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Competition Studies of Oxidative Addition of Aryl Halides to the (PNP)Rh Fragment

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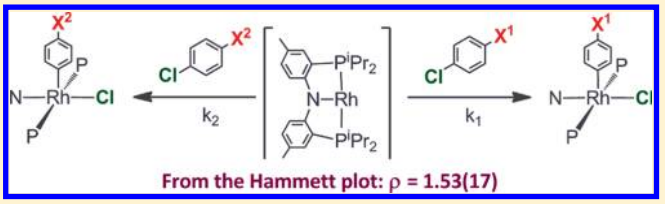
Supporting Information

ABSTRACT: The (PNP)Rh fragment (**2**) can be conveniently accessed by dissociation of L from the four-coordinate complexes (PNP)Rh(L) (L = SPr^i_2, **3**; L = $H_2C{=}CHBu^t$, **10**), which contain the tridentate PNP pincer ligand (2-^{i}Pr$_2$P-4-Me-$C_6H_4)_2N^-$. A new and a more straightforward synthesis of **10** is reported, yielding 65% of **10** based on $RhCl_3(H_2O)_x$. A number of new aryl halide oxidation addition products (AHOAP) of the general formula (PNP)Rh(Ar)(Hal) (Hal = Cl, Br, I) have been synthesized through oxidative addition (OA) reactions of meta- and para-substituted aryl halides with **3** or **10**. The rotation about the Rh−C_{aryl} bond is restricted, resulting in rotamers for the meta-substituted aryls that are distinct on the NMR spectroscopy time scale. Reactions of some aryl halides containing a *p*-NO_2 or *p*-CO_2Me with **3** or **10** led to the observation of products of C−H OA that are ostensibly stabilized by coordination to the NO_2 or CO_2Me group. Analogous C−H OA products were observed for the halide-free nitrobenzene and ethyl benzoate, as well. However, the C−H OA products are thermodynamically unstable with respect to the isomeric AHOAP, to which they convert upon thermolysis. A Hammett-style analysis of the relative electronic effects of the para substituents X in the OA reactions of *p*-HalC_6H_4X with **10** was carried out. The positive values of ρ obtained (ρ = 1.51(15) for Ar−Cl, ρ = 0.70(9) for Ar−Br, and ρ = 0.92(9) for Ar−I) illustrate the increase in the OA rate with increasing electron-withdrawing effect of X. Issues relating to the usefulness of the Hammett parameters in comparing various OA reactions are discussed. Comparison with analogous studies on the OA of aryl halides to Pd(0) complexes leads to the notion that the electronic effects have an impact on the rate similar to, but less pronounced than, that of the (PNP)Rh system, possibly indicative of an earlier transition state for the OA of aryl halides with (PNP)Rh.



INTRODUCTION

Oxidative addition (OA) of aryl halides (Ar−Hal) is a critical step in the versatile chemistry of metal-catalyzed carbon−carbon and carbon−heteroatom coupling.[1,2] OA appears to be increasingly difficult for the lighter halides in Ar−Hal. In the case of the lightest halogen, aryl fluorides rarely undergo OA and, in fact, explorations of their OA chemistry have historically been treated somewhat separately[3] from the analogous reactions of Ar−Cl, Ar−Br, and Ar−I. OA of aryl halides is most common with zerovalent group 10 metal complexes, especially those of Pd.[1,2] However, the number of examples of the OA of Ar−Hal to Rh^I complexes has been steadily rising in the recent years.[4] In the same vein, Rh complexes have also been used to effect catalytic coupling reactions of aryl halides that likely rely on the OA of Ar−Hal as one of the key mechanistic steps.[5]

Our group has reported on the OA of Ar−Hal to a three-coordinate Rh transient (PNP)Rh (**2**),[6−8] in which the Rh^I center is supported by a diarylamido/bis(phosphine) PNP pincer ligand.[9,10] We demonstrated that OA indeed requires the formation of the 14-electron (PNP)Rh fragment **2**, accessible either via dissociation of a placeholder ligand (e.g., from **3**) or via C−C reductive elimination (RE) from a five-coordinate Rh^{III} precursor (e.g., **1**, Scheme 1). We surmised that our (PNP)Rh system presents a very convenient framework for the exploration of competitive OA of various Ar−Hal with Rh. In this paper, we report our findings, ultimately focused on the influence of the substituents in Ar−Hal on the rate of OA. Analogous literature studies of the OA of Ar−Hal to Pd^0 complexes[11−14] provide a backdrop for the comparison with this first study for the OA of Ar−Hal to Rh^I.

RESULTS AND DISCUSSION

Optimized Synthesis of a Rh(I) Precursor. Our previous investigations demonstrated the intermediacy of **2** in the OA reactions of aryl halides. Complex **3** has served as a convenient masked form of **2** in reactions with aryl halides and with silyl halides. The synthesis of **3** is depicted in Scheme 2. It consists of several steps, and while each reaction is intrinsically high-yielding, the losses incurred in isolation of all the intermediates decrease the overall yield; considerable time is spent on isolation and purification as well. In addition, the synthesis of **3** requires the N-methylated PNP ligand **4**, which requires one more

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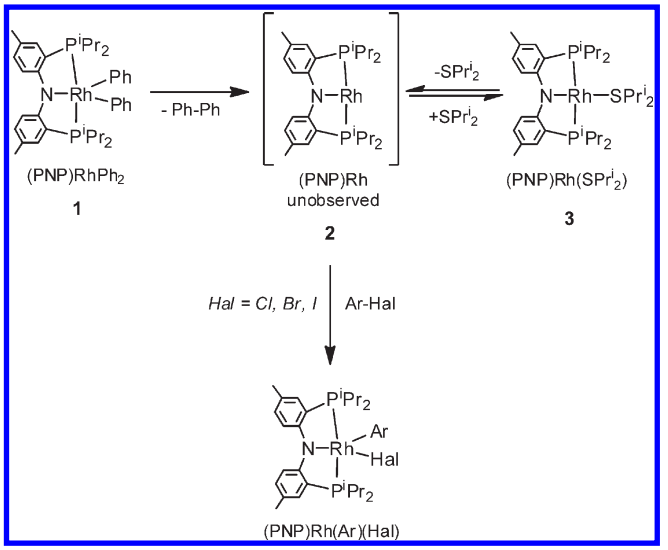
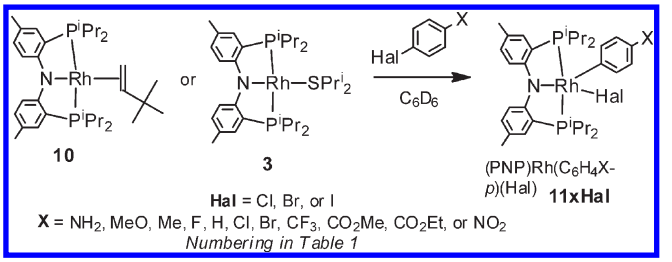
synthetic step than its NH relative **7** (Scheme 3). We saw benefit in developing a new synthesis of a synthon for **2** which minimizes the time involved and maximizes the yield. To this end, we envisioned a synthesis of **10**, shown in Scheme 3. While it cannot be carried out in a "one-pot" fashion, it can be performed as a "single-sequence" synthesis, without isolating or purifying the intermediates beyond the removal of volatiles under vacuum. We have previously reported related one-sequence syntheses of the (PNP)Ir complexes.[15]

