)−S(2)	2.373(2)	S(2)−Rh(1)−S(3)	92.30(7)
Rh(1)−S(3)	2.396(2)	S(1)−Rh(1)−S(2)	167.72(6)
Rh(1)−C(1)	1.922(7)	S(1)−Rh(1)−C(1)	87.9(2)
Rh(1)−B(1)	2.155(7)	S(2)−Rh(1)−C(1)	85.9(2)
Rh(1)−P(1)	2.523(2)	Rh(1)−C(1)−N(1)	175.5(5)
N(12)−B(1)	1.549(9)	C(1)−N(1)−C(2)	172.5(7)
N(22)−B(1)	1.538(9)	N(12)−B(1)−N(22)	114.4(5)
N(32)−B(1)	1.565(8)	N(12)−B(1)−N(32)	107.5(5)
		N(22)−B(1)−N(32)	107.7(5)

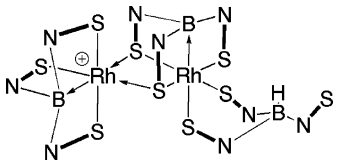
Complex $\mathbf{9}^+$

Rh(1)−S(1)	2.366(1)	S(1)−Rh(1)−S(3)	92.94(3)
Rh(1)−S(2	2.370(1)	S(2)−Rh(1)−S(3)	94.08(2)
Rh(1)−S(3)	2.408(1)	S(1)−Rh(1)−S(2)	167.50(2)
Rh(1)−C(1)	1.917(3)	S(1)−Rh(1)−C(1)	85.31(7)
Rh(1)−B(1)	2.146(3)	S(2)−Rh(1)−C(1)	86.65(7)
Rh(1)−P(1)	2.505(1)	Rh(1)−C(1)−N(1)	179.5(2)
N(12)−B(1)	1.556(3)	C(1)−N(1)−C(2)	174.1(3)
N(22)−B(1)	1.561(3)	N(12)−B(1)−N(22)	113.5(2)
N(32)−B(1)	1.556(3)	N(12)−B(1)−N(32)	108.1(2)
		N(22)−B(1)−N(32)	108.0(2)

Complex $\mathbf{14}^+$

	molecule A	molelcule B		molecule A	molecule B
Rh−S(1)	2.377(2)	2.358(2)	S(1)−Rh−S(3)	91.20(8)	90.11(9)
Rh−S(2)	2.359(2)	2.368(2)	S(2)−Rh−S(3)	92.26(9)	92.22(8)
Rh−S(3)	2.418(2)	2.432(3)	S(1)−Rh−S(2)	167.30(9)	168.18(9)
Rh−P(1)	2.459(3)	2.471(3)	S(1)−Rh−P(1)	95.96(9)	93.31(9)
Rh−P(2)	2.293(3)	2.292(3)	S(2)−Rh−P(1)	96.42(9)	98.32(9)
Rh−B	2.153(11)	2.148(10)	S(1)−Rh−P(2)	90.45(9)	91.37(9)
N(12)−B	1.559(12)	1.561(12)	S(2)−Rh−P(2)	85.72(10)	85.73(9)
N(22)−B	1.551(12)	1.552(11)	N(12)−B−N(22)	114.9(8)	114.5(7)
N(32)−B	1.576(12)	1.540(13)	N(12)−B−N(32)	105.9(7)	107.2(7)
			N(22)−B−N(32)	107.7(6)	106.1(7)

Chart 2. Dirhodaboratrane Cation in the Salt $[Rh_2\{B(mt)_3\}_2\{\kappa^2\text{-}S,S'\text{-}HB(mt)_3\}]Cl$ (7·Cl)

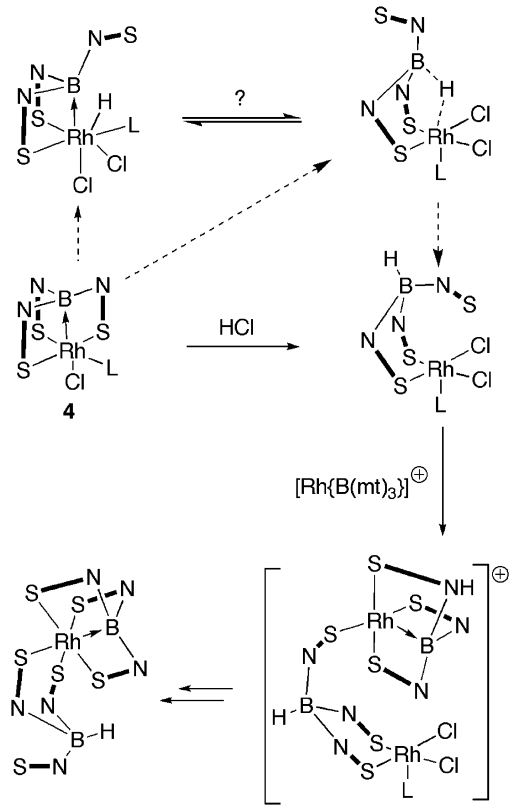


displacement of PPh_3, but rather the rhodaboratrane salts [Rh(PPh$_3$)(CNR){B(mt)$_3$}]Cl (R = ^{t}Bu **8·Cl**, Xyl **9·Cl**, Mes **10·Cl**), resulting from displacement of chloride (Scheme 4). In each case, the product identity is apparent from spectroscopic data (Table 1), with NMR signals associated with both the coordinated isonitriles (additionally verified by characteristic C≡N stretching modes in the infrared spectra) and PPh_3 being apparent in the ^{1}H NMR spectrum, along with those of the borane ligand. The bulk compositions were further confirmed by observation of the parent cations in the positive mode ESI mass spectrum (*m*/*z* 798 $\mathbf{8}^+$, 846 $\mathbf{9}^+$, 860 $\mathbf{10}^+$) and largely consistent elemental microanalytical data.[19] Phosphine retention is also apparent from the $^{31}P\{^1H\}$ NMR spectra, which are devoid of resonances associated with either free PPh_3 or its oxide. In the case of **8·Cl**, the $^{31}P\{^1H\}$ NMR spectrum also suggests that the isonitrile lies *cis* to the *Rh*→*B* linkage; the single resonance appears appreciably broadened (hhw 260 Hz), consistent with a *trans* disposition for phosphorus and boron, a feature that has been verified crystallographically (Figure 1, vide infra). That the phosphine disposition of **8** differs from that of the parent rhodaboratrane **4** would seem to imply a thermodynamic preference for *trans* P−*Rh*→*B* in the former, relative to the situation in **4**. Indeed, it has become a pragmatic observation that metallaboratranes exhibit a thermodynamic preference for the dative metal→boron linkage to lie *trans* to the weaker π-acid. This is reinforced by the fact that the less π-acidic aromatic isonitriles CNXyl and CNMes afford, under comparable conditions, mixtures of both isomers; that is, with *cis* (**a**) and *trans* (**b**) dispositions of the phosphine and borane ligands. The *cis* arrangement has been confirmed as the kinetic product, since the relative proportions of **9a·Cl** and **10a·Cl** present decrease as the mixing times are prolonged and are the sole products when the reactions are quenched after just 1 h. Once isolated, both **9a·Cl** and **10a·Cl** isomerize in solution to afford, after 3 days (ambient conditions), exclusively the thermodynamic isomers **9b·Cl** (Figure 2) and **10b·Cl**, a process conveniently monitored by infrared spectroscopy. This process can be accelerated by heating isolated **9a·Cl** or **10a·Cl** in dichloromethane under reflux and is thereby complete within 12 h. Alternatively **9b·Cl** and **10b·Cl** may be prepared directly under these conditions.

