ORGANOMETALLICS

Volume 25, Number 25, December 4, 2006

Communications

Synthesis of a Heterobimetallic Rhodium−Iron Complex Containing an η^3-Interaction between Rhodium and the B−C$_{ipso}$−C$_{ortho}$ Unit of a Triarylborane

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Received October 3, 2006

*Summary: Reaction of [{RhCl(CO)$_2$}$_2$] with a phosphine/thioether/borane ligand (TXPB) gave [Rh(μ-Cl)(CO)(TXPB)] (**1**), a rare example of a complex containing a M−Cl−BR$_3$ bridging interaction. Reaction of **1** with K[CpFe(CO)$_2$] gave [(TXPB)Rh(μ-CO)$_2$Fe(CO)Cp] (**2**), which contains an unprecedented η^3-interaction between rhodium and the B−C$_{ipso}$−C$_{ortho}$ unit of a triarylborane. DFT calculations suggest a bonding description intermediate between that expected for an isolated borane/alkene complex and a fully delocalized allyl-like complex.*

A thorough understanding of the interactions possible between arylboranes and transition metal complexes is of particular importance given their prominent position as cocatalysts and reagents in transition metal chemistry. For example, arylboronic esters play a key role as reagents in Suzuki−Miyaura coupling[1] and triarylboranes occupy a position of prime importance as activators for insertion polymerization.[2] Until recently, the vast majority of homogeneous polymerization catalysis involved the use of d^0 metal complexes. However, the discovery of effective mid and late transition metal catalysts[3] greatly expands the range of metal−borane reactivity that may be encountered.

Beyond alkyl or hydride abstraction, reported modes of reactivity between an arylborane and an organometallic complex include phosphine abstraction,[4] adduct formation,[5] or reaction with an ancillary ligand (e.g., to form a boratacyclopentadienyl[6] dianion). In late transition metal chemistry, arylboranes have also been shown to react directly with the metal[7−9] to form unusual metal borane complexes. Herein, we describe the preparation of a rhodium complex containing an η^3-interaction between rhodium and the B−C$_{ipso}$−C$_{ortho}$ unit of a triarylborane. We recently reported the preparation of a rigid phosphine−thioether−borane ligand (TXPB, Scheme 1), which has been shown to be effective in positioning a borane in close proximity to palladium.[10] Reaction of TXPB with [{Rh(μ-Cl)(CO)$_2$}$_2$] gave yellow [Rh(μ-Cl)(CO)(TXPB)] (**1**) in 83% isolated yield (Scheme 1). Selected spectroscopic features include a sharp doublet ($^1J_{\mathrm{Rh,P}}$ 161 Hz) at 63.8 ppm in the ^{31}P NMR spectrum and ν(CO)(Nujol) = 2010 cm^{-1}. The solid-state structure of **1** (Figure 1) reveals that the TXPB ligand is *P,S*-coordinated to square planar rhodium, and the borane unit of TXPB engages in a rare M−Cl−B bridging interaction.[9,11] Boron is considerably pyramidalized [C−B−C = 111.9(7)°, 113.5(6)°, and 114.4(7)°], and the B−Cl distance [1.995(9) Å] is only 0.05−0.15 Å longer than that observed for aryl-substituted chloroborane Lewis base adducts or chloroborates (cf. 1.893(2) Å in Ph$_2$BCl(THF)[12] and 1.937(5) Å in [PPN][{PhClB(η^5-C$_5$H$_4$)$_2$}-

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10.1021/om060903m CCC: $33.50

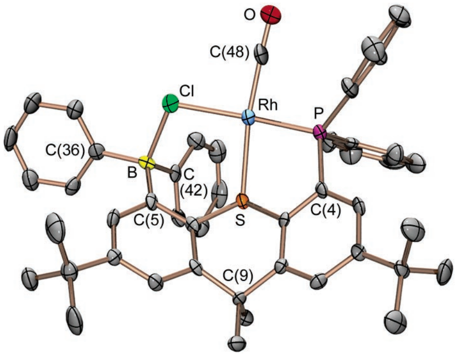
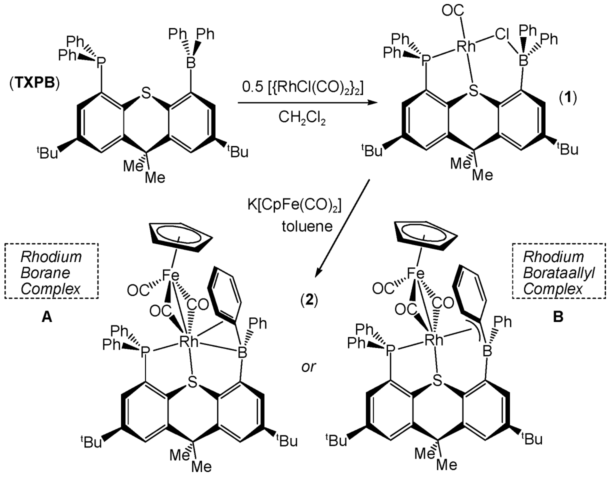