The formation of $[(COD)RhCl]_2$ is essentially quantitative,[16] and it can be used as is in the next step. It is preferable to use a small excess of (PNP)H (**7**) in the reaction with $[(COD)RhCl]_2$ to ensure errors in measurement and the non-100% purity do not lead to a deficiency of **7**. Free **7** does not react with any further (PNP)Rh complexes here, and its relatively high solubility allows for its facile separation during the purification of the final product **10**. The reaction of **7** and $[(COD)RhCl]_2$ leads to **8**, as previously described. Complex **8**, as is, can then be converted to the dihydride **9** by using potassium *tert*-butoxide in ^{i}PrOH (which should make KOPr^i) and H_2. Both the isopropoxide (via transfer of β-hydride) and H_2 (by formation of an H_2 adduct and deprotonation of the latter with a base) can serve as the source of the second hydride in **9**. We have not investigated whether only one source of hydride is sufficient. The use of nontertiary alcohols as sources of H_2 or of hydride (with base) is very common in the synthesis of late-metal hydride complexes.[17] We had anticipated that applying an excess of H_2 would help consume the cyclooctadiene byproduct from the previous step. However, if cyclooctadiene was not removed prior to addition of base and H_2, complexes other than **10** formed and persisted. This was evidenced by the observation of broad signals in the $^{31}P\{^1H\}$ NMR spectra around δ 34 and 43 ppm, which we tentatively ascribe to (PNP)Rh(olefin) complex(es) where the olefin is one of the isomers of cyclooctadiene or perhaps a cyclooctene. Apparently, **9** is a poor hydrogenation catalyst. Therefore, we found it critical to completely remove the C_8 volatiles from the reaction mixture prior to the conversion of **8** into **9**. Addition of $H_2C{=}CHCMe_3$ (TBE) to **9** led to the formation of the desired complex **10**. The two hydrides of **9** may be simply displaced as H_2 or consumed in the hydrogenation of TBE. TBE, being present in excess, may also be able to displace C_8 olefins from the residual (PNP)Rh(olefin) impurities. All in all, we were able to isolate **10** in 65% yield based on Rh in $RhCl_3(H_2O)_n$.

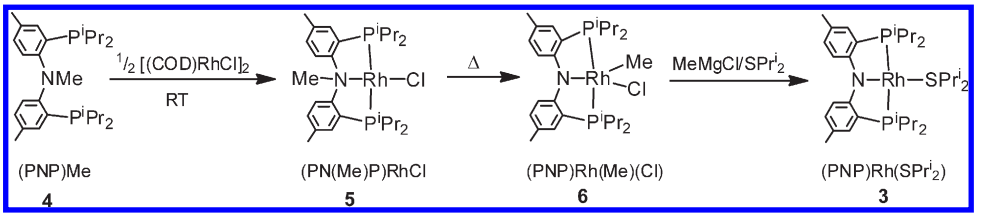
Scheme 1



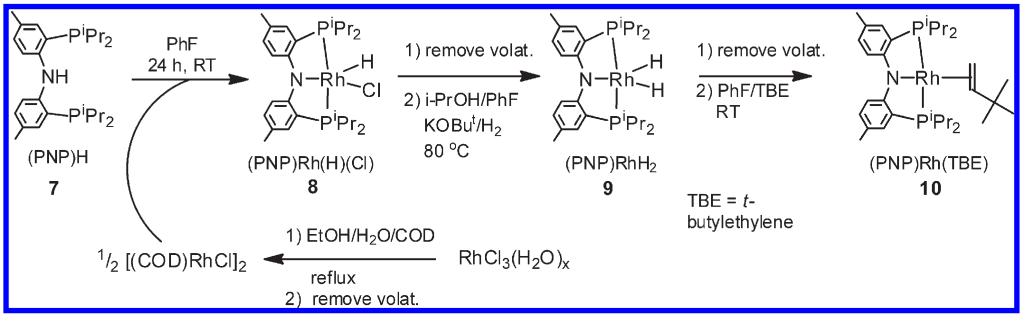
Scheme 4



Scheme 2



Scheme 3



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Scheme 5

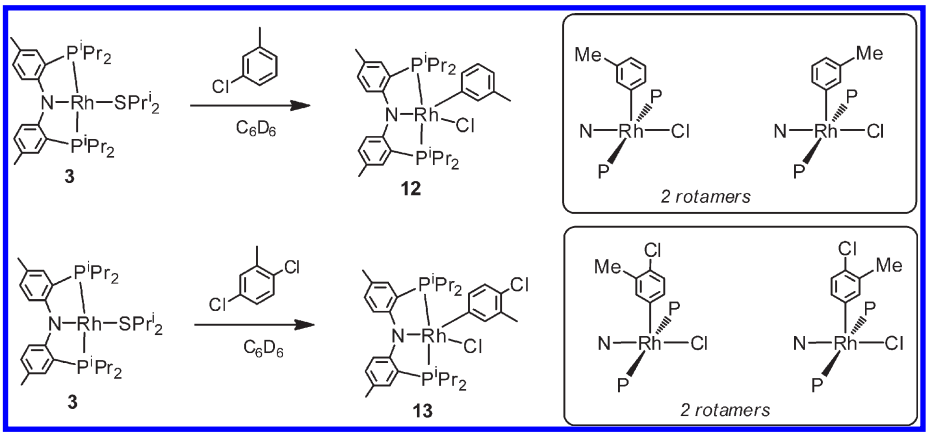

Table 1. ^{1}H NMR Chemical Shifts (in C_6D_6 Solvent) of the Resonances of the PNP Ligands in the Various AHOAP of the General Formula (PNP)Rh(C_6H_4X-*p*)(Hal) (11xHal)