Given the ease with which isonitriles would seem to displace the chloride ligand of **4**, the inherent lability of the triphenylphosphine ligand, and an emerging propensity for the formation of cationic rhodaboratranes with even weak donors, we reasoned that the "in situ" approach should be equally applicable to a range of neutral and anionic ligands, e.g., PR_3/AgX (PR_3 = PPh_3, dppe; X = BF_4, PF_6), CO, $^-S_2CNR_2$ (R = Et, Me). This approach has surprisingly met with only limited success,

(19) We note that while all other data (spectroscopic and microanalytical) unequivocally confirm the identity and high-purity of compounds **8·Cl** to **10·Cl**, carbon analyses have routinely been found to be significantly in error. Given the reproducibility of this error and the lack of deviation for other elemental compositions (H, N, S, Cl), we must conclude this to be a peculiarity of the rhodaboratrane isonitrile salts for which we are currently unable to account.

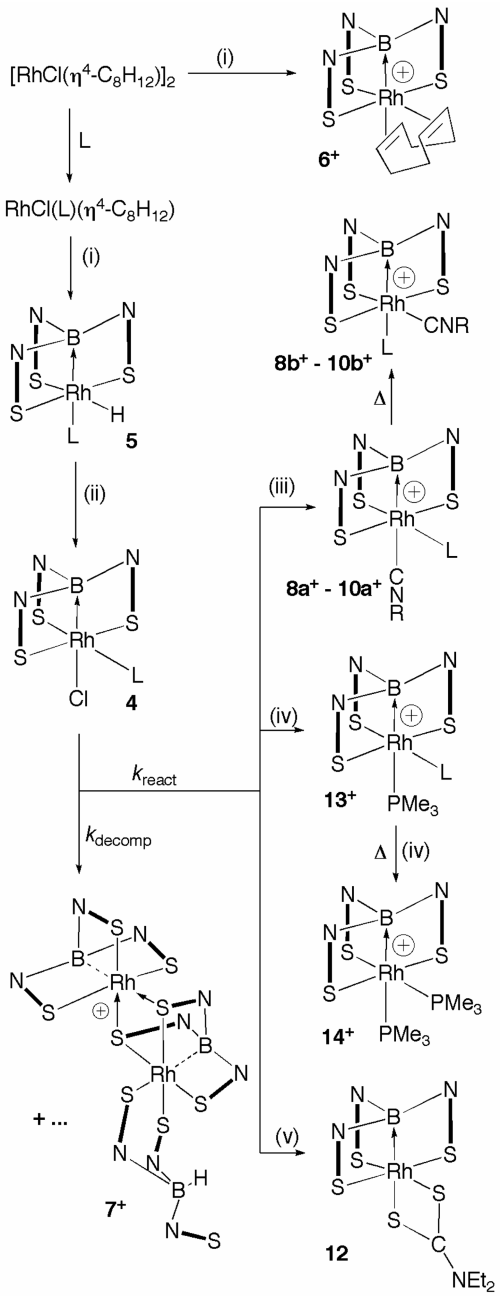
Scheme 3. Proposed Generation and Bimolecular Transfer of a $HB(mt)_3$ Ligand during Formation of 7·Cl (L = PPh_3)



more typically affording complex and often intractable mixtures, although with the complete consumption of **4**, thus implying either inherent instability of the products or prohibitively slow reaction rates (i.e., $k_{react.} \ll k_{decomp.}$). Where more selective outcomes prevailed, purification proved impracticable and the reproducibility questionable, though the identity of the major products could be convincingly inferred on the basis of spectroscopic (^{1}H and ^{31}P NMR) data. The formation, in quantity, of both $[Rh(PPh_3)_2\{B(mt)_3\}]PF_6$ (**11·PF$_6$**) and $[Rh(S_2NEt_2)\{B(mt)_3\}]$ (**12**) can thus be concluded (Table 1), despite the persistence of intractable contaminants, the formulation of both being further supported by the observation of parent ions (*m*/*z* 978 **11**$^+$; 601 **12**) and characteristic fragments in the ESI+ mass spectra.

Greater success followed from the reaction between **4** and 1 equiv of PMe_3, which affords quantitatively, after 1 h, the complex salt $[Rh(PMe_3)(PPh_3)\{B(mt)_3\}]Cl$ (**13·Cl**, Rh→B). Once again, the identity of **13·Cl** was established from key spectroscopic data (Table 1), with the $^{31}P\{^1H\}$ NMR spectrum verifying both the retention of the triphenylphosphine ligand and that its disposition to the borane has been maintained (δ_P 30.8, d, $^1J_{RhP}$ 121 Hz), in addition to the presence of a single PMe_3 ligand lying *trans* to boron (δ_P −39.7, hhw 300 Hz). The solution stability of **13·Cl** is, however, limited, gradual loss of the PPh_3 ligand being apparent, leading ultimately to an intractable mixture. In the presence of excess PMe_3, this process instead leads to replacement of PPh_3 by the more potent σ-donor, to afford after several days the bis(phosphine) complex $[Rh(PMe_3)_2\{B(mt)_3\}]Cl$ (**14·Cl**), which can alternatively be generated within 12 h in dichloromethane under reflux. Once formed, **14·Cl** exhibits appreciable solution stability, which has allowed its characterization by single-crystal X-ray diffraction (Figure 3), in support of spectroscopic data. The acquisition of reliable microanalytical data has, however, been complicated by the

Scheme 4. Ligand Substitution Reactions of Rhodaboratranes (L = PPh_3)[a]



[a] (i) $Na[HB(mt)_3]$; (ii) $CHCl_3$/HCl; (iii) CNR (R = ^{t}Bu, $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6); (iv) PMe_3; (v) $Na[S_2CNEt_2]$.

surprising persistence of $OPMe_3$, which is apparently generated during synthesis, or workup from the excess of PMe_3 required to effect useful conversion rates. This oxidized species was initially presumed to arise due to the use of dichloromethane/ethanol solvent mixtures, but continued to plague the synthetic protocol even in its absence, despite attempts at the rigorous exclusion of air/moisture.

