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Oxidative Annulation of Anilides with Internal Alkynes Using an (Electron-Deficient η^5-Cyclopentadienyl)Rhodium(III) Catalyst Under Ambient Conditions

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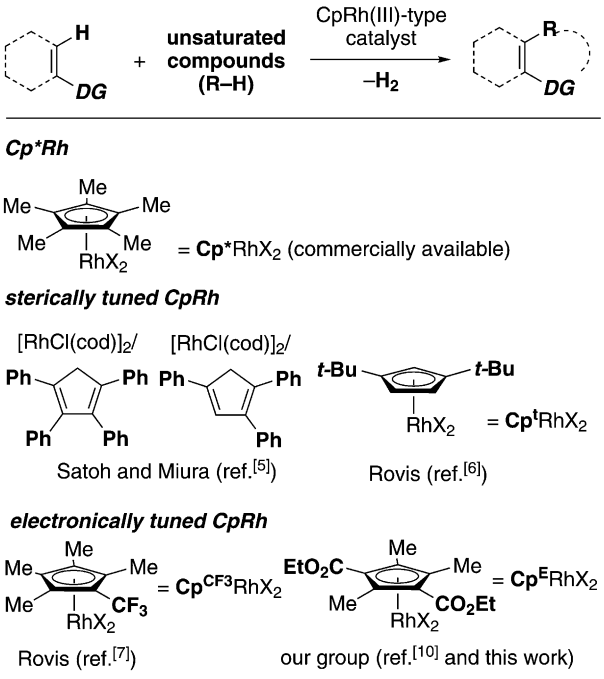
Abstract: A dinuclear (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex was synthesized on a preparative scale *via* the rhodium-catalyzed cross[2+2+1]cyclotrimerization of silylacetylenes and two alkynyl esters, leading to substituted silylfulvenes, followed by reductive complexation with rhodium(III) chloride in ethanol. The thus obtained dinuclear (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex is a highly active precatalyst for the oxidative annulation of anilides with internal alkynes under ambient conditions (at room temperature under air). A preference for annulation across electron-rich substrates over electron-deficient substrates was observed using this electron-deficient rhodium(III) complex.

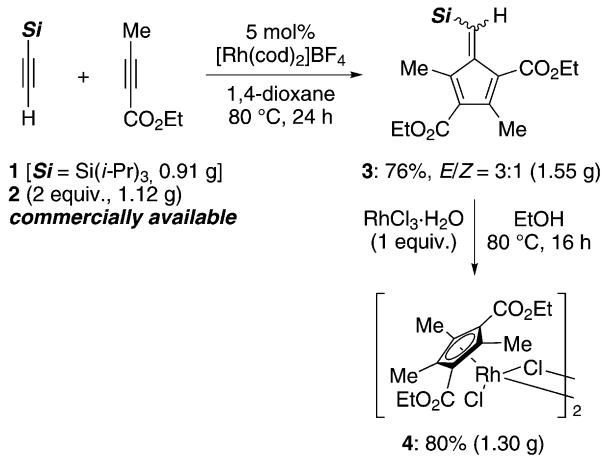
Keywords: alkynes; anilides; annulation; C–H bond functionalization; rhodium

Introduction

The C–H bond functionalization reactions catalyzed by (η^5-cyclopentadienyl)rhodium(III) complexes[1] have been widely examined and numerous successful examples have been reported.[2] The majority of reports employed a commercially available (η^5-pentamethylcyclopentadienyl)rhodium(III) complex (Cp^*RhX_2) as the catalyst. In order to improve the selectivity and reactivity, sterically or electronically tuned cyclopentadienyl ligands have been investigated recently in rhodium catalysis (Scheme 1).[3–7] For examples of sterically tuned cyclopentadienyl ligands, Satoh, Miura, and co-workers reported that the use of phenyl-substituted cyclopentadienes as ligands could improve the catalytic activity and change the reaction pathway in the rhodium-catalyzed oxidative C–H bond functionalization.[5] Rovis and co-workers reported that the use of a *tert*-butyl-substituted cyclopentadienylrhodium(III) complex (Cp^tRhX_2) improves the regioselectivity in the oxidative pyridone synthesis[6] and inverts the regioselectivity in the oxidative pyridine synthesis.[7] However, only a single example has been reported for the electronically tuned cyclopentadienyl ligand. Rovis and co-workers tested a trifluoromethyl-substituted cyclopentadienyl-



Scheme 1. Directed C–H bond functionalization catalyzed by CpRh(III)-type complexes.