			chem shift (δ, ppm)									
AHOAP	Hal	X	CH_{Ar}	CH_{Ar}	CH_{Ar}	CH_{iPr}	CH_{iPr}	Me_{Ar}	Me_{iPr}	Me_{iPr}	Me_{iPr}	Me_{iPr}
11aCl	Cl	NH_2	7.98 (d, 9)	6.90	6.81 (d, 9)	2.96 (m)	2.30 (m)	2.13	1.47 (dvt, 8)	1.07 (dvt, 8)	1.00 (dvt, 7)	0.51 (dvt, 7)
11bCl	Cl	OMe	8.00 (d, 8)	6.89	6.82 (d, 9)	2.96 (m)	2.29 (m)	2.13	1.44 (dvt, 8)	1.06 (dvt, 8)	1.00 (dvt, 6)	0.45 (dvt, 8)
11cCl	Cl	Me	7.98 (d, 9)	6.89	6.81 (d, 9)	2.96 (m)	2.29 (m)	2.13	1.45 (dvt, 8)	1.07 (dvt, 8)	1.00 (dvt, 6)	0.44 (dvt, 8)
11dCl	Cl	F	7.93 (d, 9)	6.85	6.79[a]	2.92 (m)	2.24 (m)	2.13	1.38 (dvt, 8)	1.02 (8)	0.98 (7)	0.35 (dvt, 7)
11eCl	Cl	H	7.97 (d, 8)	6.88	6.80 (d, 8)	2.96 (m)	2.29 (m)	2.12	1.42 (dvt, 8)	1.07 (dvt, 8)	0.99 (dvt, 6)	0.41 (dvt, 8)
11fCl	Cl	Cl	7.91 (d, 9)	6.84	6.81−6.77[b]	2.91 (m)	2.21 (m)	2.12	1.36 (dvt, 8)	1.00	0.95	0.34 (dvt, 8)
11gCl	Cl	Br	no ^{1}H data									
11hCl	Cl	CF_3	7.93 (d, 10)	6.83−6.79[a,c]	6.83−6.79[a,c]	2.90 (m)	2.19 (m)	2.13	1.32 (dvt, 8)	0.99 (dvt, 8)	0.94 (dvt, 7)	0.26 (dvt, 8)
11iCl	Cl	CO_2Me	7.92 (d, 9)	6.79	6.82 (d, 8)	2.92 (m)	2.20 (m)	2.12	1.36 (dvt, 8)	1.01 (dvt, 8)	0.95 (dvt, 6)	0.32 (dvt, 8)
11kCl	Cl	NO_2	7.88 (d, 9)	6.81[c]	6.81[c]	2.86 (m)	2.17 (m)	2.13	1.27 (dvt, 8)	0.96	0.92 (7)	0.19 (dvt, 8)
11aBr	Br	NH_2	8.00 (d, 9)	6.91	6.81 (d, 8)	3.13 (m)	2.33 (m)	2.13	1.53 (dvt, 8)	1.01 (6)	0.99 (8)	0.47 (dvt, 8)
11bBr	Br	OMe	8.00 (d, 9)	6.89	6.82 (d, 9)	3.1[a]	2.30 (m)	2.12	1.50 (dvt, 8)	1.00 (6)	0.98 (8)	0.39 (dvt, 8)
11cBr	Br	Me	8.00 (d, 8)	6.90	6.82 (d, 8)	3.14 (m)	2.32 (m)	2.13	1.52 (dvt, 8)	1.01 (6)	0.99 (8)	0.40 (dvt, 8)
11dBr	Br	F	7.95 (d, 8)	6.86	6.81 (d, 8)	3.09 (m)	2.26 (m)	2.12	1.44 (dvt, 8)	0.97 (6)	0.93 (8)	0.30 (dvt, 8)
11eBr	Br	H	7.98 (d, 8)	6.88	6.80 (d, 8)	3.14 (m)	2.30 (m)	2.10	1.48 (dvt, 8)	0.98[c]	0.98[c]	0.35 (dvt, 8)
11fBr	Br	Cl	7.92 (d, 8)	6.85	6.81 (d, 9)	3.07 (m)	2.25 (m)	2.13	1.42 (dvt, 8)	0.95[c]	0.95[c]	0.30 (dvt, 8)
11hBr	Br	CF_3	7.95 (d, 9)	6.87[a−c]	6.87[a−c]	3.07 (m)	2.23 (m)	2.12	1.40 (dvt, 8)	0.94 (6)	0.91 (8)	0.21 (dvt, 8)
11jBr	Br	CO_2Et	7.94 (d, 8)	6.80	6.84 (d, 8)	3.09 (m)	2.25 (m)	2.12	1.42 (dvt, 8)	0.94[a−c]	0.94[a−c]	0.26 (dvt, 8)
11kBr	Br	NO_2	7.90 (d, 9)	6.81[a−c]	6.81[a−c]	3.03 (m)	2.20 (m)	2.13	1.34 (dvt, 8)	0.93 (dvt, 6)	0.87 (dvt, 8)	0.15 (dvt, 8)
11aI	I	NH_2	8.03 (d, 8)	6.92	6.83 (d, 9)	3.39 (m)	2.35 (m)	2.13	1.61 (dvt, 8)	1.00 (dvt, 6)	0.86 (dvt, 8)	0.42 (dvt, 8)
11bI	I	OMe	8.04 (d, 9)	6.91	6.84 (d, 8)	3.39 (m)	2.32 (m)	2.12	1.59 (dvt, 8)	0.99 (dvt, 6)	0.86 (dvt, 8)	0.35 (dvt, 8)
11cI	I	Me	8.02 (d, 9)	6.91	6.83 (d, 8)	3.40 (m)	2.33 (m)	2.13	1.59 (dvt, 8)	1.00 (dvt, 6)	0.86 (dvt, 8)	0.34 (dvt, 8)
11dI	I	F	7.97 (d, 9)	6.87	6.82 (d, 8)	3.36 (m)	2.28 (m)	2.12	1.52 (dvt, 8)	0.95 (6)	0.81 (dvt, 8)	0.25 (dvt, 8)
11eI	I	H	8.01 (d, 8)	6.90	6.82 (d, 8)	3.40 (m)	2.34 (m)	2.11	1.57 (dvt, 8)	1.00 (dvt, 6)	0.87 (dvt, 8)	0.32 (dvt, 8)
11fI	I	Cl	7.95 (d, 9)	6.86	6.82 (d, 9)	3.34 (m)	2.28 (m)	2.12	1.50 (dvt, 8)	0.95 (dvt, 6)	0.79 (dvt, 8)	0.24 (dvt, 7)
11gI	I	Br	7.94 (d, 8)	6.85	6.82 (d, 9)	3.30 (m)	2.28 (m)	2.12	1.50 (dvt, 8)	0.95 (dvt, 6)	0.78 (dvt, 8)	0.24 (dvt, 8)
11iI	I	CO_2Me	7.97 (d, 9)	6.81	6.84 (d, 7)	3.39 (*)	2.26 (m)	2.12	1.50 (dvt, 8)	0.95 (6)	0.80 (dvt, 8)	0.21 (dvt, 8)
11kI	I	NO_2	7.93 (d, 8)	6.83[b,c]	6.83[b,c]	3.29 (m)	2.22 (m)	2.12	1.43 (dvt, 8)	0.91 (dvt, 6)	0.75 (dvt, 8)	0.07 (dvt, 8)

[a] Fine structure assignment and precise chemical shift determination complicated by overlap with excess free aryl halide. [b] Fine structure assignment and precise chemical shift determination complicated by overlap of the PNP resonance with the resonance of the aryl group in the AHOAP. [c] Fine structure assignment and precise chemical shift determination complicated by accidental overlap of two resonances of the PNP ligand in the AHOAP.

Oxidative Addition of Various Aryl Halides. We set out to prepare an array of aryl halide oxidative addition products of the general formula (PNP)Rh(Ar)(Hal). We will refer to them as AHOAP for the sake of brevity. The oxidative addition reactions

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were performed by treatment of **3** or **10** with 3 equiv of the corresponding aryl halide (Schemes 4 and 5). We have previously established the relative rates of reaction for the parent phenyl halides to be PhI > PhBr > PhCl, and this appears to hold true in this study as well. However, we did not attempt to optimize the reaction conditions, and the reported reaction times (6 h to 4 days) and temperatures (room temperature to 70 °C) are not necessarily indicative of the relative reaction rates. The formation of AHOAP is irreversible,[6] as indicated by the lack of observable changes upon thermolysis of select AHOAP with other aryl halides (details in the Supporting Information).

We have previously characterized other closely related AHOAP in detail, both structurally and spectroscopically.[6−8] Here we report a number of new AHOAP. Only a few were isolated; others were observed in situ. The AHOAP were easily identified, because they possess very similar ^{1}H and ^{31}P NMR spectroscopic features and presumably also similar near-square-pyramidal structures with an apical aryl group.[18] In the ^{1}H NMR spectra, all AHOAP display an unusually upfield-shifted resonance (δ 0.2−0.5 ppm) for one of the four diastereotopic pairs of Me groups of the PPr^{i}_{2} arms. Similarly anomalous chemical shifts have been observed in (PNP)Rh(Ph)(SPh)[7] and (PNP)Ir(Ph)(Hal),[15] which all likely possess similar structures with the aryl group at the apex of the square pyramid. In contrast, this anomaly is not observed for (PNP)Rh(Me)(Cl) (**6**),[19] (PNP)Rh(H)(Cl) (**8**),[19] or (PNP)Rh(SiR_3)(Hal),[8] which are square pyramidal but do not contain a Rh−aryl group. In these compounds, all the Me groups in the isopropyls resonate in the δ 0.9−1.6 ppm range typical for most PNP complexes. The Me chemical shift anomaly is also not observed in the (PNP)Ir(Ar)(H)[15] compounds or in (PNP)PdPh,[20] which do have a metal−aryl fragment but are either non square pyramidal or possess a hydride instead of an aryl at the apical position cis to N. However, this anomaly is indeed observed in the (PNP)Ir(Ph)(Hal) complexes, which possess essentially the same square-pyramidal structure of the Rh AHOAP.[15] We attribute the Me chemical shift anomaly to the selective ring current influence of an apical aryl group on a pair of Me groups. In the apical position (cis to N_{PNP}), the aryl ring is sandwiched between the two PPr^{i}_{2} arms, with a pair of Me groups positioned to occupy the space above and below the ring plane. This effect would indeed only be observed with an aryl group present, and only in the apical position. It is not specific to the PNP ligand. For example, Milstein et al. reported a [(POCOP)-Rh(Ar)][BAr^{F}_{4}] complex with PPr^{i}_{2} arms and a presumably apical aryl group where one of the pairs of Me groups resonated at δ 0.35 ppm.[21]

In fact, all of the ^{1}H NMR resonances of the PNP ligand in various AHOAP form a fingerprint pattern, especially for the AHOAP with the same halide. Table 1 presents these data for all non-meta-substituted AHOAP. Table 1 provides a numbering scheme for the products of the OA of para-substituted aryl halides (**11** in Scheme 4) of the general form **11xHal**, where **x** denotes the para substituent and **Hal** (Cl, Br, or I) stands for the Rh-bound halide. Not every combination of "x" and "Hal" in **11xHal** was prepared in this study. Table 1 includes every compound **11xHal** that has been observed in this study and excludes compounds **11jCl**, **11gBr**, **11iBr**, **11hI**, and **11jI**, which were not.