Taken together with the isomerization of **9a** and **10a** (kinetic) to **9b** and **10b** (thermodynamic), which presumably occurs via a dissociative process, the formation of **14·Cl** from **13·Cl** would seem to emphasize the heightened lability of the weaker σ-donor PPh_3, when disposed *cis* to the dative *Rh*→*B* linkage, relative to a *trans* arrangement as in **9b·Cl** and **10b·Cl**. It is, however, interesting to note that on no occasion have we observed the replacement of PPh_3 within **8·Cl**, **9·Cl**, or **10·Cl** by a second

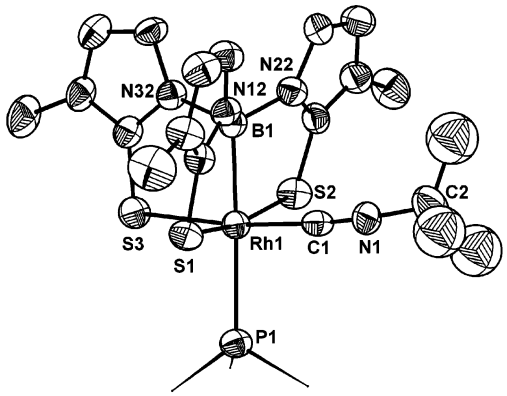


Figure 1. Molecular geometry of the cation $[Rh(PPh_3)(CN^tBu)\{B(mt)_3\}]^+$ (**8**$^+$) in crystals of nonstoichiometrically solvated **[8]·Cl**. Hydrogen atoms and phosphine substituents are omitted for clarity (50% displacement ellipsoids). The tertiary butyl group is rotationally disordered and refined across two sites with isotropic displacement parameters (one orientation shown).

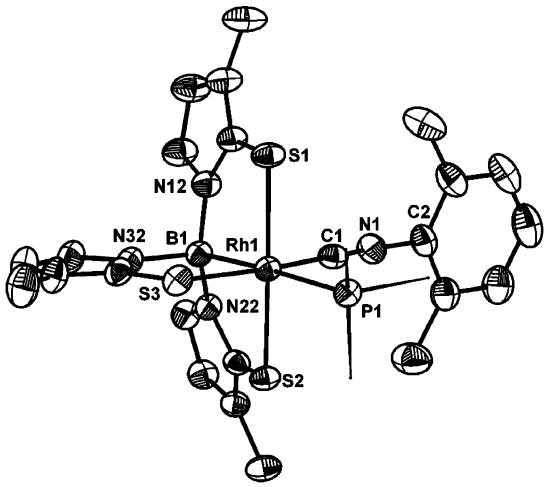


Figure 2. Molecular geometry of the cation $[Rh(PPh_3)(CNXyl)\{B(mt)_3\}]^+$ (**9**$^+$) in crystals of **[9]·Cl·CHCl$_3$**. Hydrogen atoms and phosphine substituents omitted for clarity (50% displacement ellipsoids).

isonitrile ligand, despite the use of excess CNR (R = ^{t}Bu, Xyl, Mes). Thus steric factors may also play a role. In the interests of completeness, we therefore sought to prepare the complex $[Rh(CN^tBu)_2\{B(mt)_3\}]Cl$, commencing from the salt **6·Cl**, $[Rh(\eta^4\text{-}C_8H_{12})\{B(mt)_3\}]Cl$ (vide supra), in which the lability of the cyclooctadiene ligand has been inferred. However, when **6·Cl** is treated with an excess (>2 equiv) of CN^{t}Bu, the rhodaboratrane fragment is surprisingly destroyed, affording a largely intractable mixture with a predominance of the $[Rh(CN^tBu)_4]^+$ cation presumably present as the chloride salt, which was identified on the basis of ^{1}H NMR and infrared data.[20] A more controlled reaction ensues when an exact stoichiometric ratio (2 equiv of CN^{t}Bu) is employed, such that the formation of $[Rh(CN^tBu)_2\{B(mt)_3\}]Cl$ would seem possible on the basis of ESI+ mass spectrometric data (*m*/*z* 619.1 $[M]^+$, 536.1 $[M - CN^tBu]^+$, 453.0 $[M - 2\ CN^tBu]^+$), although the ^{1}H NMR data are ambiguous, apparently indicating the presence of three magnetically distinct methimazolyl units, which would seem inconsistent with the simplest formulation. Moreover, the magnetic and chemical inequivalence of the *tert*-butyl protons

(20) (a) Branson, P. R.; Green, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1303. (b) Dart, J. W.; Lloyd, M. K.; Mason, R.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2039.

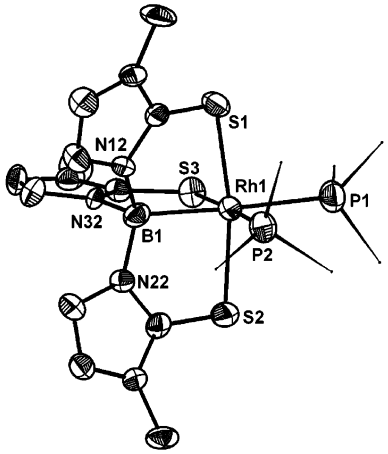
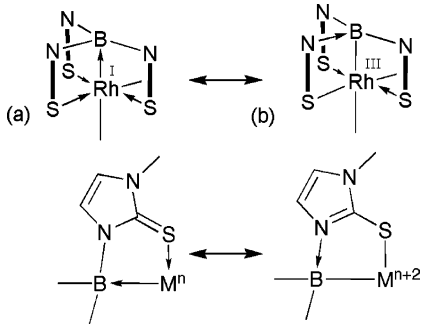


Figure 3. Molecular geometry of the cationic complex $[Rh(PMe_3)_2\{B(mt)_3\}]^+$ (**14**$^+$) in crystals of solvated **[14]·Cl**. Hydrogen atoms and phosphine substituents are omitted for clarity (50% displacement ellipsoids). The asymmetric unit comprises two unique molecules (one shown) with comparable internal geometries.

Chart 3. Canonical Forms for (a) Metallaboratrane and (b) Base-Stabilized σ-Boryl Complex



is not clearly distinguishable, perhaps implying some degree of fluxionality. Interpretation of the data is further confounded by the presence of intractable and inseparable contaminants, and accordingly we have not further pursued the isolation of $[Rh(CN^tBu)_2\{B(mt)_3\}]Cl$.

Solid-State Structures. The molecular cations **8**$^+$, **9**$^+$, and **14**$^+$ each adopt a distorted octahedral geometry about rhodium, with *cis* angles at the metal in the ranges 83.40(2)−96.54(6)° for **8**$^+$, 84.83(7)−97.88(2)° for **9**$^+$, and 83.00(3)−96.42(9)° for **14**$^+$ **A** [**B**: 83.2(3)−98.32(9)°]. These data are largely comparable to those reported for the neutral rhodaboratrane complex $[RhCl(PPh_3)\{B(mt)_3\}]$ (**4**) [two crystallographically independent molecules: **A** 80.14(5)−101.20(6)°; **B** 81.01(5)−100.65(5)°],[13] but more closely to those of the cationic bimetallic complex $[Rh_2\{B(mt)_3\}_2\{\kappa^2\text{-}S,S'\text{-}HB(mt)_3\}]^+$ (**7**$^+$) [81.23(4)−97.30(4)°],[17] which also has predominantly neutral donors about rhodium. The Rh−B distances of **8**$^+$, **9**$^+$, and **14**$^+$ are comparable within 2σ, but are marginally longer (2σ−3σ) than those observed for **4**, which is consistent with the reduced donor capacity of a cationic metal center relative to the neutral case. This confirms that the anomalously short Rh−B separations observed for the bimetallic **7**$^+$ [2.098(6) and 2.091(5) Å][17] are not intrinsic to its cationic character, which might have implied a significant contribution from the σ-boryl canonical form of the B(mt)$_3$Rh cage (Chart 3, vide infra). Rather, it seems more likely that they are inherent from the yet to be quantified influence of the additional (π-dative) sulfur donors within the coordination sphere. We have previously noted that the influence of the ligand

trans to the *Rh*−*B* linkage is also unquantified, owing to a dearth of structural data. Although the compounds herein would seem appropriate to this end, the data remain less than conclusive.

