C–H Activation

DOI: 10.1002/ange.201303507

Rhodium(III)-Catalyzed Coupling of Arenes with 7-Oxa/Azabenzonorbornadienes by C–H Activation**

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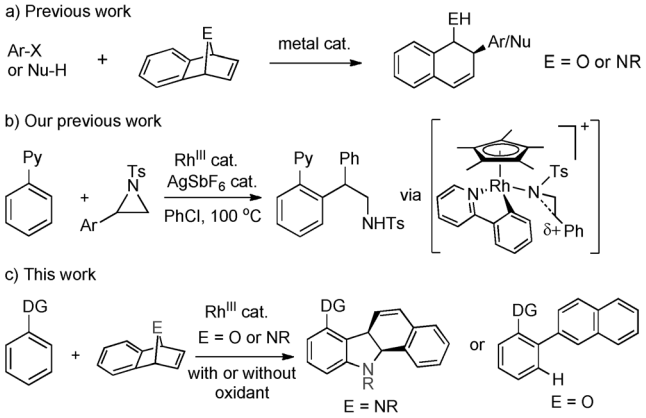
In the past decades, metal-catalyzed C–H activation/coupling reactions have been widely explored and have allowed the development of various synthetic methods employed in the construction of complex structures.[1] Palladium, ruthenium, iridium, and copper catalysts are particularly well known to serve this purpose.[2] Despite the significant progress, it is necessary to explore other metal catalysts because of the structural diversity of both coupling partners. In this regard, rhodium(III)-catalysts stood out with high activity, high selectivity, broad scope, and functional-group tolerance.[3] Thus {Cp*Rh^{III}} complexes have been recently increasingly employed in C–H bond activation and subsequent couplings with various unsaturated molecules, including alkenes,[4] alkynes,[5] ketones and aldehydes,[6] imines,[7] isocyanates,[8] isonitriles,[9] carbene precursors,[10] azides,[11] and aziridines (Scheme 1 a,b).[12]



Scheme 1. Metal-catalyzed ring-opening coupling. DG = directing group, Ts = 4-toluenesulfonyl.

In contrast, the use of transition-metal catalysts for the ring-opening of strained 7-oxa/azabenzonorbornadienes has been well studied in the coupling with aryl halides, amines, phenols, and organomain-group reagents, thus leading to important methods to construct C–F, C–C, C–N, and C–O bonds.[13] Despite the significance of this chemistry and chemistry of C–H activation, these two areas were developed separately, and there has been no report which integrates C–H activation with subsequent ring-opening coupling with 7-oxa/azabenzonorbornadienes. Furthermore, reports are also limited on C–H activation and subsequent (ring-opening) coupling with other ring structures,[14] and examples are even rarer for rhodium(III) catalysis.[12] We reasoned that the incipient Rh^{III}–C bond generated by C–H activation may insert into the strain-activated C=C bond in 7-oxa/azabenzonorbornadienes with subsequent ring opening. We now report the coupling of arenes with 7-oxa/azabenzonorbornadienes under redox-neutral and oxidative conditions (Scheme 1 c).

The coupling of 2-phenylpyridine (**1a**) with 7-oxabenzonorbornadiene (**2a**) was studied first. [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (4 mol%) could effect this coupling, but the conversion was low in a variety of solvents (see the Supporting Information), and the product **3aa** (for structure see Scheme 2) was obtained as the sole product (26–40%) through a dehydrative C–H naphthylation process.[2p,15] Introduction of CF_3COOH improved the yield of **3aa** to 60% (1,4-dioxane, 130 °C), and is likely due to the facilitation of both the C–H activation[2b] and the dehydration processes. Of note, the efficiency was further improved (71%) when a [{RhCp*Cl$_2$}$_2$]/AgSbF$_6$ catalyst was employed in the presence of PivOH (Scheme 2).