We previously noted that the rotation about the Rh−C_{aryl} bond is restricted in AHOAP, resulting in the observation of five broadened ^{1}H NMR resonances for the five inequivalent hydrogen atoms of a phenyl group in (PNP)Rh(Ph)(Hal) (**11eCl**, **11eBr**, **11eI**).[6] Likewise, all AHOAP in this study displayed inequivalence of the ortho and meta hydrogens in para-substituted aryls. This is a common phenomenon for complexes with a phenyl group in a *mer* arrangement with two bulky trans phosphines.[22] When the aryl group contained a meta substituent (**12** and **13**), we observed a mixture of two AHOAP rotamers (Scheme 5). The pairs of rotamers were distinct by NMR spectroscopy at ambient temperature, although the differences in the chemical shifts of the resonances of the PNP ligand were small to imperceptible.

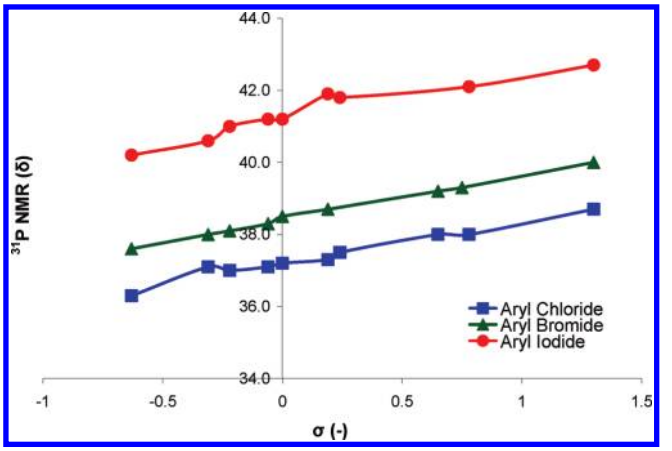

Figure 1. Illustration of the reliable correlation of the ^{31}P NMR chemical shift of (PNP)Rh(C_6H_4X-p)(Hal) (**11xHal**) on the nature of both X and Hal. The horizontal axis corresponds to σ^{-} values (vide infra) of various X.

The ^{31}P{^{1}H} NMR spectra of all aryl halide oxidative addition products displayed a single doublet resonance ($^{1}J_{P-Rh} \approx 103-109$ Hz). Although the differences between various AHOAP are small, the exact ^{31}P NMR chemical shift reliably identifies a particular AHOAP. We illustrate this in Figure 1, where the ^{31}P NMR chemical shifts of the AHOAP are plotted versus the Hammett σ^{-} values (vide infra) of the para substituents in the aryl groups. Although there is a decent correlation, we do not seek to analyze the relationship between the chemical shifts and the electronic properties quantitatively. Here, we merely wish to point out that, for a given aryl group, the Rh−Cl, Rh−Br, and Rh−I compounds are readily distinguishable and, vice versa, for a given halide in the AHOAP, the ^{31}P chemical shift is distinctive for each aryl.

C−H Oxidative Addition. In the oxidative addition reactions of *p*-$ClC_6H_4NO_2$, *p*-$BrC_6H_4NO_2$, and *p*-$ClC_6H_4CO_2Me$, we initially observed a mixture of the expected AHOAP and another product that converted to the AHOAP over time (Scheme 6). We assign these intermediates as C−H oxidative addition products **14**, **15**, and **17** on the basis of their distinctive NMR spectroscopic features. In addition to a doublet resonance (Table 2) in the ^{31}P{^{1}H} NMR spectra, each of these complexes displayed a telltale hydride resonance in the ^{1}H NMR spectra as a doublet of triplets (Table 2). Surmising that the C−Hal functionality is not necessary for the formation of these products of C−H oxidative addition, we performed reactions of **10** and **3** with nitrobenzene and ethyl benzoate (Scheme 6). These reactions cleanly produced **16** and **18**, which possessed key NMR spectroscopic features similar to those of **14**, **15**, and **17** (Table 2).

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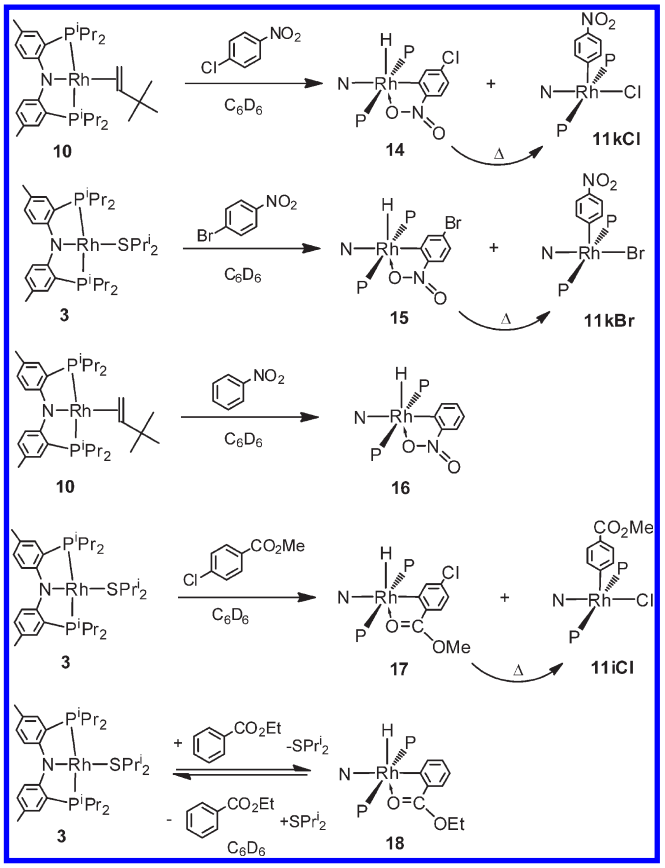
We propose that the relative stability of the C−H oxidative addition products with the nitro and carbethoxy substituents that allows for their observation arises from the stabilizing effect of the coordination of the O donor. Because of this, we assume that the observed C−H activation products are the ortho isomers. This assumption is consistent with the observed hydride chemical shifts. They are less negative than the chemical shift of the hydride (ca. −30 ppm) in the five-coordinate, square-pyramidal (PNP)Rh(H)(Cl) and closely related $(R_3P)_2Rh(H)(Cl)_2$.[23] The hydride chemical shift is quite sensitive to the nature of the occupant of the trans coordination site. The chemical shifts of **14**−**18**, six-coordinate compounds with oxygen donors trans to the hydride, compare well to the chemical shift (ca. − 22 ppm) of the hydride in Meyer and Kaska's (PNP*)Rh(H)(Cl)(THF), where the hydride is trans to THF (PNP* is bis(*o*-(diphenylphosphino)phenyl)amide).[24]

Goldman and co-workers studied the C−H oxidative addition of nitrobenzene to the closely related (PCP)Ir fragment and concluded that the ortho selectivity in C−H activation is of thermodynamic, not kinetic, origin.[25] This conclusion likely applies here as well. Precoordination of the "directing" group is in fact likely counterproductive, as it blocks the coordination site necessary for the C−H OA.