A feature common to each of the structurally characterized rhodaboratranes is the apparent exertion of an appreciable *trans* influence by the *Rh*→*B* linkage, as determined by comparison of the *trans* Rh−L distances against relevant examples deposited in the Cambridge Crystallographic Data Center. No doubt this contributes to the *trans* effect implicit in both the lability of metallaboratranes and the stereochemistry of the kinetic products of ligand substitution. This might appear counterintuitive, given that an inverse *trans* influence would be anticipated for a σ-retrodative bond. Nonetheless, the anomaly is confirmed by the data for **14**$^+$ in which the presence of two equivalent PMe_3 ligands lying *cis* [**A** 2.293(3); **B** 2.292(3) Å] and *trans* [**A** 2.459(3); **B** 2.471(3) Å] to boron provides an internal standard. It might be argued that this is indicative of the bridgehead boron(III) atom behaving not as a σ-Lewis acid but rather as an internally base-stabilized σ-boryl, for which a strong *trans* influence would be expected.[21] This would represent a counterpoint to our favored "metallaboratrane" description, which is however an extreme scenario, and contributions from such a canonical form cannot be unequivocally discounted. Our assertion that this linkage is predominantly, if not exclusively, σ-retrodative in character is based largely upon electroneutrality arguments, which would seemingly preclude oxidation of the metal center by boron, especially for the formally isoelectronic group 10 systems.[15] Geometric data for the rhodium compounds do, however, reveal flattening of two of the mt buttresses away from local C_{3v}-B(mt)$_3$Rh symmetry (Figure 4), reflected also in the NMR spectroscopic data (vide supra), which could be argued to support a contribution from the boryl form. However, while moderate deviations between the three B−N linkages are in each case apparent [**4** 1.534(10)−1.567(9); **7**$^+$ 1.552(7)−1.566(7); **8**$^+$ 1.538(9)−1.565(8); **9**$^+$ 1.556(3)−1.561(3); **14**$^+$ **A** 1.551(12)−1.576(12); **B** 1.540(13)−1.561(12) Å], these do not correlate with the similarity noted for the Rh−S distances, when variations might be anticipated for a base-stabilized boryl thiolato complex. Moreover, variations in the C−S distances are insignificant ($\leq 2\sigma$) and offer no tangible evidence for differing bond orders. We thus conclude that, as for group 8 metallaboratranes,[7,8] the geometric deviations are inherent from accommodating the constraints attending a tetrahedral boron center in proximity to octahedral rhodium and, thus, serve only to alleviate strain within the chelate rings.

The conformation adopted by the boratrane cage imposes significant constraints upon the ancillary geometry about the metal. Thus, while the complex cation **14**$^+$ readily accommodates two PMe_3 ligands (Figure 5), within **8**$^+$ and **9**$^+$, where the ligand *trans* to boron is the larger PPh_3, the isonitrile occupies an apparent "pocket" in the coordination sphere, which is seemingly inadequate to easily accommodate a more sterically demanding ligand. Indeed, this is consistent with the difficulties encountered in cleanly isolating the salt [Rh(PPh$_3$)$_2${B(mt)$_3$}]PF$_6$ (**11**·**PF**$_6$) and the lability ascribed to this salt and [Rh(PMe$_3$)(PPh$_3$){B(mt)$_3$}]Cl (**13**·**Cl**). Moreover, it might be argued that the thermodynamic preference for *trans* disposition of boron and phosphorus in **8**$^+$, **9**$^+$, and **10**$^+$ (vide supra) is, at least in part, a function of the steric perturbation that would be incurred by accommodating a PPh_3 ligand within the cavity presented by the S1- and S3-based heterocycles, rather than an intrinsic predilection for the weaker π-acid to lie *trans* to boron. Indeed, this perturbation is clearly apparent from the greater displacement of the boron atom from the [P, Rh, S1, S2] mean plane within **4** [B→Rh−Cl, **A** 0.483, **B** 0.512 Å] as compared with **7**$^+$−**9**$^+$ and **14**$^+$ [**7** 0.049, 0.078 Å; **8**$^+$ 0.204 Å; **9**$^+$ 0.193 Å; **14**$^+$ **A** 0.321, **B** 0.278 Å]. Nonetheless, the electronic argument retains credence, since the observation is common to a range of metallaboratranes, regardless of steric considerations.

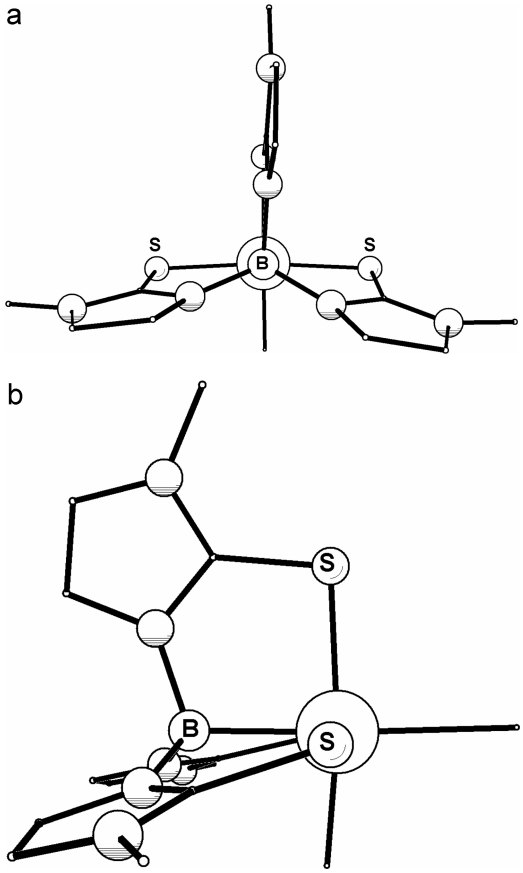


Figure 4. Projections of the simplified structure of **8**$^+$ along (a) B−Rh and (b) S1−S2 vectors illustrating distortion from local C_{3v}-B(mt)$_3$Rh symmetry.