Figure 1. ORTEP of [Rh(μ-Cl)(CO)(TXPB)]•hexane (**1**) with solvent and hydrogen atoms omitted for clarity (50% thermal ellipsoids). Selected bond lengths (Å): Rh−C(48) 1.817(11), Rh−P 2.205(2), Rh−S 2.379(2), Rh−Cl 2.381(2), B−Cl 1.995(9), B−C(42) 1.611(12), B−C(36) 1.619(12), B−C(5) 1.612(12).

Scheme 1. Preparation of Complexes 1 and 2



ZrCl$_2$][13]), indicative of a strong B−Cl interaction. In keeping with this observation, the ^{11}B NMR chemical shift for **1** occurs at 11.5 ppm, compared with 69 ppm in free TXPB. However, the Rh−Cl bond in **1** seems largely unperturbed, with Rh−Cl = 2.381(2) Å, compared to 2.381(1) Å in [{*o*-C$_6$H$_4$(PPh$_2$)(SMe)}RhCl(CO)][14] and 2.370(2) Å in [(POT)RhCl(CO)][15] (POT = a neutral, bidentate, chiral triarylphosphine/dialkylthioether ligand). For comparison, the B−Cl interaction in [Pd(η^3-allyl)(μ-Cl){(Cy$_2$B)(*i*Pr$_2$P)C$_6$H$_4$-*o*}], a close relative of **1**, appears to be substantially weaker, with B−Cl = 2.16 Å, $\sum$(C−B−C) = 349°, and ^{11}B NMR δ = 47 ppm.[9]

In order to probe whether a metal−boron interaction might be accessible by replacement of chloride with a nucleophilic metal anion, complex **1** was reacted with K[CpFe(CO)$_2$], resulting in the formation of olive green [(TXPB)Rh(μ-CO)$_2$Fe(CO)Cp] (**2**) in 69% yield (Scheme 1). The presence of a doublet ($^1J_{\mathrm{Rh,P}}$ 175 Hz) at 46.0 ppm in the ^{31}P NMR spectrum and carbonyl stretching frequencies of 1960 and 1771 cm^{-1} (Nujol) confirm that **2** contains both bridging and terminal carbonyl ligands and that the TXPB ligand remains bound to rhodium. A broad singlet in the ^{11}B NMR spectrum at 2 ppm demonstrates that **2** does *not* contain a neutral three-coordinate triarylborane. The ^{1}H NMR of **2** shows broad P-*Ph* and B-*Ph* signals and a single C*Me*$_2$ peak at 20 °C,[16] but at −75 °C is well resolved and corresponds to a single C_1 symmetric product. Of particular interest are five signals originating from one phenyl ring, several of which are observed at unusually high field [7.16 (*o*), 6.93 (*m*), 6.52 (*p*), 6.25 (*m*), 3.60 (*o*) ppm].

After many attempts, crystals of **2**•solvent were obtained by slow diffusion of hexanes into a 1,2-dme/toluene solution of **2** at −30 °C. The solid-state structure of **2** shows that the TXPB ligand is bound to rhodium not only via phosphorus and sulfur but also through boron and the *ortho*- and *ipso*-carbons of one B-phenyl ring (Figure 2). This coordinated phenyl ring provides an explanation for the unusually shielded aromatic protons in the ^{1}H NMR spectrum. The complex has a total of 36 electrons and a Rh−Fe single bond with two approximately symmetrical bridging carbonyl ligands (located in a plane with Rh and Fe) and one terminal carbonyl on iron. Rhodium is trigonal bipyramidal, excluding the Rh−Fe bond and with C(42), C(49), and P in the trigonal plane. The geometry at boron is more planar than pyramidal; $\sum$(C−B−C) = 357(3)°, although C42 lies 0.421(66) Å above the C5−B−C36 plane.[17]

