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Rhodium Phosphine Olefin Complexes of the Weakly Coordinating Anions $[BAr^F{}_4]^-$ and [1-*closo*-$CB_{11}H_6Br_6]^-$. Kinetic versus Thermodynamic Factors in Anion Coordination and Complex Reactivity

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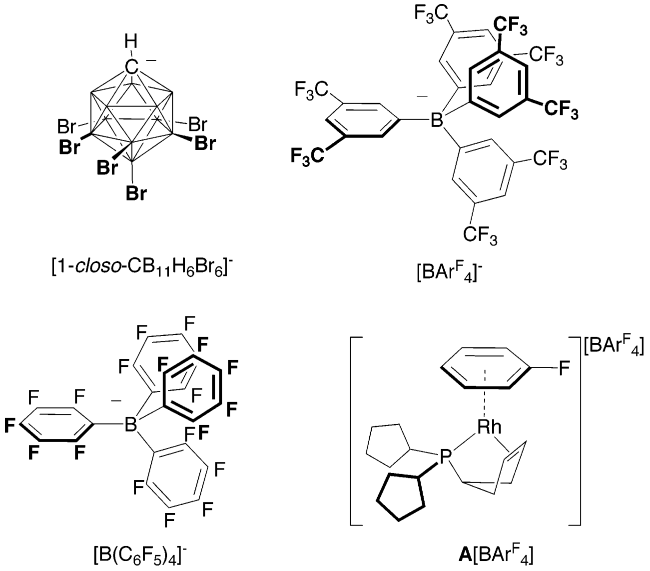
Summary: Solution and solid-state structures for the pair of complexes Rh{P(Cyp$_2$)(η^2-C_5H_7)}{η^6-($C_6H_3(CF_3)_2$)$BAr^F{}_3$} and Rh{P(Cyp$_2$)(η^2-C_5H_7)}(1-closo-$CB_{11}H_6Br_6$), which contain bound weakly coordinating anions, are reported. While thermochemical data show that enthalpically [1-closo-$CB_{11}H_6Br_6]^-$ binds less strongly with the metal fragment and it is the large entropy loss for the overall process of coordination of the $[BAr^F{}_4]^-$ anion that results in the latter anion being thermodynamically more weakly coordinating. Qualitative kinetic data arising from reaction with H_2 indicates that the carborane anion is displaced more readily, attributable to the ability of the carborane to lift a Rh−Br interaction.

Chart 1



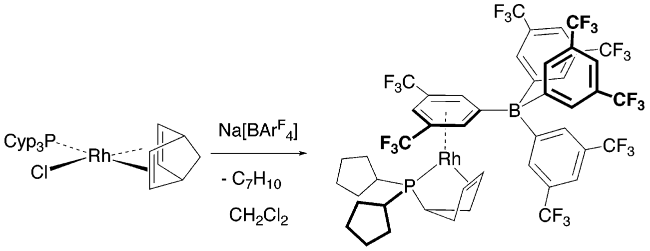
[1-*closo*-$CB_{11}H_6Br_6]^-$

$[BAr^F{}_4]^-$

$[B(C_6F_5)_4]^-$

A$[BAr^F{}_4]$

Scheme 1



The [1-*closo*-$CB_{11}H_6Br_6]^-$- and $[BAr^F{}_4]^-$-type anions (Chart 1; $Ar^F = C_6H_3(CF_3)_2$) are commonly referred to as being among the least nucleophilic and most stable anions known.[1] Comparisons between these classes of anions have been reported in terms of the synthesis of free silylium cations[2] and protonated arenes,[3] in relative anion basicities,[4] and in catalysis when partnered with cationic transition-metal fragments.[5] The solid-state structures of Ag^+ salts of these two anions are also known.[6,7] However, systems where a direct structural and thermochemical comparison can be made between the coordination properties of these counterions when they are partnered with transition-metal fragments, as far as we are aware, have not been reported. This is because, in order to do this, each anion must cleanly form a complex in both the solution and the solid state with the transition-metal fragment, and this is understandably difficult to achieve, given their weakly coordinating properties. Thermochemical data are well established for early-transition-metal (metallocene) cations partnered with $[MeB(Ar^F{}_3)]^-$ anions where complexes between cation and anion can be systematically made.[8] We communicate here the synthesis and solid-state and solution structures of a cationic rhodium phosphine fragment partnered with either a coordinated $[BAr^F{}_4]^-$ or [1-*closo*-$CB_{11}H_6Br_6]^-$ anion. This affords, for the first time we believe, a comparison of simple structural, thermodynamic, and kinetic factors that influence anion coordination between these two anions.

