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Dihydrogen Loss from a 14-Electron Rhodium(III) Bis-Phosphine Dihydride To Give a Rhodium(I) Complex That Undergoes Oxidative Addition with Aryl Chlorides

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Summary: Dihydrogen loss from the 14-electron Rh(III) bis-phosphine dihydride $[Rh(P^iBu_3)_2H_2][BAr^F_4]$ *forms a complex tentatively identified as* $[Rh(P^iBu_3)_2(L_2)][BAr^F_4]$ *(*L_2 *= solvent or agostic interactions), which reacts with dichloroethane or fluorobenzene to form* $[Rh(P^iBu_3)_2(ClCH_2CH_2Cl)][BAr^F_4]$ *and* $[Rh(P^iBu_3)_2(\eta^6\text{-}C_6H_5F)][BAr^F_4]$*, respectively.* $[Rh(P^iBu_3)_2(L)_2][BAr^F_4]$ *or its adducts undergo oxidative addition of aryl halides (*C_6H_5X*; X = Cl, Br) at room temperature to give the dimeric species* $[Rh(P^iBu_3)_2(C_6H_5)(\mu\text{-}X)]_2$*.*

The use of haloarene substrates is ubiquitous in organic chemistry, and the oxidative addition of C−halogen bonds to low-coordinate transition metals, in particular Pd(0),[1] is a key step in cross-coupling reactions.[2] Recently a number of examples of oxidative addition of aryl halides to rhodium and iridium complexes have been reported,[3] reactions which are suggested to proceed through low-coordinate electronically unsaturated intermediates. Examples of well-characterized group 9 species capable of oxidative addition with aryl halides are particularly useful in the study of the emerging fields of C−C and C−N coupling[4] and polychloroarene dehydrohalogenation[5] reactions mediated by group 9 metals.

We have previously reported that bis-dihydrogen dihydride complexes $[Rh(PR_3)_2H_2(\eta^2\text{-}H_2)_2][BAr^F_4]$ (R = ^{i}Pr, Cy; $Ar^F = C_6H_4(CF_3)_2$) are formed from addition of H_2 to CD_2Cl_2 solutions of $[Rh(PR_3)_2(nbd)][BAr^F_4]$ (nbd = norbornadiene).[6] Removing the H_2 atmosphere results in loss of the dihydrogen ligands and formation of dihydride species, suggested to be stabilized by solvent molecule coordination or by agostic C−H···Rh interactions. We now report that, on changing the phosphine ligand to triisobutylphosphine (P^iBu_3), removing the H_2 atmosphere results instead in the generation of a complex with no hydride ligands that can be considered as the kinetic equivalent of “12-electron” $[Rh(P^iBu_3)_2][BAr^F_4]$. This complex undergoes clean oxidative addition with unactivated aryl bromides and chlorides at room temperature to give coordinatively unsaturated Rh(III) aryl halides.

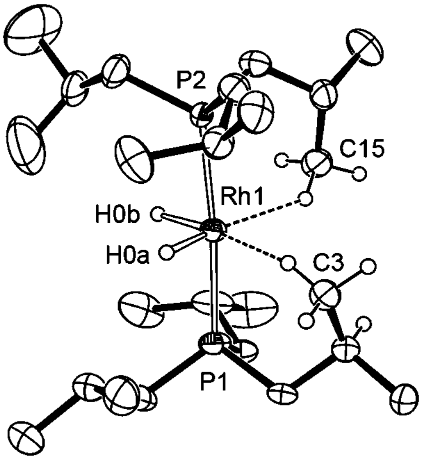

Figure 1. $[Rh(P^iBu_3)_2H_2][BAr^F_4]$ (**1**; 40% probability ellipsoids). The anion, minor disordered components, and most hydrogen atoms have been omitted for clarity. Key bond distances (Å) and angles (deg): Rh1−P1, 2.3067(12); Rh1−P2, 2.2990(11); Rh1−C3, 2.90(3); Rh1−C15, 2.891(5); P1−Rh1−P2, 175.09(4).