Complex **2** could be considered to contain either (A) an η^2-coordinated phenyl ring and a σ-interaction between rhodium and an approximately planar borane or (B) a conjugated borataallyl (B−C−C) ligand (Scheme 1). Neither class of metal−ligand interaction has precedent in the literature. However, calculations[18] have shown that in certain cases an unsymmetrical μ-boryl complex[18,19] can be considered a metal−

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(5) See for example adducts with organometallic complexes bearing the following ligands: (a) oxo: Sánchez-Nieves, J.; Frutos, L. M.; Royo, P.; Castaño, O.; Herdtweck, E., *Organometallics* **2005**, *24*, 2004. (b) nitrido: Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059. (c) carbyne: van der Eide, E. F.; Piers, W. E.; Romero, P. E.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 314. (d) alkylidene: Cook, K. S.; Piers, W. E.; Woo, T. K.; McDonald, R. *Organometallics* **2001**, *20*, 3927. (e) halide: References 9 and 11a. (f) cyano or vinyl cyanide: Brunkan, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627. Rocchini, E.; Rigo, P.; Mezzetti, A.; Stephan, T.; Morris, R. H.; Lough, A. J.; Forde, C. E.; Fong, T. P.; Drouin, S. D. *Dalton Trans.* **2000**, 3591. (g) carbonyl: Choukroun, R.; Lorber, C.; Lepetit, C.; Donnadieu, B. *Organometallics* **2003**, *22*, 1995. (h) nitrile: Choukroun, R.; Lorber, C.; Vendier, L.; Donnadieu, B. *Organometallics* **2004**, *23*, 5488. García, J. J.; Arévalo, A.; Brunkan, N. M.; Jones, W. D. *Organometallics* **2004**, *23*, 3997. (i) enolate: Spaether, W.; Klass, K.; Erker, G.; Zippel, F.; Fröhlich, R. *Chem. Eur. J.* **1998**, *4*, 1411. (j) acyl: Anderson, G. D. W.; Boys, O. J.; Cowley, A. R.; Green, J. C.; Green, M. L. H.; Llewellyn, S. A.; von Beckh, C. M.; Pascu, S. I.; Vei, I. C. *J. Organomet. Chem.* **2004**, *689*, 4407. (k) enone: Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944. Reference 10.

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(16) The ^{1}H NMR spectrum of **2** at 20 °C is consistent with exchange between coordinated and noncoordinated B−*Ph* rings, presumably via a σ-bonded M−BR$_3$ intermediate or by complete B−C$_{ipso}$−C$_{ortho}$ dissociation.

(17) Accurate B−C bond lengths were not accessible from the X-ray crystal structure of **2**, and hydrogen atoms were not located.

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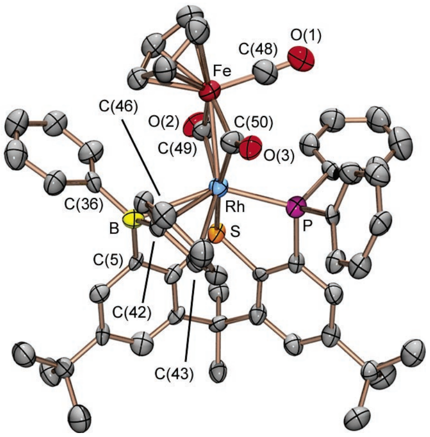

Figure 2. ORTEP of [(TXPB)Rh(μ-CO)$_2$Fe(CO)Cp]$\cdot$solvent (**2**) with disordered solvent (~6.5 carbon atoms) and hydrogen atoms omitted for clarity (50% thermal ellipsoids). Selected bond lengths (Å): Rh−Fe 2.665(3), Fe−C(48) 1.73(2), Fe−C(49) 1.92(2), Fe−C(50) 1.88(2), Rh−C(49) 1.97(2), Rh−C(50) 2.03(2), Rh−P 2.346(5), Rh−S 2.354(5), Rh−B 2.63(2), Rh−C(42) 2.33(2), Rh−C(43) 2.46(2), B−C(42) 1.50(3), B−C(36) 1.57(3), B−C(5) 1.63(3), C(42)−C(43) 1.41(2).

borane adduct, even in the absence of significant pyramidalization at boron. In addition, allyl-like (C−B−C) chelation of a borane-bridged diylide to Zr and Pd was recently reported.[20]