The competition between C−H and C−Hal activation in pincer-supported Ir and Rh systems has recently been a subject of intense scrutiny, with complementary findings by the Milstein group and ours that were also examined computationally by Hall et al.[6,15,26−28] The observation of **14**, **15**, and **17** suggests that C−H OA is kinetically competitive with C−Cl and C−Br OA in the (PNP)Rh system, but the products are long-lived enough for observation only when the aryl carries an ortho-chelating (and electron-withdrawing) substituent. In an earlier report,[6] we attempted to generate (PNP)Rh(C_6H_4Cl-*p*)(H), only to detect (PNP)Rh(Ph)(Cl) (**11eCl**), the apparent product of its rearrangement favoring the C−Cl over C−H OA. The lack of the observation of the C−H OA products in reactions with nitrophenyl and carbethoxyphenyl iodides suggests that the C−Hal OA is faster (i.e., more competitive with the C−H OA) for heavier halides. On the other hand, the isomerization of **14**, **15**, and **17** into the corresponding AHOAP (**11kCl**, **11kBr**, **11iCl**) demonstrates that the C−Hal OA is thermodynamically preferred to the C−H OA even when the C−H OA products are stabilized by the ortho group.

Competition between Different C−Hal Bonds. *p*-Dihalobenzenes as substrates provide an opportunity to test the preference for the OA of the various C−Hal bonds in the intramolecular setting. Within the set of para-substituted substrates (Scheme 4, Table 1), there were six possible dissymmetric permutations of *p*-$C_6H_4(Hal)_2$ where Hal = F, Cl, Br, I. We used NMR spectroscopy (Figure 1) to determine which halide was bound to Rh and which remained bound to C in the resultant AHOAP. In all six cases, the OA of the C−Hal bond with the heavier halide was preferred. Only in the case of *p*-BrC_6H_4Cl were both possible AHOAP observed by NMR spectroscopy: 96% of the C−Br OA (**11fBr**) and 4% of the

Scheme 6



Scheme 7

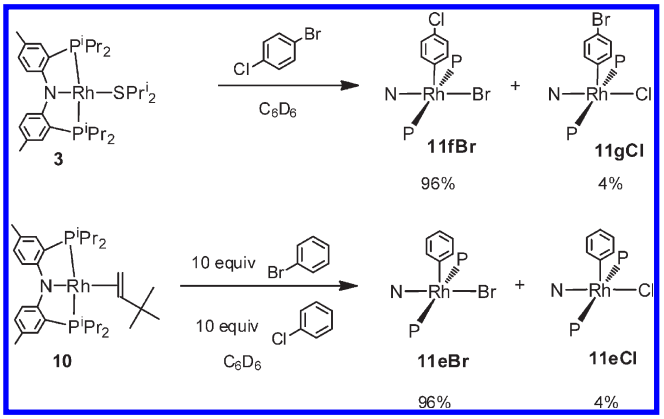


Table 2. Select NMR Spectroscopic Data for Products of C−H OA (14−18) in Reactions with Various Aryl Reagents

aryl reagent	C−H OA product	$^{31}P\{^1H\}$ NMR (δ)	^1H NMR (δ)
4-chloronitrobenzene	**14**	56.6 (d, J = 105 Hz)	−18.19 (dt, J_{H-Rh} = 33 Hz, J_{H-P} = 13 Hz)
4-bromonitrobenzene	**15**	56.9 (d, J = 106 Hz)	−18.22 (dt, J_{H-Rh} = 34 Hz, J_{H-P} = 12 Hz)
nitrobenzene	**16**	56.1 (d, J = 107 Hz)	−18.02 (dt, J_{H-Rh} = 34 Hz, J_{H-P} = 12 Hz)
methyl 4-chlorobenzoate	**17**	52.7 (d, J = 108 Hz)	−19.71 (dt, J_{H-Rh} = 35 Hz, J_{H-P} = 13 Hz)
ethyl benzoate	**18**	52.2 (d, J = 109 Hz)	−19.53 (dt, J_{H-Rh} = 35 Hz, J_{H-P} = 13 Hz)

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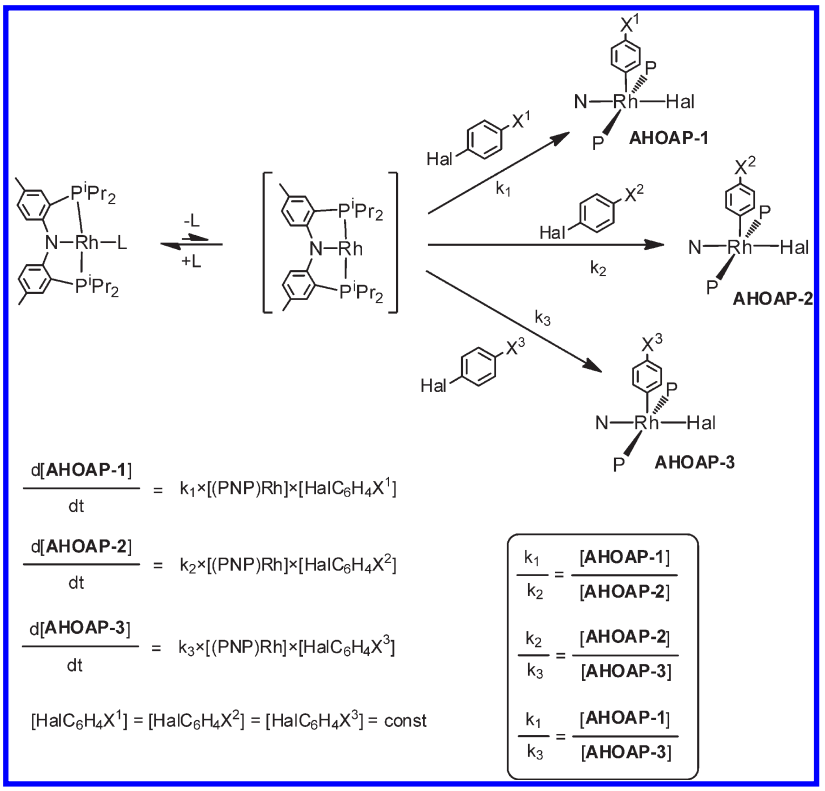
Scheme 8



C−Cl OA (**11gCl**). In an intermolecular competition (Scheme 7), reaction of **10** with equal excesses of PhBr and PhCl also produced a mixture of 96% C−Br OA (**11eBr**) and 4% C−Cl OA (**11eCl**). We have previously established qualitatively that the relative rates of OA to **3** were in the order PhI > PhBr > PhCl. Fluorobenzene does not react with **3**, even under forcing thermolysis conditions, and so the lack of C−F activation[29] in *p*-$C_6H_4(Hal)_2$ was expected. The general preference for a heavier halide in the Ar−Hal OA reactions is not surprising and follows the corresponding trend for the OA of aryl halides to Pd^0 complexes.

Intermolecular Competition among Differently Substituted Aryl Halides. In order to assess the electronic influence of the substituents in an aryl halide on the rate of oxidative addition, we performed an array of intermolecular competition reactions. Here, we assumed that the mechanism of OA is the same for all aryl halides: that is, that the formation of the three-coordinate species **2** precedes interaction of Rh with the aryl halide and **2** is thus a common intermediate. We previously obtained evidence in support of this mechanism, although we have not unequivocally established that for each aryl halide under study.[7]

For each halide (Cl, Br, and I), we selected a series of para-substituted aryl halides with substituents ranging in electronic effect from carbalkoxy and nitro as the most electron-withdrawing groups to methoxy and amino as the most electron-donating. For each halide, we carried out 12 experiments in which **10** was allowed to react to completion with a mixture of three aryl halides (same halide), each in 10-fold molar excess, in C_6D_6 as solvent. The ratios of the AHOAP were measured in situ by ^{31}P NMR spectroscopy. Each substituent was used in at least three separate experiments for each halide.