Addition of H_2 (4 atm) to $[Rh(P^iBu_3)_2(nbd)][BAr^F_4]$ in CH_2Cl_2 solution results in the immediate formation of $[Rh(P^iBu_3)_2H_2][BAr^F_4]$ **1** (eq 1), which has been characterized by NMR and IR spectroscopy, ESI-MS, and X-ray crystallography. Complex **1** can be characterized in CD_2Cl_2 solution under an argon atmosphere. The molecular structure of **1** is shown in Figure 1 and reveals two Rh···H−C agostic interactions trans to the (located) hydride ligands (Rh···C(3) = 2.90(3) Å, Rh···C(15) = 2.891(5) Å) and is closely related to “14-electron” iridium bis-phosphine and *N*-heterocyclic carbene hydrides reported by Caulton[7] and Nolan,[8] respectively. ^{1}H and $^{31}P\{^1H\}$ NMR spectra are consistent with the solid-state structure. In the $^{31}P\{^1H\}$ NMR

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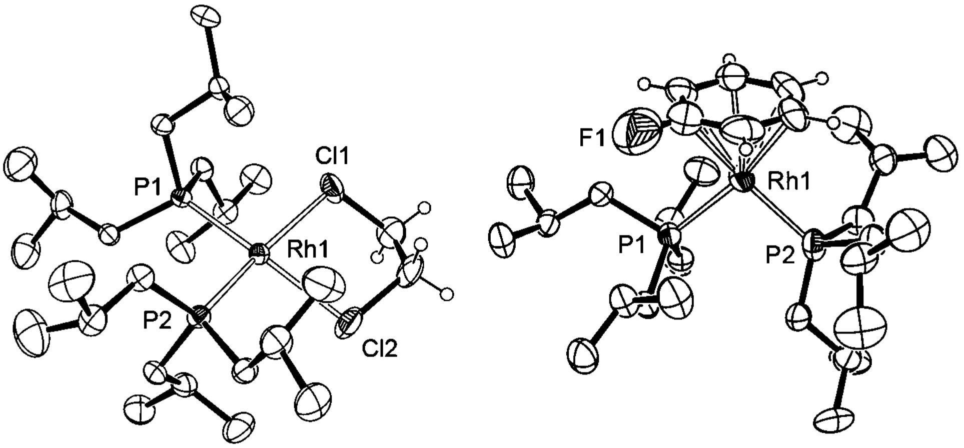
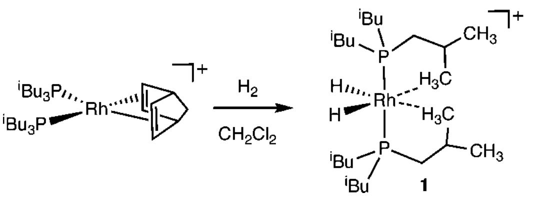


Figure 2. [Rh(P^{i}Bu$_3$)$_2$(ClCH$_2$CH$_2$Cl)][BAr^F$_4$] (**3b**) and [Rh(P^{i}Bu$_3$)$_2$(η^6-C$_6$H$_5$F)][BAr^F$_4$] (**3c**) (40% probability ellipsoids). The anions, minor disordered components, and most hydrogen atoms have been omitted for clarity.

spectrum a single environment is observed that shows coupling to rhodium (δ 28.3, J(RhP) = 107 Hz). The ^{1}H NMR spectrum displays a high-field doublet of triplets for hydrides, while a single set of resonances is observed for the ^{i}Bu protons, indicating rapid exchange between agostic and free C−H groups. This exchange is not frozen out at 190 K. The IR spectrum (CD$_2$Cl$_2$) shows a very broad, medium-intensity band characteristic of agostic interactions at 2668 cm^{-1}.[7] Using a slightly different protocol (starting from Rh(P^{t}Bu$_3$)$_2$H$_2$Cl and Na[BAr^F$_4$]) the analogous complex [Rh(P^{t}Bu$_3$)$_2$H$_2$][BAr^F$_4$] (**2**) was also synthesized (Supporting Information).