The Rh−B distance of 2.63(2) Å is longer than that observed in Hill, Bourissou, Parkin, and Connelly's rhodium borane complexes [2.09−2.31 Å][8,21] or Rh−B in Westcott et al.'s unsymmetrical μ-boryl complex [2.444(9) Å].[18] However, M−B is intermediate between that observed in Shapiro's palladium [2.200(5) Å] and zirconium [2.754(4) Å] boron-bridged diylide complexes[20] and is considerably shorter than that observed for group 8 metallocenylboranes [2.8−3.3 Å].[22]

In complex **2**, as with metallocenylboranes, the M−B distance will be strongly influenced by geometric constraints imposed by the rigid ligand backbone. However, the ^{11}B NMR chemical shift of 2 ppm rules out the possibility that the borane is three-coordinate and neutral and is held in close proximity to rhodium solely as a consequence of a Rh−(η^2-arene) interaction. In addition, the B···P distance of 4.770(21) Å in **2**, which is considerably shorter than that of 5.442(9) Å in **1** or 5.774(4) Å in [Pd(dba)(TXPB)],[10] demonstrates that the borane unit is not positioned in close proximity to rhodium as a simple consequence of ligand rigidity and that a significant Rh−(BCC) interaction must exist. In fact, while important to control and direct borane reactivity, it is conceivable that the rigidity of TXPB may in fact enforce longer bond lengths between Rh and the BCC unit (especially Rh−B) than would otherwise be observed.

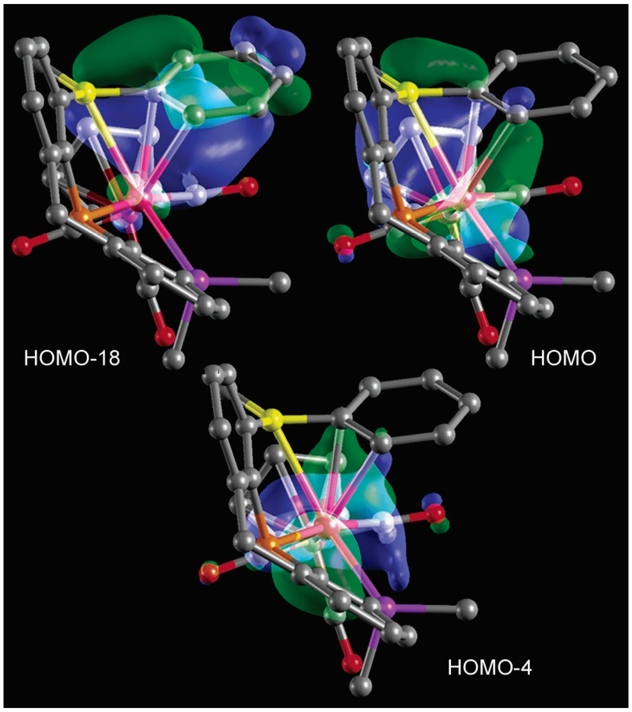

Figure 3. Localized molecular orbitals of **2**. Peripheral Me and CMe$_3$ groups and the *o*-, *m*-, and *p*-carbon atoms of three phenyl rings hidden for clarity.

The bridging carbonyl ligands in **2** give rise to ν(CO) = 1771 cm^{-1}, compared with 1673 and 1712 cm^{-1} for [(Me$_3$P)$_2$Rh(μ-CO)$_2$Fe(PMe$_3$)Cp][23] and 1708 cm^{-1} for [Cp*Rh(μ-CO)$_2$Fe(C$_6$Me$_6$)],[24] despite a greater electron count on **2** (36 versus 34 if Rh−Fe bonds can be considered to be single in all complexes). Complex **2** also undergoes an irreversible reduction at E_p(red) = −1.81 V in THF (cf. $E_{1/2}$ = −1.97 V for TXPB reduction in THF), consistent with reduction of the Rh−Fe core of **2**. While it is tempting to interpret these data with respect to formal charges on the Rh−Fe core as a result of either borane/alkene or borataallyl ligand bonding, there are problems inherent with assigning formal charge to ligands such as these in significantly covalent complexes. This point has been highlighted in a recent article focused on the nature of metal−boron σ-bonding in transition metal borane complexes, [L$_x$M−BR$_3$].[25] Therefore, for **2**, the major distinction between a borane/alkene complex (A) and a borataallyl complex (B) must be the nature of the B−C$_{ipso}$−C$_{ortho}$ molecular orbitals involved in M−(BCC) bonding (Figures 3 and 4), rather than the charge on the BCC unit.