With the establishment of the optimal reaction conditions, the scope and limitations of this reaction were next explored (Scheme 2). Substrates bearing both electron-donating and electron-withdrawing groups at different positions of the phenyl ring all coupled smoothly with **2a**, and the naphthylation products were isolated in 56–78% yields (**3aa–3ga**). In particular, when a *meta* substituent was introduced, the reaction occurred at the less hindered position (**3ea**, **3fa**). The directing group is not limited to a simple pyridyl, and introduction of a methyl group at different positions of the pyridine ring caused no detrimental effects (**3ha–3ja**). In contrast, the selectivity was switched to diarylation when a *meta*-chloro group was introduced (**3la**), thus implicating an electronic effect. In addition, quinolinyl and pyrimidyl are also effective directing groups, although both mono- and diarylation products were obtained (**3ma, 3maa, 3na, 3naa**). Significantly, when directed by the same groups, heterocycles such as thiophene and furan underwent more efficient coupling and the products **3oa–3ra** were isolated in 86–90% yields. Finally, the bicyclic olefin substrate is not limited to **2a**, and (di)arylation products (**3ab, 3ac, 3acc**) were isolated in moderate yields when substituted 7-oxabenzonorbornadienes were used.

To better define the substrate scope, the aza analogue of **2a** was employed and an amide-retentive coupling was

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[**] This work was supported by the NSFC (No. 21272231) and Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303507.

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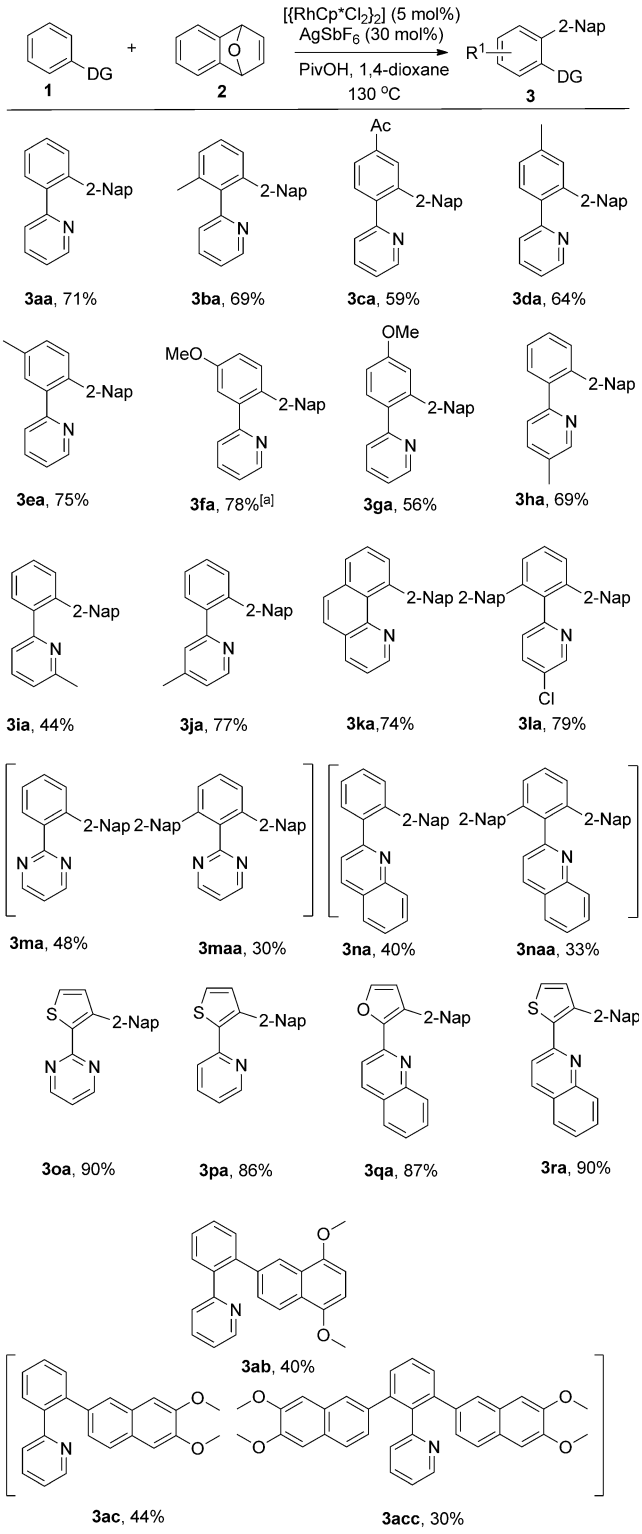
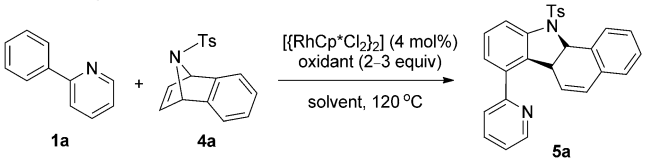