A generic experiment and the corresponding rate equations are depicted in Scheme 8. The large and equal excess of each aryl halide ensures that the concentration of each aryl halide is approximately constant throughout the experiment. The concentration of the (PNP)Rh (**2**) that confronts the three aryl halides in the same mixture is the same from the point of view of each aryl halide at any point in time, even though it is not constant. From this, we can derive that the ratio of the rate constants for the reaction of an aryl halide with **2** should be equal to the ratio of the corresponding AHOAP.[30]

Because we observed some C−H OA products **14**, **15**, and **17** in reactions with *p*-$ClC_6H_4NO_2$, *p*-$BrC_6H_4NO_2$, and *p*-$ClC_6H_4CO_2Me$, it was necessary to wonder whether C−H OA in effect "directs" the Rh center toward the C−Hal bond in the same molecule. To test this, we attempted to examine whether the selectivity in the formation of the AHOAP from a mixture of aryl halides was skewed by the C−H OA. The reaction of **10** with a mixture (10 equiv each) of *p*-$ClC_6H_4NO_2$ and *p*-$ClC_6H_4CF_3$ at complete consumption of **10** produced **14** (57%), **11kCl** (30%), and **11hCl** (13%). However, heating this mixture until **14** was completely converted to the AHOAP resulted in an 87:14 mixture of **11kCl** and **11hCl**. This result suggests that, ostensibly, once formed, **14** is converted exclusively to **11kCl**. Because of this, we excluded *p*-$ClC_6H_4NO_2$ from our studies.

Analogous reactions of **10** with of *p*-$BrC_6H_4NO_2$ and *p*-$BrC_6H_4CF_3$ yielded less emphatic results. For one, the proportion of **15** initially formed was small (<20%) and while thermolysis of **15** appeared to favor **11kBr** more so than the initial reaction with **10**, the preference was less pronounced than with **14**. Thermolysis of a mixture of *p*-$BrC_6H_4NO_2$ and *p*-$BrC_6H_4CF_3$ produced similar ratios with both **3** and **10** as

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Table 3. Logarithmic Values of the Relative Rate Constants for the Various Aryl Halides

		$\log_{10}(k_i/k_0)$		
para substituent	X	*p*-XC_6H_4Cl	*p*-XC_6H_4Br	*p*-XC_6H_4I
a	NH_2	−0.72(7)	−0.38(5)	−0.30(4)
b	OMe	−0.52(5)	−0.24(6)	−0.20(4)
c	Me	−0.17(6)	−0.09(7)	−0.05(5)
d	F	−0.15(8)	0.00(8)	−0.04(6)
e	H	0	0	0
f	Cl	0.47(7)		0.34(5)
g	Br			0.46(5)
h	CF_3	1.04(8)	0.52(9)	
i	CO_2Me	1.34(9)		0.87(6)
j	CO_2Et		0.70(8)	
k	NO_2		0.87(10)	1.36(8)

sources of (PNP)Rh. All in all, the deviation potentially caused by the C−H OA in the case of bromides was small and was probably within experimental error. It is possible that the C−H OA may play a role with other substrates (besides nitroaryl halides), but it is likely to be even smaller.

The rate constants for the reactions involving the unsubstituted PhCl, PhBr, and PhI were set to unity. Each group of 12 experiments generated 36 pairwise determinations of rate constant ratios. In practice this number was slightly reduced, because overlap of $^{31}P\{^1H\}$ resonances did not allow for signal discrimination in a few cases. Nonetheless, the amount of original data was quite sufficient to solve for the 7 or 8 unknowns (relative rate constants corresponding to various para substituents) using the LINEST function in Microsoft Excel. The rate constants relative to the corresponding Ph-Hal are shown in the $\log_{10}$ form in Table 3.

Hammett Studies. With the relative rate constant values in hand, we set out to perform a Hammett-type analysis.[31−35] A Hammett plot analysis is a fairly common exercise for the study of the electronic effects of substituents, including in the studies of oxidative addition of aryl halides.[11−14] Plotting logarithmic rate constants against a known set of σ values appears to be straightforward; however, closer scrutiny of the literature unveils a more equivocal picture. First, there exist at least a few different sets of standard σ values.[33] The original σ values proper are derived from the pK_a values of substituted benzoic acids. Complementary σ^- values arise from the pK_a values of substituted phenols; they ostensibly better capture the resonance effects of strongly electron withdrawing groups stabilizing a developing negative charge.[33] A similar set of σ^- values has been derived from the pK_a values of substituted anilinium cations.[36] On the other hand, σ^+ values have been developed for use with reactions where resonance stabilization of the developing positive charge is especially significant.[33] The existence of "competing" sets of standard σ values naturally leads to the selection, somewhat arbitrary, of the best-matching ones for a particular comparison or even a mix-and-match combination of σ values from different sets. Compounding the situation, most of the σ proper and σ^- values are based on the pK_a determinations in water, whereas organometallic reactions typically take place in solvents of low polarity and the solvation differences may well skew the effects of various substituents. The experimental uncertainty in the reported σ values is not always known. In addition, Hammett plot *graphics* are much more common in publications than complete disclosure of raw measurement data, precise sources of the σ constants used, or error analysis. This often makes comparisons of different studies quite tentative. All of these considerations make the Hammett analysis of the organometallic OA reactions much less quantitative than a cursory look may suggest. Nonetheless, with appropriate mathematical caution, Hammett plots can provide some information on the relative influence of substituents on the relative rates of the reaction. If nothing else, they serve as an organized method to evaluate qualitatively whether the reaction rate is uniformly accelerated by electron-withdrawing (or electron-donating) substituents.

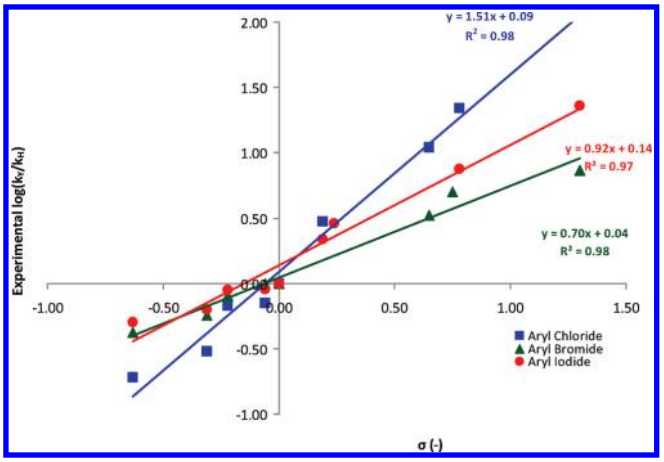

Figure 2. Overlaid Hammett plots for the reactions of aryl chlorides (blue), aryl bromides (green), and aryl iodides (red) of the general formula *p*-$HalC_6H_4X$. The horizontal axis corresponds to σ^- values (from anilinium pK_a's)[36] of various X.