We have recently reported that addition of $Na[BAr^F{}_4]$ to Rh(nbd)(PCyp$_3$)Cl (PCyp$_3$ = tricyclopentylphosphine) in fluorobenzene solvent results in the elimination of NaCl and the facile dehydrogenation of one of the cyclopentyl groups to afford [Rh(η^6-C_6H_5F){P(Cyp$_2$)(η^2-C_5H_7)}]$[BAr^F{}_4]$ (**A**$[BAr^F{}_4]$; Chart 1), which has a chelating phosphine−olefin ligand and coordinated fluorobenzene ligand.[9] We reasoned that repeating this reaction in CH_2Cl_2, a solvent much less likely to coordinate to

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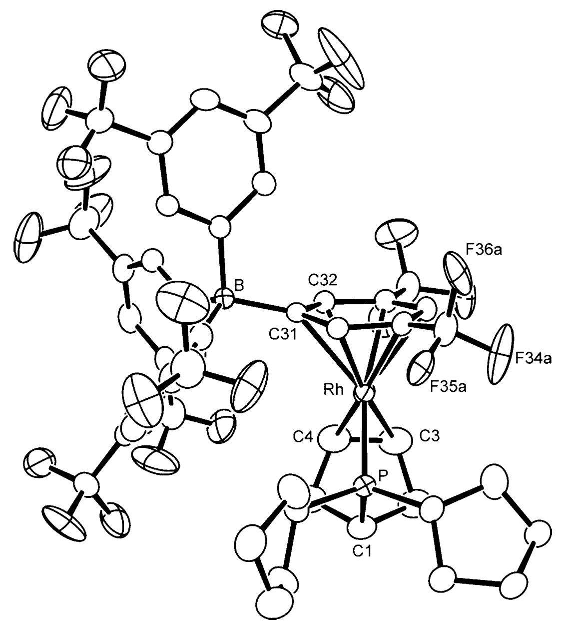
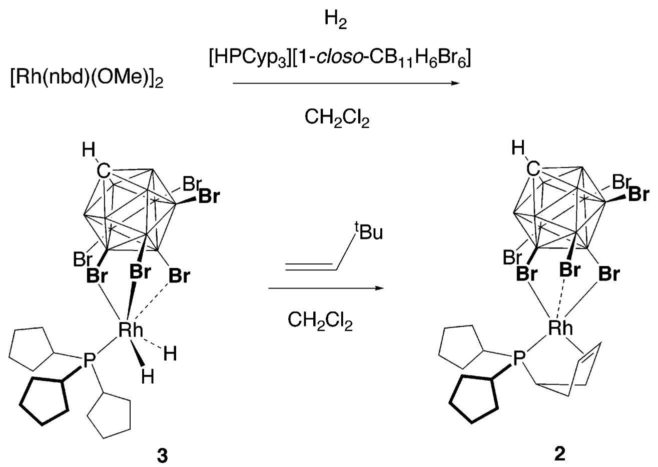


Figure 1. Solid-state structure of **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−C(31) = 2.426(3), Rh−C(32) = 2.308(3), Rh−P = 2.2608(8), Rh−C(4) = 2.131(3), Rh−C(3) = 2.158(3); B−C(31)−C(34) = 167.3(2).

the metal center, would afford the new complex Rh{P(Cyp$_2$)(η^2-C$_5$H$_7$)}{η^6-(C$_6$H$_3$(CF$_3$)$_2$)BAr$^F_3$} (**1**), in which the [BAr$^F_4$]$^-$ anion is now a ligand coordinated through one of its aryl rings. This is indeed the case, and complex **1** can be isolated in 54% yield (Scheme 1). Solutions of **1** slowly decompose to unidentified products, some of which appear to have undergone B−C cleavage of the anion.[10] The solid-state structure of **1** is shown in Figure 1 and clearly demonstrates the η^6 coordination of the weakly coordinating [BAr$^F_4$]$^-$ anion through one of its aryl rings (d(Rh−C$_{aryl}$) = 2.263(3)−2.426(3) Å), with the longest Rh−C$_{aryl}$ interaction being not surprisingly with the ipso carbon, C(31). Solution NMR data demonstrate that the anion also remains coordinated in CD$_2$Cl$_2$ solution. In particular the coordinated aryl protons are shifted upfield in the ^{1}H NMR spectrum and the ^{19}F NMR spectrum displays two environments in the ratio 1:3. As far as we are aware, there are only two other examples of [BAr$^F_4$]$^-$ coordinated to a metal center, with {Rh(cod)}$^+$ and Ag$^+$ fragments,[6] while there are only a handful of crystallographically characterized examples of the analogous [B(C$_6$F$_5$)$_4$]$^-$ anion coordinated through M···F interactions, all with early transition metals or lanthanides.[11] Although it is η^6-coordinated, the [BAr$^F_4$]$^-$ anion in **1** can be displaced by weak ligands. Addition of 1 equiv of fluorobenzene establishes an equilibrium between **1** and **A**[BAr$^F_4$], so that a ratio of 1:1, respectively, is observed at 298 K. Addition of excess fluorobenzene affords **A**[BAr$^F_4$] quantitatively.