Scheme 2. Dehydative coupling with 7-oxabenzonorbornadienes. Reaction conditions: arene (0.2 mmol), $[\{RhCp^*Cl_2\}_2]$ (5 mol%), $AgSbF_6$ (30 mol%), PivOH (0.4 mmol), 7-oxabenzonorbornadiene (0.3 mmol), 1,4-dioxane (2 mL), 130°C, 24 h. Yield is that of product isolated after column chromatography. [a] Used: arene (0.2 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (4 mol%), TFA (0.4 mmol), and 7-oxabenzonorbornadiene (0.3 mmol), 1,4-dioxane (2 mL), 130°C, 24 h. Cp* = C_5Me_5, Piv = pivaoyl.

expected. However, essentially no reaction occurred when we translated the above redox-neutral conditions to the coupling of 2-phenylpyridine with the 7-azabenzonorbornadiene **4a**. Thus we pondered the possibility of oxidative coupling. It was found that when $[\{RhCp^*Cl_2\}_2]$ was used as a catalyst, AgOAc proved to be an optimal oxidant and 1,4-dioxane was the best solvent (Table 1, entry 2). To our delight, the product **5a** was

Table 1: Optimization studies.[a,b]



Entry	Catalyst [mol%]	Oxidant	Solvent	Yield [%]
1	**A** (6)	AgOAc	1,4-dioxane	42
2	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc	1,4-dioxane	73
3	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc	THF	40
4	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc	DCE	46
5	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc	CH_2Cl_2	43
6	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc	PhCl	38
7	$[\{Cp^*RhCl_2\}_2]$ (4)	$Cu(OAc)_2$	1,4-dioxane	n.d.[d]
8	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOPiv	1,4-dioxane	65
9	$[\{Cp^*RhCl_2\}_2]$ (4)	Ag_2CO_3	1,4-dioxane	n.d.[d]
10	$[\{Cp^*RhCl_2\}_2]$ (4)	AgOAc[c]	1,4-dioxane	90

[a] Reaction conditions: 2-phenylpyridine (0.2 mmol), azacycle **4a** (0.26 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (**A**, 6 mol%) or $[\{RhCp^*Cl_2\}_2]$ (4 mol%), 1,4-dioxane (2 mL), oxidant (2.2 equiv), 120°C, 24 h, sealed tube under argon. [b] Yield of isolated product. [c] Used 3 equiv. DCE = 1,2,-dichloroethane, THF = tetrahydrofuran. [d] Not detectable.

isolated in 90% yield when an excess of AgOAc was used (entry 10). Product **5a** was fully characterized as a *cis*-fused dihydrocarbazole. It should be noted that double C–H activation of arenes are rare in rhodium catalysis.[16]