As some others before us,[13,14] we have found that the correlation between the OA rates and the σ proper values deviates significantly from linearity. On the other hand, σ^- values provided a much better fit. The σ^- values based on the acidity of phenols and of anilinium cations are very similar for all substituents pertinent to this study, except for the NH_2 group. Strangely, the σ^- value for *p*-NH_2 from the phenol series is −0.15, whereas the values for *p*-OMe and *p*-Me are −0.26 and −0.17, respectively.[33] This implies that the *p*-NH_2 group is less donating than either *p*-OMe or *p*-Me groups, which seems simply incorrect. This odd value originally stems from a 1928 determination of the pK_a of *p*-$H_2NC_6H_4OH$ in neat water (not made in the context of Hammett substituent analysis).[37] The uncertainty in that determination is unknown, and it is also possible that nontrivial solvation effects alter the acidity of *p*-aminophenol specifically in water. Notably, in 20% water/80% ethanol, the acidity of *p*-$H_2NC_6H_4OH$ is lower than that of either *p*-$MeOC_6H_4OH$ or *p*-MeC_6H_4OH.[38] In our study, the amino-substituted aryl halides displayed the lowest rates of OA, grossly inconsistent with a σ^- value of −0.15. Largely for that reason, we favor the anilinium series of σ^- values (used in Figures 1 and 2).[36] The corresponding Hammett plots for the aryl halide OA reaction rates are depicted in Figure 2. The ρ values from these plots are 1.51(15) for Ar−Cl, 0.70(9) for Ar−Br, and 0.92(9) for Ar−I.[39]

In all cases, the increase in the electron-withdrawing ability of the substituents clearly correlated with the acceleration of OA ($\rho > 0$). The uncertainty in the determination of the ρ values does

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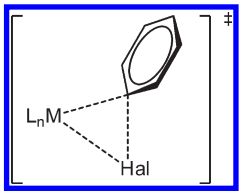

Figure 3. Schematic representation of the three-centered transition state for the concerted OA of a phenyl halide.

not allow us to discriminate with confidence between the values obtained for Ar−I and Ar−Br. Nonetheless, the ρ values for Ar−Br and Ar−I are close and meaningfully smaller than that for Ar−Cl. The positive sign of ρ indicates a buildup of partial negative charge on the aromatic ring in the transition state (TS) and is generally consistent with a three-center transition state for the concerted OA that lies on the continuum toward an S_NAr-type reaction.[1] In this TS (Figure 3), the degree of rupture of the Ar−Hal bond should correlate with an increased transfer of electron density from the metal to Ar−Hal and thus increased partial negative charge on the Ar unit. It seems reasonable to propose that a more positive ρ value corresponds to a "later" TS. From this perspective, since the cleavage of Ar−Br and Ar−I bonds should be more facile, the higher positive value of ρ for Ar−Cl makes sense.

It is also instructive to compare the ρ values in this study to the ρ values reported[11−14] in the literature for the OA of aryl halides to Pd(0) complexes. Literature ρ values for the OA of aryl halides to Pd(0) were recently tabulated by Mayr et al. and in 2004 by Dupont et al.[11] The groups of Milstein in 1993[13] and Buchwald in 2008[14] determined the ρ values for the OA of Ar−Cl to Pd complexes supported by strongly donating trialkyl- or aryldialkylphosphines. The Milstein report[13] erroneously used the natural logarithm of the rates for the Hammett analysis (instead of the decadic logarithm), and their reported value of $\rho = 5.2$ (vs the σ^- set) should be treated as $\rho = 5.2/(\ln 10) = 2.3$ for purposes of comparison with other Hammett studies. This matches the value obtained in the Buchwald communication.[14] The ρ value of +2.3 for the Ar−Cl OA in these Pd studies vs +1.51(15) in our study suggests that the TS for the OA of Ar−Cl is "earlier" for the (PNP)Rh system than even for the most electron rich phosphine/Pd(0) systems. This may be taken to reflect the greater facility of the concerted OA with the (PNP)Rh fragment. This line of reasoning is supported by computational studies. Hall et al.[26] analyzed the OA of PhCl to a truncated (PNP)Rh system and found the C−Cl distance of 1.935 Å in the TS, whereas Norrby et al.[40] calculated much longer C−Cl distances of 2.15 and or 2.17 Å in the TS for the OA of *p*-$CHOC_6H_4Cl$ and *p*-$MeOC_6H_4Cl$, respectively, to ($^tBu_3P$)Pd. The C−Cl bond length in free PhCl has been determined by various experimental methods to be ca. 1.74 Å.[41] The literature ρ values for the Ar−Br and Ar−I OA to Pd(0) vary broadly, from +0.6 to +2.5.[11,12] In some of these cases, the nature of the Pd(0) fragment undergoing the OA step is not at all clear. With $(Ph_3P)_4Pd$ as the Pd reagent, ρ values in the +2.0 to +2.5 range have been reported for the Ar−Br and Ar−I OA.[11,12] It may be expected that the ρ values for the Ar−I and Ar−Br OA should be lower than for Ar−Cl, but Ph_3P-supported Pd(0) is much less electron rich (in fact, incapable of the Ar−Cl OA) and we would predict much lower ρ values for the Ar−Br and Ar−I OA with trialkyl- or aryldialkylphosphines.

CONCLUSION

Investigations of the electronic influence of the substituents on the aromatic ring on the oxidative addition (OA) of aryl halides to the (PNP)Rh transient (**2**) have shown that the OA is accelerated by the presence of electron-withdrawing groups. This influence was semiquantitatively evaluated using the Hammett relationships. The electronic influence of the substituents is greater for the OA of aryl chlorides than for aryl bromides and aryl iodides. We also conclude that the electronic influence of the substituent in the OA of aryl chlorides to **2** is less pronounced than in the analogous studies with OA of aryl chlorides to Pd(0) complexes with strongly electron donating phosphines. Lesser electronic influence (smaller positive ρ value in the Hammett analysis) may indicate an earlier transition state in a concerted OA process.

Competitive experiments between different carbon−halogen bonds to **2** clearly showed the preference for the OA of a carbon−halogen bond with the heaviest halide. In some instances, relatively long lived C−H OA products were observed, when stabilized by a donating substituent ortho to the Rh−C bond. However, in all cases, the C−Hal OA (Hal = Cl, Br, I) was thermodynamically preferred to the C−H OA.

EXPERIMENTAL SECTION

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, and pentane were dried and deoxygenated (by purging) using a solvent purification system[17] by MBraun and stored over molecular sieves in an Ar-filled glovebox. C_6D_6 and THF were dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene was dried with and then distilled from CaH_2 and stored over molecular sieves in an Ar-filled glovebox. The liquid aryl halides 4-bromoanisole, ethyl 4-bromobenzoate, 1-bromo-4-fluorobenzene, 1-bromo-4-chlorobenzene, 4-bromobenzotrifluoride, 4-bromotoluene, bromobenzene, 4-chlorobenzotrifluoride, 2,5-dichlorotoluene, 3-chlorotoluene, chlorobenzene, 4-chloroanisole, 1-chloro-4-fluorobenzene, 4-chlorotoluene, iodobenzene, 1-fluoro-4-iodobenzene, and nitrobenzene were degassed prior to use and stored in an Ar-filled glovebox. The solid aryl halides 4-bromonitrobenzene, 4-bromoaniline, 1,4-dichlorobenzene, 4-chloroaniline, methyl 4-chlorobenzoate, 4-iodonitrobenzene, methyl 4-iodobenzoate, 1-bromo-4-iodobenzene, 4-iodotoluene, 4-iodoanisole, 1-chloro-4-iodobenzene, 4-iodoaniline, and ethyl benzoate were introduced under vacuum into and stored in an Ar-filled glovebox as well. (PNP)Rh(S^iPr_2) (**3**), (PNP)Rh(Ph)(Cl) (**11eCl**), (PNP)Rh(Ph)(Br) (**11eBr**), and (PNP)Rh(Ph)(I) (**11eI**) were synthesized as previously described.[6,7] Compounds **11fCl**, **11hCl**, and **11dBr** have been previously reported.[6] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz; ^{19}F NMR, 376.104 MHz) spectrometer. For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at 0 ppm. ^{19}F NMR spectra were referenced externally using 1 M trifluoroacetic acid in $CDCl_3$ at −78.5 ppm. Elemental analyses were performed by CALI Laboratories, Parsippany, NJ.