Scheme 2



In order to compare the two anions, we have developed a synthesis of the complex directly analogous to **1** with the [1-*closo*-CB$_{11}$H$_6$Br$_6$]$^-$ anion (Scheme 2). Reaction of the hydrogen acceptor *tert*-butylethene with Rh(PCyp$_3$)H$_2$(1-*closo*-CB$_{11}$H$_6$Br$_6$) (**3**; see the Supporting Information for the synthesis of **3**) results in the dehydrogenation of one cyclopentyl ring and formation of Rh{P(Cyp$_2$)(η^2-C$_5$H$_7$)}(1-*closo*-CB$_{11}$H$_6$Br$_6$) (**2**) in 69% isolated yield. By comparison, the analogous complex using the [1-*closo*-CB$_{11}$H$_6$Cl$_6$]$^-$ anion could not be prepared cleanly by this route. The solid-state structure of **2** is shown in Figure 2. The carborane anion coordinates with the rhodium fragment through three Rh−Br interactions. One of these is significantly longer than the other two (2.9514(6) Å versus 2.6504(5), 2.6702(5) Å), and we describe the geometry of **2** as pseudo trigonal bipyramidal with one weaker equatorial Rh···Br interaction. In solution (CD$_2$Cl$_2$) the anion is fluxional, as C_{5v} symmetry is observed for the boron cage, in contrast to the approximate C_s symmetry observed in the solid state. As with **1**, addition of 1 equiv of fluorobenzene to **2** results in an equilibrium between **2** and **A**[1-*closo*-CB$_{11}$H$_6$Br$_6$], being observed in a 1:2.7 ratio, respectively. Addition of an excess of fluorobenzene results in the quantitative formation of **A**[1-*closo*-CB$_{11}$H$_6$Br$_6$], which has been spectroscopically characterized by independent synthesis (see the Supporting Information).

With complexes **1** and **2** in hand, we have a unique opportunity to determine the relative strengths of binding of these two anions with a late-transition-metal fragment. Addition of 1 equiv of [NBu$_4$][BAr$^F_4$] to **2** slowly (hours at 298 K) establishes an equilibrium between **1** and **2** (Scheme 3). Measuring the relative ratios of these two complexes over the

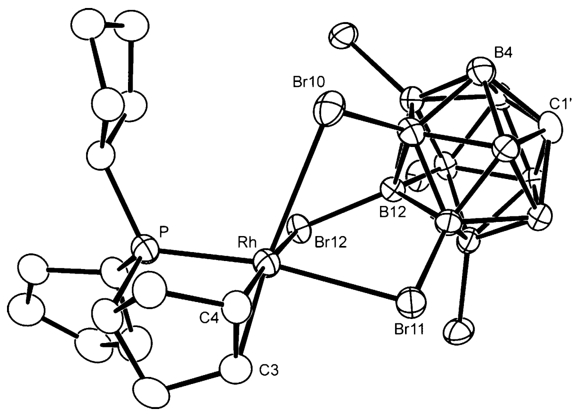


Figure 2. Solid-state structure of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−Br(11) = 2.6504(5), Rh−Br(12) = 2.6702(5), Rh−Br(10) = 2.9514(6), Rh−P = 2.197(1), Rh−C(4) = 2.077(5), Rh−C(3) = 2.109(5); P−Rh−centC(3)/C(4) = 84.0(2), Br(12)−Rh−centC(3)/C(4) = 153.8(2), P−Rh−Br(11) = 171.32(4).