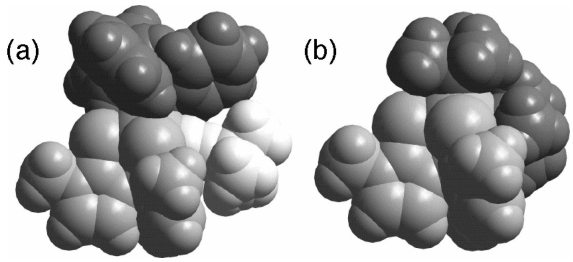
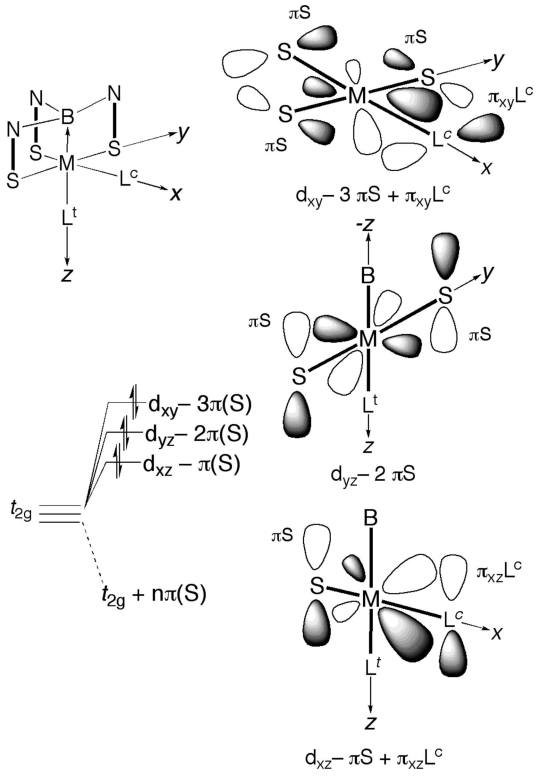


Figure 5. Space-filling models of (a) [Rh(PPh$_3$)(CN^{t}Bu){B(mt)$_3$}] (**8**$^+$) and (b) [Rh(PMe$_3$)$_2${B(mt)$_3$}] (**14**$^+$) projected along the S2−Rh−S1 axes. B(mt)$_3$, light gray; isonitrile, white; phosphines, dark gray.

Two stereochemical observations noted above call for comment. First, there appears to be a developing trend in metallaboratrane chemistry that, under thermodynamic control, the preferred geometry in octahedral complexes of the form B(mt)$_3$ML^{1}L^2 involves the weaker π-acid assuming the position *trans* to the M→B interaction. The second observation is that there appears to be a significant *trans* influence exerted by the M→B group (confirmed for **14**$^+$ where L^1 = L^2) and that this

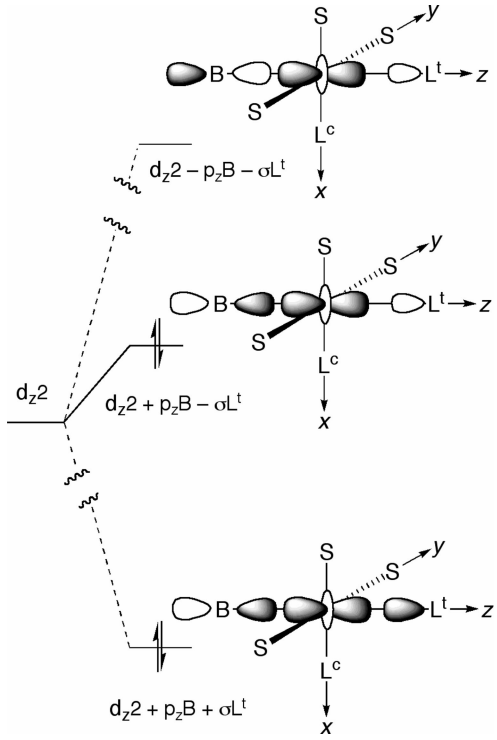
(21) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittel, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

Chart 4. Interactions of Orbitals with π-Symmetry with Respect to Metal−Ligand Axes[a]



[a] πS = methimazolyl-based π-donor orbital; πL^c = acceptor orbitals on a π-acid ligand positioned *cis* to the *M*→*B* bond; L^t = ligand *trans* to *M*→*B* bond.

Chart 5. Origins of *trans* Influence in Octahedral d^8-Metallaboratranes



presumably contributes to a *trans* effect implicit in the general lability of metallaboratranes with respect to dissociative ligand substitution (confirmed by the stereochemistries of **9a**$^+$/**10a**$^+$ (kinetic) and **9b**$^+$/**10b**$^+$ (thermodynamic)). These issues will be considered separately, beginning with the preferred location of π-acid ligands.

The tris(methimazolyl)borate ligand has been suggested to act as a particularly effective π-donor, a feature that has been quantified with recourse to carbonyl-associated infrared data for the alkylidyne complexes [W(≡CC_6H_4Me-4)$(CO)_2$(L)] where L represents a wide range of the more commonly encountered facially tridentate ligands.[3c] It might reasonably be assumed that this superlative π-basicity is also a feature of tris(methimazolyl)borane coordination. The orbitals available for interaction with a potential π-acid in metallaboratranes (d_{xy}, d_{xz}, d_{yz}) will be destabilized to varying extents by the number (1, 2, or 3) of occupied methimazolyl π-donor orbitals (πS) with which they interact. Defining the *M*→*B* axis as "*z*" and the M−S_{unique} axis as "*x*" (Chart 4) the π-interactive metal orbitals increase in energy (i.e., π-retrobasicity) in the order (d_{xz} − πS) < (d_{yz} − 2 πS) < (d_{xy} − 3 πS). A cylindrically symmetric bifacial π-acid (CO, CNR, CR, NO) with a pair of orthogonal acceptor orbitals (πL) will interact with two of these metal orbitals. Coordination along the *x*-axis, i.e., L^c, *cis* to the *M*→*B* bond, will involve interaction with d_{xz} and d_{xy}, affording greater net stabilization (4πS) than would interaction with the d_{xz} and d_{yz} combination (3πS) presented to a ligand coordinating *trans* to boron (L^t). Conversely, coordination of a π-donor (e.g., Cl in **4**), in which case the interaction will be repulsive, would be least disfavorable were it to involve the orbitals d_{xz} and d_{yz}, i.e., coordination along the *z*-axis, with L^t *trans* to the M→B bond. Although these arguments are only qualititative, they account for the structurally authenticated stereochemistries of known octahedral metallaboratranes in addition to six ruthenium-based examples that we have yet to report. The exceptions to this are the hydrido complexes **5** and [PtH(PPh_3){B$(mt)_3$}]$^+$, wherein the position of the hydride adjacent to boron is a corollary of the mechanism of formation and the inability of hydride ligands to exchange sites by heterolytic solvolysis (cf. chloride).

The second phenomenon, the operation of a *trans* influence (linked to a *trans* effect), may be traced to the nature of the bonding in the σ-framework. Conventional (σ) *trans* influences are discussed in terms of competition between σ-donors; however in the case of octahedral metallaboratranes, only one of the two *trans*-disposed metal substituents (B and L^t) is a Lewis base (L^t). Chart 5 depicts the σ orbitals on boron and the *trans* ligand L^t in combination with the d_{z^2} orbital on the metal in a manner that is bonding and antibonding with regard to M−B and M−L^t, respectively. NB: In a homoleptic d^8-ML_6 complex this combination has zero net overlap between metal and ligand orbitals; rather, the conventional e_g* orbitals, which are in all directions M−L antibonding, are generally considered. For the d^8 case where one metal substituent is a σ-Lewis acid, population of this orbital combination would be expected to strengthen the M−B bond but weaken the M−L^t bond, accounting for the observed *trans* influence in the ground-state structures observed to date. In considering the observed *trans* effect, this M−L^t ground-state destabilization may be one contributory factor; however transition-state stabilization might also be considered. The transition state for L^t departure might be viewed as akin to the electronically favorable d^8-square planar geometry, in which the d_{z^2} orbital is further stabilized by interaction with the B^{III} center.