(PNP)Rh(H_2C=$CHBu^t$) (10). Under a steady flow of Ar, [$RhCl_3$-(H_2O)] (2.51 g, 11.0 mmol) was transferred into a 100 mL Schlenk flask. A mixture of ethanol (23.8 mL) and water (7.1 mL) was then added to the flask. This was degassed for 10 min by bubbling Ar into the solution through a pipet. Cyclooctadiene (4.15 mL, 33.7 mmol) was added to the flask and similarly degassed for an additional 5 min. The

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solution was then allowed to reflux at 80 °C for 18 h. During this time, an orange precipitate formed and the solution changed from dark red to yellow. The volatiles were then removed in vacuo. In an Ar-filled glovebox, the residue was redissolved in fluorobenzene (40 mL) and PNP(H) (**7**; 4.82 g, 11.2 mmol) was added to the solution. This was then stirred for 24 h, causing the solution to change from orange to dark green. The volatiles were then removed in vacuo. Toluene (4 mL) was added to the flask and immediately removed in vacuo; this was repeated two more times to aid in the removal of free C_8 hydrocarbons. The residue was then redissolved in fluorobenzene (40 mL), and the solution was transferred to a Teflon-stoppered gastight round-bottom flask. Potassium *tert*-butoxide (1.61 g, 14.3 mmol) was dissolved in isoproptl alcohol and degassed by bubbling Ar into the solution through a pipet for 10 min. This solution was then added to the flask under a steady flow of Ar. The flask was briefly placed under vacuum. The flask was then filled with 1 atm of H_2 gas and placed in an 80 °C oil bath for 1 h. During this time, the solution changed from dark green to dark red. The flask was then refilled with 1 atm of H_2 gas and placed back in the 80 °C oil bath, and the mixture was stirred for 18 h. An aliquot of the solution was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, revealing ca. 75% formation of (PNP)RhH_2 (**9**), 5% of (PNP)H (**7**), and 20% of a unknown byproduct. The flask was placed back under 1 atm of H_2 gas and the solution stirred in a 100 °C oil bath for 48 h. An aliquot was taken again, but the ratio of (PNP)Rh(H)(H) to byproduct did not change in the $^{31}P\{^1H\}$ NMR spectra. The volatiles of the solution were then removed in vacuo, and the residue was redissolved in fluorobenzene (40 mL). 3,3-Dimethyl-1-butene (7.09 mL, 55 mmol) was then added to the flask and the mixture stirred for 18 h at ambient temperature. An aliquot of the solution was then analyzed through $^{31}P\{^1H\}$ NMR spectroscopy to confirm the disappearance of **9** and the appearance of **10**. The volatiles of the solution were then removed in vacuo, and the residue was redissolved in diethyl ether (30 mL). The solution was filtered through a layer of Celite. The volatiles of the filtrate were removed in vacuo, and the residue was redissolved in diethyl ether (30 mL). Silica gel was added to the solution, and the mixture was stirred for 10 min and filtered through a layer of Celite once more. The volatiles of the filtrate were removed in vacuo once more. Pentane (20 mL) was then used to dissolve the residue; however, the product was not entirely soluble. The flask was then placed in a −35 °C freezer for 18 h. After this time, the solution was decanted and the solids were washed with cold pentane and dried in vacuo to yield 3.78 g of orange powder. The decanted solution was combined with the washings, and the volatiles were removed in vacuo. The residue was then redissolved in pentane, placed in the freezer, and collected in the same manner. Combined yield: 4.3 g (63%). NMR spectroscopic data were identical with those previously reported.[7] Anal. Calcd: C, 62.43; H, 8.51. Found: C, 62.36; H, 8.62.

Syntheses of 11xHal, 12, and 13. AHOAP Compounds **11xHal**, **12**, and **13** were synthesized through reactions of 3 equiv of the corresponding aryl halides with either **3** or **10** in C_6D_6. The details for each compound are described in the Supporting Information; they were typically characterized in situ in the presence of excess aryl halide and of either SPr^i_2 or TBE.

Intermolecular Competition between PhBr and PhCl. Complex **10** (20.0 mg, 32.5 μmol) was transferred to a glass vial, followed by bromobenzene (10.3 μL, 97.5 μmol), chlorobenzene (9.3 μL, 97.5 μmol), and C_6D_6 (0.58 mL). The solution was mixed and transferred to a J. Young NMR tube, which was then placed in a 75 °C oil bath. $^{31}P\{^1H\}$ NMR analysis revealed that **10** converted to the two distinct products **11eBr** and **11eCl** after 20 h, in a 96:4 ratio. During this time, the solution changed from dark red to dark green. **11eBr** was identified in situ by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, while **11eCl** was only clearly observable by $^{31}P\{^1H\}$ NMR spectroscopy.

Synthesis of (PNP)Rh(H)($C_6H_4NO_2$) (16). Compound **10** (40.0 mg, 65.0 μmol) was transferred to a glass vial, followed by nitrobenzene (20.1 μL, 195 μmol) and C_6D_6 (0.58 mL). The solution was mixed and transferred to a J. Young NMR tube, where it was then placed in a 50 °C oil bath. $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopy analysis revealed that **10** converted entirely to **16** after 24 h. The product was characterized in situ through ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. ^1H NMR (C_6D_6): δ 8.12 (d, 1H, J = 8 Hz, C_6H_4), 7.87 (d, 1H, J = 7 Hz, C_6H_4), 7.77 (overlap, 4H, C_6H_5 of nitrobenzene (2H) + Ar−*H* of PNP (2H)), 6.88−6.30 (overlap, 4H, C_6H_5 of nitrobenzene (1H) + Ar−*H* of PNP (2H) + C_6H_4 (1H)), 6.79 (br s, 2H, Ar−*H* of PNP), 6.70 (overlap, 3H, C_6H_5 of nitrobenzene (2H) + C_6H_4 (1H)), 5.80 (dd, 1H, J = 6 Hz, CH_2=C*H* of 3,3-dimethyl-1-butene), 4.89 (dd, 2H, J = 14 Hz, CH_2=CH of 3,3-dimethyl-1-butene), 2.19 (s, 6H, Ar−CH_3 of PNP), 1.99 (br m, 2H, $CH(CH_3)_2$), 1.82 (br m, 2H, $CH(CH_3)_2$), 1.04 (app quartet (dvt), 6H, J_{H-H} = 7 Hz, $CH(CH_3)_2$), 0.95 (s, 9H, $C(CH_3)_3$ of 3,3-dimethyl-1-butene), 0.88 (app quartet (dvt), 6H, J_{H-H} = 8 Hz, $CH(CH_3)_2$), 0.70 (overlap, 12H, $CH(CH_3)_2$) + $CH(CH_3)_2$), −18.0 (dt, 1H, J_{H-Rh} = 34 Hz, J_{H-P} = 12 Hz, Rh−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.1 (d, J_{P-Rh} = 107 Hz, PPr^i_2).

Observation of (PNP)Rh(H)($C_6H_4CO_2Et$) (18). Compound **3** (20 mg, 31 μmol) was dissolved in 0.80 mL of C_6D_6 and treated with ethyl benzoate (13.3 μL, 92 μmol) in a J. Young NMR tube. The mixture was placed into a 60 °C oil bath. After 7 h, the reaction mixture contained a ca. 63:37 mixture of **18** and **3**, as well as the corresponding amounts of liberated SPr^i_2 and excess ethyl benzoate. Further thermolysis at 60 °C for another 55 h did not result in a noticeable change in the ratio of **18** to **3**. Selected NMR spectroscopic data for **18** are as follows (some resonances could not be reliably identified, owing to overlaps). ^1H NMR (C_6D_6): δ 7.89 (t, 1H, 6 Hz, Ar−*H* of $C_6H_4CO_2Et$), 7.83 (d, 1H, 8 Hz, Ar−*H* of PNP), 6.92 (br s, 1H, Ar−*H* of PNP), 6.84 (d, 1H, 8 Hz, Ar−*H* of PNP), 3.92 (q, 2H, 7 Hz, OCH_2CH_3), 2.23 (s, 6 H, Ar−CH_3 of PNP), 2.09 (m, 2 H, $CHMe_2$), 2.03 (m, 2 H, $CHMe_2$), 0.97 (t, 3H, 7 Hz, OCH_2CH_3), −19.53 (dt, J_{H-Rh} = 35 Hz, J_{H-P} = 13 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.2 (d, J_{P-Rh} = 109 Hz).

■ ASSOCIATED CONTENT

Supporting Information. Text, tables, figures, and a spreadsheet giving experimental details and mathematical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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