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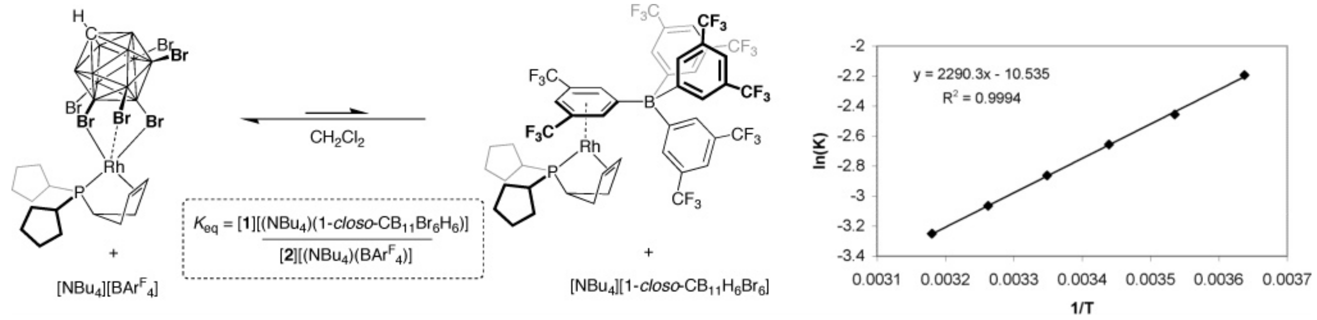
Scheme 3[a]



[a] The insert gives a van't Hoff plot for the equilibrium established between **1** and **2**.

temperature range 275−313 K[13] affords a van't Hoff plot from which $\Delta H° = -19.0 \pm 0.3$ kJ mol^{-1}, $\Delta S° = -87.6 \pm 0.8$ J K^{-1} mol^{-1}, and $\Delta G°(298) = +7.0 \pm 0.5$ kJ mol^{-1} were determined. Interestingly, this shows that although enthalpically the $[BAr^F_4]^-$ anion binds more strongly than the carborane anion ($\Delta H°$ is negative), it is the large negative entropic contribution involved in the coordination of the $[BAr^F_4]^-$ anion/dissociation and solvation of the carborane anion that overall results in the [1-*closo*-$CB_{11}H_6Br_6]^-$ anion being marginally favored ($\Delta G°$ is small but positive). Addition of 1 equiv of $[NBu_4]$[1-*closo*-$CB_{11}H_6Cl_6]$, an anion which is ranked as being less basic that its bromo congener,[4] to **2** did *not* result in an equilibrium being established to the detection limits of ^1H and ^{31}P NMR spectroscopy after 24 h at room temperature, with **2** remaining unchanged and no decomposition observed. This demonstrates that, in this system at least, [1-*closo*-$CB_{11}H_6Cl_6]^-$ must be more weakly coordinating even than $[BAr^F_4]^-$.

Reaction of H_2 (1 atm, 298 K) with **2** affords **3** in 3 h, whereas no reaction is observed with **1**, even after 12 h. We explain this by the $[BAr^F_4]^-$ anion being unable to create a vacant site on the 18-electron metal center in **1** required for addition of H_2, whereas the [1-*closo*-$CB_{11}H_6Br_6]^-$ can presumably lift the already weak Rh−Br interaction to reveal a reactive 16-electron rhodium center. With stronger ligands such as THF or MeCN reaction is effectively instantaneous for both to form the previously reported metal fragment $[Rh\{P(Cyp_2)(\eta^2\text{-}C_5H_7)\}(L)_2]^+$ (L = MeCN, THF).[9]

In conclusion we report a rare example of $[BAr^F_4]^-$ coordinated to a transition-metal center and present the first comparative structural, thermodynamic, and reactivity data with the weakly coordinating carborane anion [1-*closo*-$CB_{11}H_6Br_6]^-$ in a transition-metal system. These show that although the $[BAr^F_4]^-$ anion forms a slightly weaker complex than [1-*closo*-$CB_{11}H_6Br_6]^-$, kinetically it is substitutionally less labile with the weak ligand H_2 in the weakly coordinating solvent CH_2Cl_2. This is a consequence of the η^6 binding of the $[BAr^F_4]^-$ compared with the carborane anion that can act in a hemilabile manner. Given that there are a growing number of organic transformations mediated by cationic late-transition-metal fragments in weakly coordinating solvents such as CH_2Cl_2 (e.g. hydrogenation, hydroacylation, cyclizations, and cycloadditions[12]) such subtle differences between anions as we disclose here may prove to be important.

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Supporting Information Available: Text, tables, figures, and CIF files giving full experimental data for the synthesis of complexes **1**, **2**, and **3**, details of the anion exchange experiments, NMR spectra for complex **1**, and crystallographic data for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The collection of equilibrium data over a wider temperature range was frustrated by the very slow time taken to reach equilibrium at each temperature: e.g., 16 h at 275 K.