(1)

Evaporating a pale yellow solution of **1** to dryness and placing the residue under vacuum (16 h, 5 × 10^{-2} Torr) resulted in the slow loss of H$_2$ to give an air-sensitive orange solid that we tentatively formulate as [Rh(P^{i}Bu$_3$)$_2$(L$_2$)][BAr^F$_4$] (**3a**) (eq 2, L$_2$ = solvent, agostic or anion coordination). Alternatively, rapid H$_2$ removal from **1** in CH$_2$Cl$_2$ solution can be achieved by addition of *tert*-butylethylene (tbe, 5 equiv, 5 min) as a hydrogen acceptor, evaporating the solution to dryness, and washing the resulting orange powder with pentane to remove excess tbe. ^{1}H and ^{31}P{^{1}H} NMR spectra are identical for both preparation methods, indicating that tbe is not bound to the metal. The ^{1}H NMR spectrum (CD$_2$Cl$_2$, 298−190 K) of **3a** shows peaks due to a single P^{i}Bu$_3$ environment, a featureless hydride region, and no evidence for coordination of the [BAr^F$_4$]$^-$ anion through a η^6-arene interaction.[9] The ^{31}P{^{1}H} and ^{19}F NMR spectra (CD$_2$Cl$_2$) both show single environments at δ 44.9 (J(RhP) = 207 Hz) and δ −61.1, respectively. The latter observation further suggests that the anion is not bound through a η^6-arene interaction in solution.[9a] Additional evidence comes from changing the [BAr^F$_4$]$^-$ anion in **3a** for the carborane anion [*closo*-HCB$_{11}$(CH$_3$)$_{11}$]$^-$,[10] which resulted in no change in the chemical shift or coupling constant in the ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$). The ^{31}P{^{1}H} NMR spectrum of **3a** remains relatively sharp and unchanged in chemical shift between 298 and 190 K, suggesting that reversible C−H activation of one of the alkylphosphines, which would result in inequivalent phosphorus environments as recently reported by Caulton for (PNP)Rh (PNP = ^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N), is probably not occurring.[11] Crystalline material obtained from CH$_2$Cl$_2$/pentane solutions showed a grossly disordered solid-state structure from which, unfortunately, no useful structural information could be obtained. Microanalysis and ESI-MS data were consistent with a formulation that *does not* contain CH$_2$Cl$_2$, a ^{1}H NMR spectrum (C$_6$H$_5$F) of dissolved crystals showed no liberated CH$_2$Cl$_2$, and a solid-state ^{2}H NMR experiment of a sample of **3a** prepared in CD$_2$Cl$_2$ showed no deuterium signal, consistent with the absence of coordinated CD$_2$Cl$_2$. In the solid state, in the absence of coordinated solvent, such a complex would undoubtedly have supporting Rh···HC agostic interactions[12] or interactions with the [BAr^F$_4$]$^-$ anion,[9] while in *solution* a bound CH$_2$Cl$_2$ solvent molecule[13] or agostic interactions are likely present, given that we have no evidence for anion coordination. Infrared spectroscopic measurements on microcrystalline **3a** (KBr) or dissolved **3a** (CD$_2$Cl$_2$) show no characteristic stretches for agostic C−H interactions, thus suggesting anion and solvent coordination, respectively. However, given that those signals observed in **1** are particularly broad, we cannot discount that they are present but are too broad to be observed. A d^8 ML$_2$ fragment would be expected to be bent rather than linear and thus be well set up for interactions with solvent, arene, or agostic C−H bonds.[14]

Whatever the precise structure of **3a**, solvent-trapping experiments confirm that the {Rh(P^{i}Pr$_3$)$_2$}$^+$ fragment has been formed.