The interaction between Rh and the BCC unit was further examined using DFT (ADF 2005.01, TZP, VWN, PW91, ZORA). The geometry of a model analogue of **2** with H in place of CMe$_3$ groups was fully optimized using frozen cores (up to 3d for Rh and below the valence shell for all other atoms) and closely matches the experimental structure. It also reveals nonplanarity at both B and C43 ($\sum$(C−B−C) = 354.4°; C42 lies 0.605 Å above the C5−B−C36 plane; C46−C43−H43 = 168.58°) and a slight shortening of B−C42 relative to B−C36 and B−C5 (1.567 vs 1.587 and 1.593 Å).[17]

The compositions of relevant orbitals were examined by applying the Boys−Foster localization method to the result of an all-electron calculation. Three localized molecular orbitals involve significant *Rh−(BCC) bonding* interactions (Figure 3):

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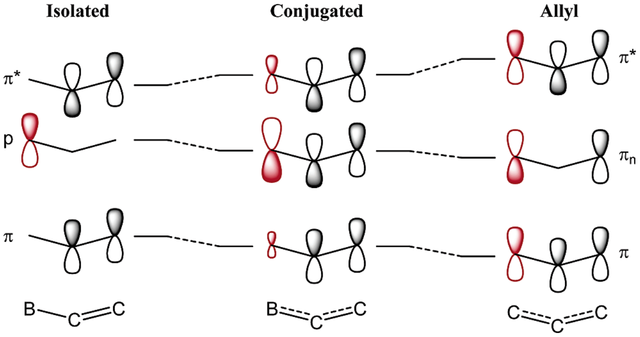

Figure 4. Schematic representations of the π-manifold for an ECC ligand (E = B or C) in the two extreme bonding descriptions (an isolated borane/alkene ligand and a fully delocalized allyl ligand) and an intermediate situation for a conjugated BCC ligand.

The HOMO-18 shows π-delocalization across the BCC fragment, consistent with π-bonding borataallyl character. The HOMO-4 is $\pi^*(C_{ipso}-C_{ortho})$ in character with no significant contribution from boron, as would be expected for a borane/alkene complex. The HOMO involves a bonding interaction between $\pi^*(C_{ipso}-C_{ortho})$ and p_π-B. In a symmetrical π-allyl ligand, this orbital would correspond to the familiar π_n orbital, containing a central node as a result of equal magnitude bonding and antibonding contributions between the central carbon atom and the two equivalent terminal carbons. Overall, these calculations confirm the existence of a significant Rh−(BCC) bonding interaction and are indicative of Rh−BCC bonding character intermediate between that expected for an allyl-like ligand with fully delocalized molecular orbitals and a borane/alkene complex. This is expected since overlap between B and C_{ipso} must exist, but the extent of mixing will depend on the electronegativity difference between boron and carbon (Figure 4).

In summary, reaction of [Rh(μ-Cl)(CO)(TXPB)] (**1**) with K[CpFe(CO)$_2$] gave [(TXPB)Rh(μ-CO)$_2$Fe(CO)Cp] (**2**), in which a triarylborane group is found to engage in an η^3-interaction with rhodium via $B-C_{ipso}-C_{ortho}$. This type of interaction is without precedent, but could have unrealized significance in transition metal chemistry involving aryl or vinylboranes, especially where metal oxidation is possible. The nature of complex **2** and the Rh−($B-C_{ipso}-C_{ortho}$) interaction was investigated by NMR and IR spectroscopy, cyclic voltammetry, X-ray crystallography, and DFT calculations, which suggest a bonding description intermediate between that expected for an isolated borane/alkene complex and a fully delocalized allyl-like complex. Future work will include studies into the reactivity of **2** with nucleophiles and unsaturated molecules and attempts to probe the generality of the η^3(BCC)-arylborane coordination mode.

Acknowledgment. D.J.H.E. and I.V.B. thank NSERC of Canada for Discovery Grants and Canada Foundation for Innovation (CFI) and Ontario Innovation Trust (OIT) for New Opportunities Grants. D.J.H.E. thanks McMaster University for support in the form of a start-up grant. K.D.P thanks NSERC of Canada for a USRA.

Supporting Information Available: Experimental, NMR, CV, computational, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060903M