Conclusions

We have reported the first systematic study of a family of metallaboratrane complexes, based on rhodium(I), with a

selection of ancillary ligands encompassing a range of basicities, π-acidities, and steric profiles. This has revealed appreciable and generic lability for rhodaboratrane complexes that can be moderated by the judicious use of strong σ-donor ligands and/or salt formation. The application of a range of isonitriles (CNR, R = ^{t}Bu, Xyl, Mes) to this end has further illustrated an apparent thermodynamic preference for *cis* disposition of the M→B linkage and the most π-acidic ligand, the formation of [Rh(PPh$_3$)(CNR){B(mt)$_3$}]Cl (*trans*-RNC−Rh→B) as kinetic products being observed, with their subsequent isomerization to the *trans*-P−*Rh→B* isomer under thermodynamic control. This is similarly reflected in the isolation of [Rh(PMe$_3$)(PPh$_3$)-{B(mt)$_3$}]Cl (*trans*-Me$_3$P−*Rh→B*), with no evidence for the *cis* isomer, although in each case the relative contributions of electronic and steric effects remain to be determined. Indeed, crystallographic studies of [RhCl(PPh$_3$){B(mt)$_3$}], [Rh(PPh$_3$)-(CNR){B(mt)$_3$}]Cl (R = ^{t}Bu, Xyl), [Rh$_2${B(mt)$_3$}$_2${κ^2-*S*,*S*′-HB-(mt)$_3$}]Cl, and [Rh(PMe$_3$)$_2${B(mt)$_3$}]Cl leave scope for debate as to the definite covalent bonding scenario within the metallaboratrane motif and the extent to which geometric deformities are inherent from electronic versus steric influences. Qualitative arguments have been presented to account for these observations, in anticipation of a more rigorous and quantitive theoretical study. Clearly, a full understanding of metallaboratranes, in the context of their formation, structure, and reactivity, will require further substantial investigation.

Experimental Section

General Methods. Conventional Schlenk and vacuum line techniques were routinely employed throughout for the exclusion of air. Isolated products generally exhibited moderate air-stablity; thus analytical samples were typically prepared in air. Solvents were distilled under prepurified nitrogen from appropriate drying agents. The compounds [RhCl(PPh$_3$)$_3$],[22] [RhCl(η^4-C$_8$H$_{12}$)]$_2$,[23] CNC$_6$H$_2$Me$_3$-2,4,6,[24] and Na[HB(mt)$_3$][7a] were prepared according to published procedures, while [RhCl(PPh$_3$)(η^4-C$_8$H$_{12}$)] was obtained by treatment of [RhCl(η^4-C$_8$H$_{12}$)]$_2$ with 2 equiv of PPh$_3$. All other materials were obtained from commercial sources and used as supplied after spectroscopic and analytical verification of purity. All NMR spectra were recorded on a Varian Inova 300 instrument (^{1}H, 299.945 MHz, ^{13}C, 75.428 MHz, referenced to external SiMe$_4$; ^{31}P, 121.420 MHz, ref external 85% H$_3$PO$_4$; ^{11}B, 96.232 MHz, ref external BF$_3$·Et$_2$O). Carbon-13 NMR assignments were confirmed with recourse to 2-D correlation (HMQC and HMBC) spectra. In general, multiplet (ddq) resonances due to coordinated isonitrile carbon nuclei were not identified. Elemental microanalytical[19] and mass spectrometric data were provided by the ANU analytical services.

Preparation of [RhCl$_2$(C$_6$H$_5$)(PPh$_3$)$_2$] (3). Under an atmosphere of prepurified nitrogen, a flask was charged with [RhCl(PPh$_3$)$_3$] (1.226 g, 1.33 mmol) and PhHgCl (0.430 g, 1.37 mmol) in THF (40 mL), then the mixture was brought to reflux. After 3 h, during which time the mixture assumed an orange coloration, it was allowed to cool to ambient temperature. Dichloromethane (40 mL) was then added and the mixture filtered through diatomaceous earth to remove metallic mercury. The filter pad was washed with a further 40 mL of CH$_2$Cl$_2$, and then the combined filtrates were concentrated under reduced pressure until an orange solid began to form. The addition of ethanol (80 mL) completed precipitation of the orange product, which was collected by filtration, washed with ethanol (10 mL) and ether (10 mL), and then dried in vacuo. The complex could be recrystallized from a mixture of dichloromethane and ethanol. Yield: 0.706 g (69%). ^{31}P{^{1}H} NMR: δ_P 21.58 (d, $^1J_{RhP}$ 103.2 Hz). The complex was characterized by comparison of spectroscopic data with those previously published.[16]

Synthesis of [RhCl(PPh$_3$){B(mt)$_3$}] (*trans*-Cl−Rh→B) (4). A mixture of **3** (0.100 g, 0.129 mmol) and Na[HB(mt)$_3$] (0.049 g, 0.131 mmol) in dichloromethane (20 mL) and ethanol (2 mL) was stirred under an atmosphere of nitrogen for 1 h. After allowing it to settle, the mixture was filtered via cannula to a second Schlenk flask and concentrated under reduced pressure to approximately 2 mL volume. The addition of excess diethyl ether resulted in precipitation of a pale orange solid. The solvent was removed via filter-cannula and the solid dried in vacuo. Yield: 0.060 g (62%). FAB-MS: *m*/*z* 715 [M − Cl]$^+$, 453 [M − Cl − PPh$_3$]$^+$. NMR (CDCl$_3$): ^{11}B δ_B 1.7 (s br, hhw 50 Hz). Anal. Found: C, 48.0; H, 4.12; N, 10.99. Calcd for C$_{30}$H$_{30}$BClN$_6$PRhS$_3$: C, 47.98; H, 4.03; N, 11.19.

Synthesis of [RhH(PPh$_3$){HB(mt)$_3$}] (*trans*-P−Rh→B) (5). A mixture of [RhCl(PPh$_3$)(η^4-C$_8$H$_{12}$)] (0.200 g, 0.393 mmol) and Na-[HB(mt)$_3$] (0.150 g, 0.401 mmol) in dichloromethane (15 mL) was stirred anaerobically for 4 h. The product was isolated in an analogous manner to **4**, as a yellow solid, dried in vacuo, and stored under N$_2$. Yield: 0.170 g (60%). ESI+ MS: *m*/*z* 716.1 [M]$^+$, 715.1 [M − H]$^+$, 453.1 [M − H − PPh$_3$]$^+$. NMR (CDCl$_3$): ^{11}B{^{1}H} δ_B 2.1 (s br, hhw 55 Hz). Solution instability precluded acquisition of satisfactory elemental data.