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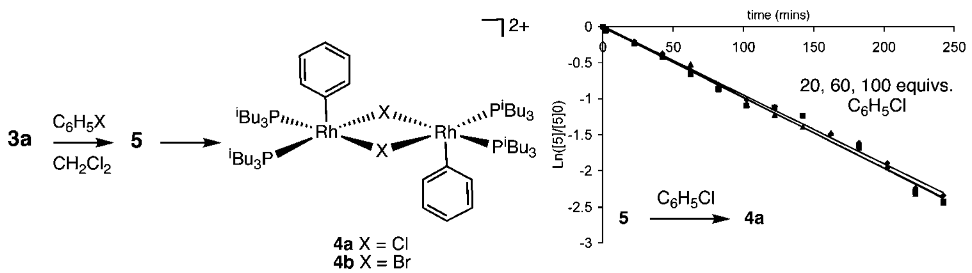


Figure 3. Synthesis of **4a**,**b** (left) and a plot illustrating first-order oxidative addition at different C_6H_5Cl concentrations (right).

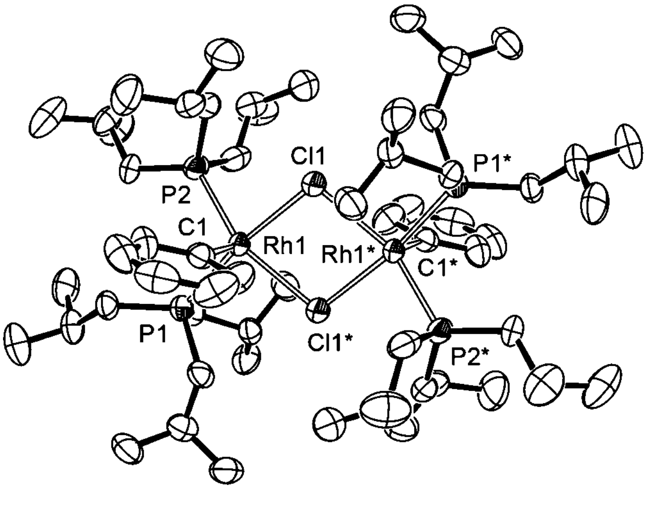
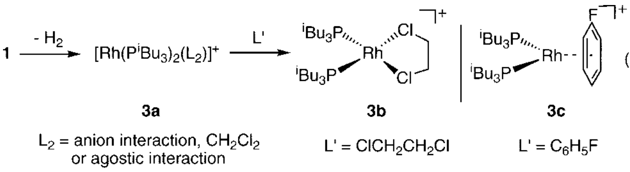


Figure 4. $[Rh(P^iBu_3)_2(C_6H_5)(\mu\text{-}Cl)]_2[BAr^F{}_4]_2$ (**4a**) (40% probability ellipsoids). The anions, minor disordered components, and hydrogen atoms have been omitted for clarity.



(2)

Thus, repeating the synthesis in $ClCH_2CH_2Cl$ rather than CD_2Cl_2 solvent afforded an air-sensitive complex with NMR spectroscopic characteristics very similar to those of **3a** in CD_2Cl_2 solution ($\delta(^{31}P)$ 32.1, $J(RhP) = 204$ Hz) that could also be characterized by X-ray crystallography as the dichloroethane adduct[15] $[Rh(P^iBu_3)_2(ClCH_2CH_2Cl)][BAr^F{}_4]$ (**3b**) (Figure 2). Use of fluorobenzene as the solvent gave the arene adduct $[Rh(P^iBu_3)_2(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$ (**3c**) (Figure 2). **3b**,**c** can also be cleanly generated by adding the appropriate ligand to CH_2Cl_2 solutions of **3a** (eq 2).