The scope of this double C–H activation/oxidative annulation reaction was examined (Scheme 3). In line with the 2-naphthylation reaction, a broad scope of directing groups has been achieved. Thus quinoline and pyridine rings bearing electron-donating, electron-withdrawing, as well as halogen groups at different positions are all viable directing groups, and the cyclization products were isolated in good to high yields (>56%). In addition, O-methyl ketoximes are also viable directing groups (**5o**, **5p**), albeit with somewhat lower efficiency. When 2-phenylpyrimidne was subjected to the standard reaction conditions, the cyclization product **5u** was also isolated as a mixture of two diasteromers (1.2:1) in addition to **5t**. Introduction of methyl and halide substituents into the *ortho* and *meta* positions of the phenyl ring is also tolerated (**5e, 5f, 5g, 5j**). However, the *para* substituent has a pronounced influence. 2-(*p*-Fluorophenyl)pyridine coupled with **4a** to give **5n** in 48% yield, while essentially no reaction took place when the *para*-fluoro group was replaced by either a *para*-methyl or *para*-methoxy group, likely as a result of the combination of electronic and steric effects at this position. Furthermore, the N substituent in the azacycle can be extended to other N sulfonyls (**5q, 5r**) and even to an N-Boc group (**5s**).

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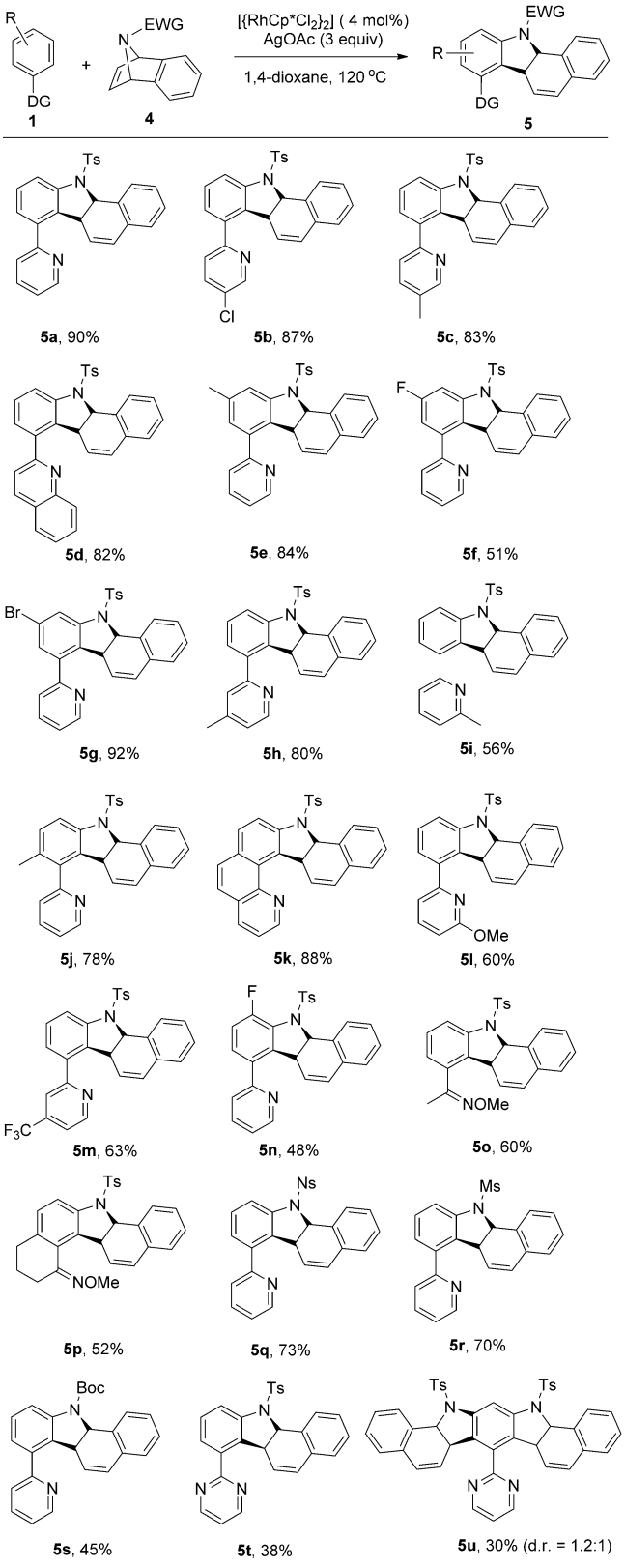
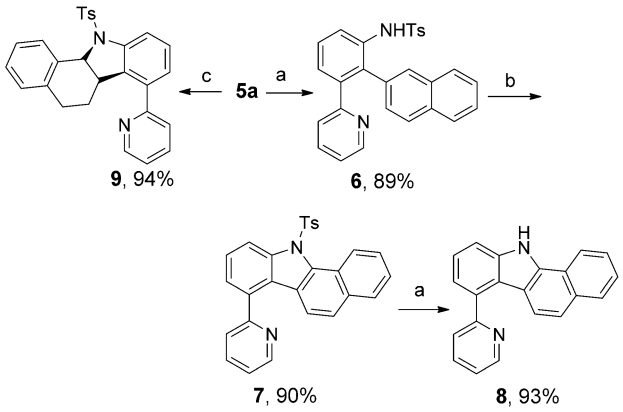