Synthesis of [Rh(CN^{t}Bu)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-P−Rh→B) (8·Cl). A solution of compound **4** was prepared, as described, from **3** (0.200 g, 0.258 mmol) and Na[HB(mt)$_3$] (0.099 g, 0.265 mmol) in a mixture of dichloromethane (20 mL) and ethanol (2 mL) over 1 h. The mixture was filtered anaerobically, and to the filtrate was added an excess of CN^{t}Bu (0.1 mL, 0.9 mmol). After stirring for 12 h the golden solution was concentrated under reduced pressure to ca. 3 mL volume and the product precipitated by the addition of excess diethyl ether. The golden yellow solid was isolated by filtration and dried in vacuo. The complex could be recrystallized from a mixture of dichloromethane and diethyl ether. Yield: 0.160 g (74%). IR: ν_{max}(C≡N) 2186 cm^{-1} (KBr). ESI+ MS: *m*/*z* 797.6 [M]$^+$, 714.8 [M − CN^{t}Bu]$^+$, 535.9 [M − PPh$_3$]$^+$. NMR (CDCl$_3$): ^{11}B{^{1}H}: $\delta_B \approx 9.0$ (s br, hhw 100 Hz). ^{13}C{^{1}H}: δ_C 29.6 [d, $^4J_{RhC}$ 14.0, C*C*H$_3$], 33.6 (2C), 34.1 (1C) [NCH$_3$], 124.1 (2C), 124.5 (1C) [N*C*H=CHNB], 119.3 (1C), 121.2 (2C) [NCH=*C*HNB], 128.5 [d, $^3J_{CP}$ 8.6, C^{3,5}(C$_6$H$_5$)], 129.7 [C^4(C$_6$H$_5$)], 133.5 [d, $^2J_{CP}$ 13.2, C^{2,6}-(C$_6$H$_5$)], 134.3 [d, $^1J_{CP}$ 23.6 Hz, C^1(C$_6$H$_5$)], 161.8 (1C), 163.5 (2C) [C=S], C≡N not identified. Anal. Found:[19] C, 46.54; H, 4.76; N, 11.78; Cl, 4.27; S, 11.00. Calcd for C$_{35}$H$_{39}$BClN$_7$PRhS$_3$: C, 50.40; H, 4.71; N, 11.76; Cl, 4.25; S, 11.53. *Crystal data*: C$_{35}$H$_{39}$BN$_7$-PRhS$_3$·Cl·(CHCl$_3$)$_{2.53}$·(H$_2$O)$_{0.3}$. M_w = 1141.32, monoclinic, *C*2/*c* (No. 15), *a* = 42.9100(12) Å, *b* = 9.8725(3) Å, *c* = 27.4618(8) Å, β = 112.2130(10)°, *V* = 10770.2(5) Å^3, *Z* = 8, D_c = 1.408 Mg m^{-3}, μ(Mo Kα) = 0.923 mm^{-1}, *T* = 200(2) K, yellow needle, 9423 independent reflections, *F* refinement R_1 = 0.0684, wR_2 = 0.0649 for 5505 independent absorption-corrected reflections [$I > 3\sigma(I)$; $2\theta_{max}$ = 50°], 609 parameters, CCDC 281910.

Synthesis of [Rh(CNXyl)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-C−Rh→B) (9a·Cl). Prepared as **8·Cl** from **3** (0.100 g, 0.129 mmol), Na[HB-(mt)$_3$] (0.050 g, 0.13 mmol), and excess CNXyl (0.075 g, 0.57 mmol). Product isolated after 1 h. Yield: 0.072 g (63%). IR: ν_{max}-(C≡N) 2125 (KBr), 2133 cm^{-1} (CH$_2$Cl$_2$). ESI+ MS: *m*/*z* 846.1 [M]$^+$, 715.1 [M − CNXyl]$^+$, 535.9 [M − PPh$_3$]$^+$, 453.1 [M − PPh$_3$ − CNXyl]$^+$. NMR (CDCl$_3$): ^{11}B{^{1}H} $\delta_B \approx 8.7$ (s br, hhw 196 Hz). ^{13}C{^{1}H}: δ_C 18.9 [C*C*H$_3$], 33.0 (2C), 34.2 (1C) [NCH$_3$], 123.9 (2C), 124.2 (1C) [N*C*H=CHNB], 119.2 (1C), 120.0 (2C) [NCH=*C*HNB], 127.6 [C^4(C$_6$H$_3$)], 128.0 [C^{3,5}(C$_6$H$_3$)], 127.2 [d, $^3J_{CP}$ 9.7, C^{3,5}(C$_6$H$_5$)], 129.8 [C^4(C$_6$H$_5$)], 133.4 [d, $^2J_{CP}$ 13.2 Hz, C^{2,6}-

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(C_6H_5)], 161.1 (1C), 163.2 (2C) [C═S], quaternary $C^{1,2,6}(C_6H_3)$, $C^1(C_6H_5)$, and C≡N not identified.

Synthesis of [Rh(CNXyl)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-P−Rh→B) (9b·Cl). As for **9a·Cl**; upon the addition of the isonitrile (CNXyl), the mixture was heated under reflux for 12 h. Isolated as described for **9a·Cl**. Yield: 0.075 g (65%). IR: ν_{max}(C≡N) 2155 (KBr), 2158 cm^{-1} (CH_2Cl_2). ESI+ MS: *m*/*z* 846.1 $[M]^+$, 715.1 $[M - CNXyl]^+$, 535.9 $[M - PPh_3]^+$, 453.1 $[M - PPh_3 - CNXyl]^+$. NMR ($CDCl_3$): $^{11}B\{^1H\}$ $\delta_B \approx 8.9$ (s br, hhw 172 Hz). $^{13}C\{^1H\}$: δ_C 17.3 [C*C*H$_3$], 33.6 (2C), 34.2 (1C) [NCH$_3$], 124.1 (2C), 124.5 (1C) [N*C*H═CHNB], 119.4 (1C) 121.4 (2C) [NCH═*C*HNB], 127.6 [$C^4(C_6H_3)$], 128.4 [$C^{3,5}(C_6H_3)$], 133.8 [$C^{2,6}(C_6H_3)$], 128.5 [d, $^3J_{CP}$ 8.8, $C^{3,5}(C_6H_5)$], 129.7 [$C^4(C_6H_5)$], 133.4 [d, $^2J_{CP}$ 13.2 Hz, $C^{2,6}(C_6H_5)$], 134.2 [d, $^1J_{CP}$ 5.7, $C^1(C_6H_5)$], 161.6 (1C), 163.0 (2C) [C═S], quaternary $C^1(C_6H_3)$ and C≡N not identified. Anal. Found:[19] C, 47.22; H, 4.70; N, 10.13; Cl, 4.60; S, 10.00. Calcd for $C_{39}H_{39}BClN_7PRhS_3$: C, 53.10; H, 4.46; N, 11.12; Cl, 4.02; S, 10.90. *Crystal data*: $C_{39}H_{39}BN_7PRhS_3 \cdot Cl \cdot 3CHCl_3$. M_w = 1240.26, triclinic, $P\bar{1}$ (No. 2), a = 10.8109(2) Å, b = 14.8035(3) Å, c = 18.0613(4) Å, α = 86.3691(10)°, β = 73.2647(12)°, γ = 74.3865(13)°, V = 2665.63(10) Å^3, Z = 2, D_c = 1.545 Mg m^{-3}, μ(Mo Kα) = 1.008 mm^{-1}, T = 200(2) K, yellow plate, 12 247 independent reflections, F refinement R_1 = 0.0431, wR_2 = 0.0529 for 9728 independent absorption-corrected reflections [$I > 3\sigma(I)$; $2\theta_{max}$ = 55.3 °], 596 parameters, CCDC 281911.