Interestingly **2** does not lose H_2 readily and addition of tbe to CH_2Cl_2 solutions results in slow decomposition. We speculate that this is because the bulky *tert*-butyl groups in **2** cannot fold back sufficiently to allow access to a trigonal transition-state with a dihydrogen-like ligand, most likely required for the loss of H_2 from **1**. Similar attempts to remove all the hydrides from $[Rh(PR_3)_2H_2(\eta^2\text{-}H_2)_2][BAr^F{}_4]$ (R = ^{i}Pr or Cy) gave mixtures of products, showing that the P^iBu_3 ligands provide just the right balance of steric and electronic support to facilitate H_2 loss and stabilize the resulting complex.

Addition of bromo- or chlorobenzene to **3a** in CH_2Cl_2 solution at room temperature resulted in the quantitative formation (NMR) of new species that have been characterized as the products of aryl halide oxidative addition at the cationic Rh(I) center: $[Rh(P^iBu_3)_2(C_6H_5)(\mu\text{-}X)]_2[BAr^F{}_4]_2$ (**4a**, X = Cl; **4b**, X = Br). The reaction with bromobenzene is instant at room temperature (<5 min), but that with chlorobenzene takes longer (8 h). In this latter case the immediate formation of an intermediate species is observed. The crystal structure of $[Rh(P^iBu_3)_2(C_6H_5)(\mu\text{-}Cl)]_2$ (**4a**) is presented in Figure 4 and shows a dimeric complex with bridging chloride ligands. Each Rh(III) is formally a 16-electron species with a vacant site in the coordination sphere, lying opposite the aryl group (Rh$\cdots$C > 3.4 Å). The intermediate species in this oxidative addition reaction has been identified spectroscopically as $[Rh(P^iBu_3)_2(\eta^6\text{-}C_6H_5Cl)][BAr^F{}_4]$ (**5**) by comparison of spectroscopic data with those of **3c**. When **5** is formed in situ from addition of chlorobenzene to **3a** in CD_2Cl_2, its transformation to **4b** follows first-order kinetics with a rate that is independent of chlorobenzene concentration (Figure 3; $k = (1.78 \pm 0.05) \times 10^{-4}\ s^{-1}$), indicating that the rate-limiting step is oxidative cleavage of the bound aryl halide to the metal center, possibly via a η^6 to η^2 ring slippage mechanism.[16] The formation of **4a**,**b** via a η^6-haloarene intermediate parallels that observed by Budzelaar and coworkers on the neutral Rh(nacnac)(coe) complex (nacnac = ArNC(Me)CHC(Me)NAr, Ar = 2,6-$Me_2C_6H_3$, coe = *cis*-cyclooctene) to give dimeric Rh(III) aryl halides.[3c] The structure of **4a** is also closely related to the dimeric alkylrhodium(III) complex $[RhCl_2(CH_2CH_3)\{P^tBu_2(CH_2CH_2C_6H_3\text{-}2,6\text{-}Me_2)\}]_2$.[17] Addition of an excess (10 equiv) of P^iBu_3 to a CH_2Cl_2 solution of **3a** inhibited oxidative addition of haloarenes, consistent with the mechanism proposed. Complexes **3b**,**c** also underwent oxidative addition of aryl halides to give the same products, but in the case of **3c** the rate is slower, presumably due to competitive exchange between the arenes.

In conclusion, we report the H_2 loss from a "14-electron" Rh(III) complex to give a series of solvent-stabilized low-coordinate cationic Rh(I) species (**3a**−**c**) in solution, which are capable of oxidative addition of unactivated aryl halides at room temperature. These products are themselves unsaturated, and it is tempting to speculate that this feature will allow them to take part in further reactivity that will result in useful coupling reactions. Studies are currently underway to probe this, and preliminary results indicate that **3a** will promote C−C coupling between 4-bromotoluene and (4-*tert*-butylphenyl)boronic acid in the presence of base. Finally, we note that species such as **3b** are inferred, but not isolated,

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intermediates in cycloaddition reactions mediated by Rh(I) bis-phosphines.[18]

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Supporting Information Available: Text, figures, and tables giving full experimental details, kinetic data, and characterization data and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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