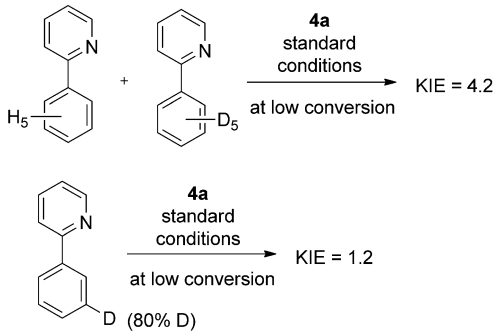
Scheme 3. Oxidative coupling with 7-azabenzonorbornadienes. Reaction conditions: arene (0.2 mmol), 7-azabenzonorbornadiene (0.26 mmol), AgOAc (0.6 mmol), and [{RhCp*Cl_2}$_2$] (4 mol%) in 1,4-dioxane (2 mL) at 120°C, 24 h. Yield is that of product isolated after column chromatography. Boc = *tert*-butoxycarbonyl, EWG = electron-withdrawing group.



Scheme 4. Transformations of dihydrocarbazole **5a**. Reaction conditions: a) **5a** or **7** (0.2 mmol), NaOH (1.4 equiv), THF/MeOH (1.4 mL/1.6 mL), 60°C, 10 h; b) **6** (0.17 mmol), $Cu(OTf)_2$ (5 mol%), CF_3COOH (3 equiv), $PhI(OAc)_2$ (1.5 equiv), DCE (2 mL), 80°C, 18 h; c) **5a** (0.15 mmol), 10% Pd/C, H_2 (balloon), PhMe, RT, 5 h. Ts = 4-toluenesulfonyl.

To demonstrate the synthetic usefulness of this method, derivatization of **5a** has been carried out (Scheme 4). Treatment of **5a** with NaOH afforded the elimination product **6** in 89% yield. Copper(II)-catalyzed oxidative C–N coupling of **6** to carbazole **7** was readily achieved by using the protocol of Chang and co-workers.[17] This cyclization process is highly regioselective, and only the α C–H bond of the naphthalene ring was functionalized (90% yield). Removal of the sulfonyl group to give **8** was readily achieved under the same basic conditions. In addition, hydrogenation of **5a** readily provides the tetralin **9**.

Several experiments have been carried out to probe the reaction mechanism. Competitive coupling of **4a** with an equimolar mixture of **1a** and [D_5]-**1a** at a low conversion gave an overall KIE = 4.2 (Scheme 5). A second KIE study was



Scheme 5. Kinetic isotope effects.

performed using a partially *meta*-deuterated 2-phenylpyridine, and a KIE value of 1.2 was estimated. These results suggest that cleavage of the first C–H bond (*ortho*), instead of the second one (*meta*), is involved in the rate-limiting step. To gain further insight into the interactions between the organorhodium species and **4a**, an equimolar mixture of rhodium complex **10**, **4a**, and $AgSbF_6$ was stirred, and the complex **11**