Synthesis of [Rh(CNMes)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-C−Rh→B) (10a·Cl). Prepared from a solution of **4**, generated in situ as described for **9·Cl**, and excess CNMes (0.080 g, 0.55 mmol). Product isolated after 1 h. Yield: 0.080 g (69%). IR: ν_{max}(C≡N) 2124 cm^{-1} (KBr). ESI+ MS: *m*/*z* 860.1 $[M]^+$, 715.1 $[M - CNMes]^+$, 598.1 $[M - PPh_3]^+$, 453.1 $[M - PPh_3 - CNMes]^+$. NMR ($CDCl_3$): $^{11}B\{^1H\}$ $\delta_B \approx -2.0$ (s br, hhw 384 Hz). Satisfactory ^{13}C NMR data not obtained due to conversion to **10b·Cl** during acquisition.

Synthesis of [Rh(CNMes)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-P−Rh→B) (10b·Cl). As described for **10a·Cl**, upon addition of the isonitrile (CNMes), the mixture was heated under reflux for 15 h. Isolated as for **10a·Cl**. Yield: 0.098 g (85%). IR: ν_{max}(C≡N) 2154 (KBr), 2165 cm^{-1} (CH_2Cl_2). ESI+ MS: *m*/*z* 860.1 $[M]^+$, 715.1 $[M - CNMes]^+$, 598.1 $[M - PPh_3]^+$, 453.1 $[M - PPh_3 - CNMes]^+$. NMR ($CDCl_3$): $^{11}B\{^1H\}$ $\delta_B \approx 9.1$ (s br, hhw 212 Hz). $^{13}C\{^1H\}$: δ_C 17.2 [C*C*H$_3$-2,6], 21.1 [C*C*H$_3$-4], 33.5 (2C), 34.2 (1C) [NCH$_3$], 124.4 (2C), 124.1 (1C) [N*C*H═CHNB], 119.4 (1C), 121.3 (2C) [NCH═*C*HNB], 128.3 [$C^{3,5}(C_6H_2)$], 133.9 [$C^{2,6}(C_6H_2)$], 138.6 [$C^4(C_6H_3)$], 128.4 [d, $^3J_{CP}$ 8.9, $C^{3,5}(C_6H_5)$], 129.7 [$C^4(C_6H_5)$], 133.4 [d, $^2J_{CP}$ 13.2, $C^{2,6}(C_6H_5)$], 134.0 [s, $^1J_{CP}$ 24.0 Hz, $C^1(C_6H_5)$], 161.7 (1C), 163.1 (2C) [C═S]. Anal. Found:[19] C, 46.41; H, 4.62; N, 11.09; Cl, 4.99; S, 10.54. Calcd for $C_{40}H_{41}BClN_7PRhS_3$: C, 53.61; H, 4.61; N, 10.94; Cl, 3.96; S, 10.73.

Synthesis of [Rh(PMe$_3$)(PPh$_3$){B(mt)$_3$}]Cl (*trans*-Me$_3$P−Rh→B) (13·Cl). A solution of **4** was prepared as described from **3** (0.100 g, 0.13 mmol) and Na[HB(mt)$_3$] (0.050 g, 0.13 mmol) in a mixture of dichloromethane (20 mL) and THF (2 mL). After stirring for 1 h, 1.1 equiv of PMe_3 (0.015 mL, 0.15 mmol) was added directly to the mixture. After a further hour the mixture was filtered to remove the inorganic halide byproducts, then concentrated under reduced pressure to ca. 3 mL. The addition of excess diethyl ether effected the precipitation of **13·Cl** as a pale orange solid, which was isolated by anaerobic filtration and dried in vacuo. Yield: 0.080 g (75%). ESI+ MS: *m*/*z* 715.1 $[M - PMe_3]^+$, 529.1 $[M - PPh_3]^+$, 453.0 $[M - PPh_3 - PMe_3]^+$. NMR ($CDCl_3$): $^{11}B\{^1H\}$ $\delta_B \approx 8.8$ (s br, hhw 250 Hz).

Synthesis of [Rh(PMe$_3$)$_2$){B(mt)$_3$}]Cl (Rh→B) (14·Cl). A solution of **4**, prepared as described for **13·Cl** from **3** (0.200 g, 0.26 mmol), and Na[HB(mt)$_3$] (0.050 g, 0.27 mmol) was filtered to remove the inorganic halides, then treated with excess PMe_3 (0.1 mL, 0.97 mmol), and the mixture was brought to reflux for 15 h. Concentration of the golden yellow solution to ca. 3 mL, followed by the addition of excess diethyl ether, led to the precipitation of **14·Cl** as a golden yellow solid, which was isolated by filtration and dried in vacuo. Yield: 0.140 g (76%). ESI+ MS: *m*/*z* 605.0 $[M]^+$, 529.1 $[M - PMe_3]^+$, 453.1 $[M - 2\ PMe_3]^+$. NMR ($CDCl_3$): $^{11}B\{^1H\}$ $\delta_B \approx 9.5$ (s br, hhw 250 Hz). $^{13}C\{^1H\}$: δ_C 17.2, 17.3 [d × 2, PCH_3, $^1J_{CP} \approx 7$ − second order], 33.7 (2C), 34.2 (1C) [NCH$_3$], 124.7 (2C), 124.1 (1C) [N*C*H═CHNB], 118.6 (1C), 120.2 (2C) [NCH═*C*HNB], 164.5 (1C), 164.8 (2C) [C═S]. Occluded $OPMe_3$ (1 equiv by NMR) is a persistent obstacle to obtaining microanalytical data from bulk samples, which also retain ill-defined solvent traces. Anal. Found: C, 34.45; H, 5.17; N, 10.49; S, 11.21; Cl, 6.73. Calcd for $C_{21}H_{42}BClN_6OP_3RhS_3$: C, 34.42; H, 5.78; N, 11.47; S, 13.13; Cl, 4.84. *Crystal data*: $C_{18}H_{33}BN_6P_2RhS_3 \cdot Cl \cdot H_2O \cdot CHCl_3 \cdot (C_4H_{10}O)_{0.25}$. M_w = 1474.06, orthorhombic, $P2_12_12_1$ (No. 19), a = 9.1802(2) Å, b = 21.9173(5) Å, c = 32.4110(8) Å, V = 6521.3(3) Å^3, Z = 4, D_c = 1.502 Mg m^{-3}, μ(Mo Kα) = 1.044 mm^{-1}, T = 200(2) K, yellow needle, 10 400 independent reflections, F refinement R_1 = 0.0405, wR_2 = 0.0402 for 6099 independent absorption-corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 48.4°], 660 parameters, CCDC 281909. NB: The structure has a non-centrosymmetric space group; the absolute structure of the crystal used was determined by refinement of a Flack parameter (0.02(4), 4538 Friedel pairs).

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Supporting Information Available: Full details of crystallographic structure determinations for solvates of **8·Cl** (CCDC 281910), **9·Cl** (CCDC 281911), and **14·Cl** (CCDC 281909) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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