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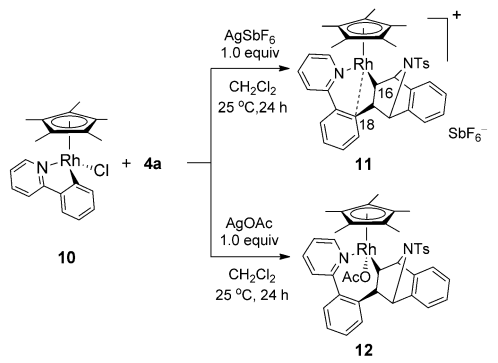


Scheme 6. Reaction intermediates.

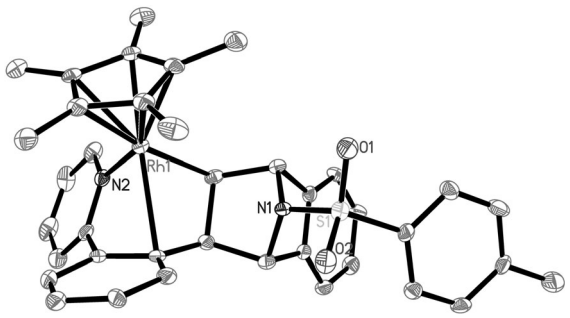
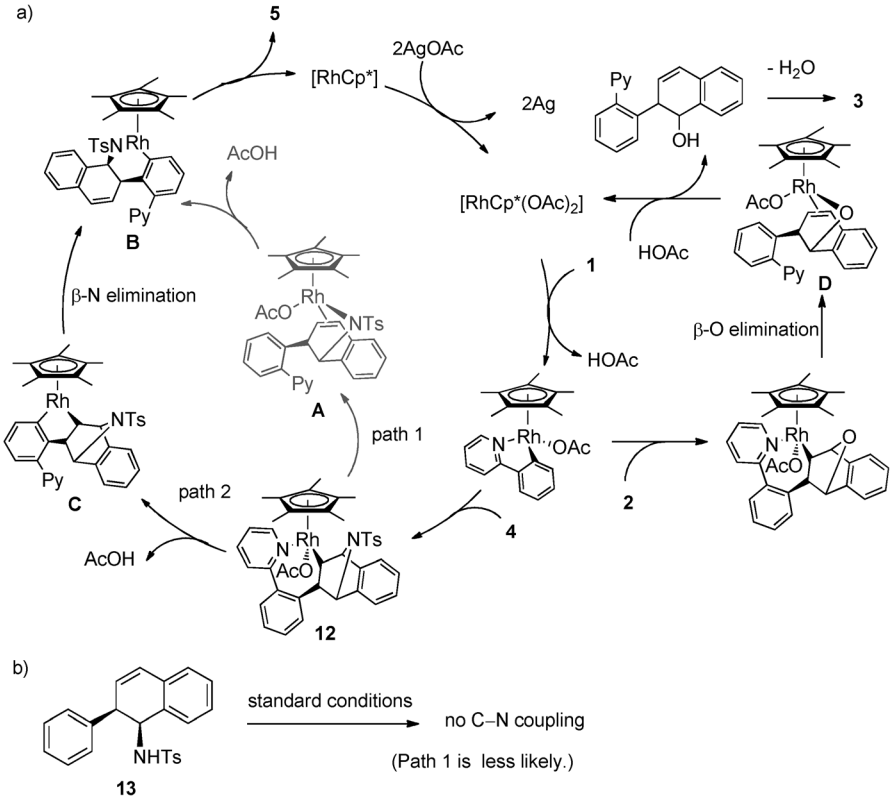


Figure 1. ORTEP diagram of complex **11**·CH_2Cl_2 (cation only). Thermal ellipsoids are drawn at a 40% probability level. Hydrogen atoms are omitted for clarity.[18]

was isolated (92%, Scheme 6). ^{1}H and ^{13}C NMR spectroscopy revealed the incorporation of a unit of **4a** with the bicyclic framework being retained. In particular, ^{13}C NMR spectroscopic data suggest disappearance of any Rh–C(aryl) bond but formation a Rh–C(alkyl) bond ($\delta = 32.7$, $^1J_{Rh\text{-}C} = 21$ Hz), thus indicating that the Rh–C(aryl) bond underwent migratory insertion into the olefin unit. The structure of **11** was ambiguously confirmed by X-ray crystallography (Figure 1),[18] and this insertion has occurred *cis* to the sulfonamide group. The most striking structural feature of **11** is the existence of a weak Rh···C18 bond [2.522(5) Å], known as the π agostic interaction,[19] which renders it significantly longer than the Rh–C16 bond [2.096(4) Å]. This weak Rh···C18 interaction in the solid state agrees with the ^{13}C NMR data (CD_2Cl_2), where C18 resonates at a high field ($\delta = 108.2$).[19] Analogously, the reaction of **10**, **4a**, and AgOAc afforded **12** in 74% yield. While no crystal structure of **12** was established, a related neutral rhodium(III) acetate structure is suggested based on NMR spectroscopic data. Both **11** and **12** (6 mol%) proved active in catalyzing the coupling of **1a** and **4a**, thus indicating that they are real catalysts (**12**) or direct precursors (**11**) in the catalytic cycle. It is noteworthy that although the migratory insertion of M–Ar bonds into 7-oxa/azabenzonorbornadienes has been well proposed in catalysis, authenticated stoichiometric reactions are rare.

As proposed in Scheme 7a, two reaction pathways can be possible after the intermediate **12** is formed. In pathway 1, *β*-nitrogen elimination occurs to give the amidate **A**, which undergoes subsequent cyclometalation to afford the six-membered rhodacycle **B**, reductive elimination of which furnishes the product **5a** together with a rhodium(I) intermediate which is reoxidized to rhodium(III) to complete a catalytic cycle. In pathway 2, cyclometalation of **12** occurs prior to the *β*-nitrogen elimination to reach the same intermediate **B**. Exactly which pathway is followed depends on the relative rate of the cyclometalation versus the *β*-nitrogen elimination. To gain further insight, the sulfonamide **13** was cyclized under the standard reaction conditions (Scheme 7b). NMR analyses revealed that essentially no C–N coupling occurred, but only a small amount of the elimination product was formed. These observations pointed to the conclusion that pathway 1 is less likely but pathway 2 is strongly preferred.[20,21] In the case of the coupling of 7-oxabenzonorbornadiene, we propose that the β-oxygen elimination takes place preferentially to give **D** after the olefin insertion (Scheme 7). Protonolysis of the Rh–O bond by an acid releases the dihydronaphthol intermediate, which is then dehydrated to give the product **3**.



Scheme 7. Mechanistic considerations.

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In conclusion, we have realized the rhodium(III)-catalyzed C–H activation and insertion of (hetero)arenes into 7-oxabenzonorbornadienes, thus leading to dehydrative naphthylation. In contrast, the coupling of these arenes with 7-azabenzonorbornadienes occurred only under oxidative conditions to furnish dihydrocarbazoles. This reaction proceeded through a double C–H activation pathway where a seven-membered rhodacyclic complex has been established as a key intermediate as a result of stereoselective insertion of the olefin into the Rh-C(aryl) bond. Experimental studies suggest that the second C–H activation likely occurs prior to the β-nitrogen elimination. Experimental and theoretical studies are underway to gain detailed mechanistic insights of these catalytic systems.

Received: April 24, 2013
Published online: July 5, 2013

Keywords: C–H activation · cross-coupling · heterocycles · rhodium · synthetic methods

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[21] A third possible but less likely mechanism is given in the Supporting Information and involves Lewis-acid-promoted ring opening of azabenzonorbornadiene to give an allyl cation intermediate. See the Supporting Information for details.

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