Scheme 2. Preparative scale synthesis of silylfulvene **3** and rhodium(III) complex **4**.

rhodium(III) complex ($Cp^{CF3}RhX_2$) in the oxidative pyridine synthesis, whereby both the product yield and regioselectivity were low.[7]

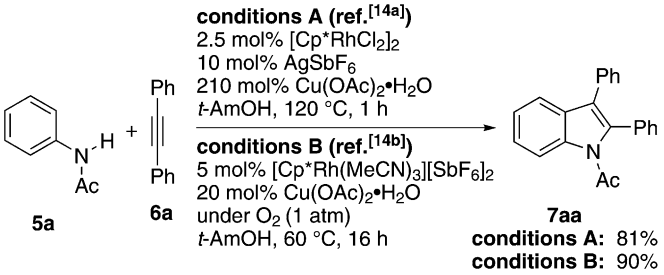
On the other hand, our research group recently reported the synthesis of an ethoxycarbonyl-substituted cyclopentadienenylrhodium(III) complex ($Cp^{E}RhX_2$) *via* the rhodium(I)-catalyzed cross[2+2+1]cyclotrimerization[8] of silylacetylenes and two alkynyl esters, leading to substituted silylfulvenes,[9] followed by reductive complexation with $RhCl_3$ (Scheme 1).[10] Pleasingly, this new electron-deficient rhodium(III) complex is a highly active and selective precatalyst for the oxidative annulation of acetanilides with an internal alkyne.[10] In this full paper, we wish to present full details of our study on the oxidative annulation of anilides with alkynes using the (electron-deficient η^5-cyclopentadienyl)rhodium(III) catalyst under ambient conditions.[11]

Results and Discussion

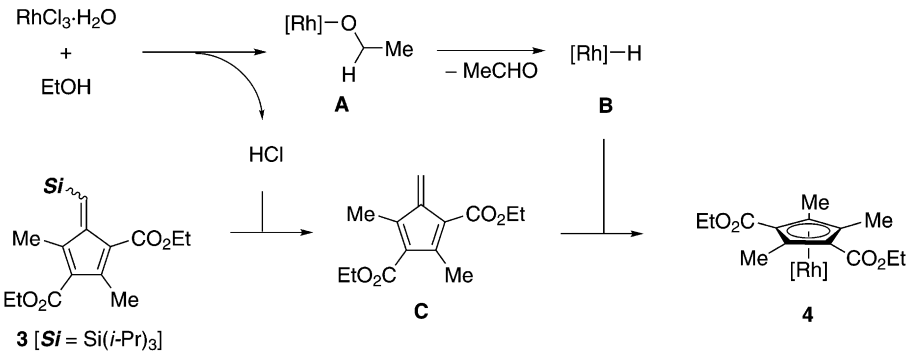
As shown in Scheme 2, silylfulvene **3** and dinuclear (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex **4** were synthesized on a preparative scale. Trimethylsilylacetylene **1** (0.91 g) and ethyl 2-butynoate **2** (1.12 g) were treated with $[Rh(cod)_2]BF_4$ (5 mol%) in dioxane at 80 °C to give the corresponding silylfulvene **3** (1.55 g) in 76% isolated yield. Subsequent reductive complexation of **3** with $RhCl_3$ in EtOH at 80 °C furnished the corresponding rhodium(III) complex **4** (1.30 g) in 80% isolated yield. These isolated yields are comparable to the small-scale synthesis [**3**: 80% isolated yield (98 mg) and **4**: 88% isolated yield (75 mg)].[10] Importantly, the use of EtOH is essential for the reductive complexation step. The use of MeOH or *i*-PrOH did not afford complex **4**.

A mechanistic proposal for the reductive complexation of silylfulvene **3** with $RhCl_3$ in EtOH, leading to (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex **4**, is shown in Scheme 3.[12] $RhCl_3{\cdot}H_2O$ reacts with EtOH to generate rhodium ethoxide **A** and HCl.[13] Elimination of acetaldehyde from **A** affords rhodium hydride **B**. The HCl-mediated desilylation of silylfulvene **3** proceeds to give fulvene **C**.[12] Rhodium hydride **B** reacts with desilylated fulvene **C** to afford rhodium(III) complex **4**.[14]

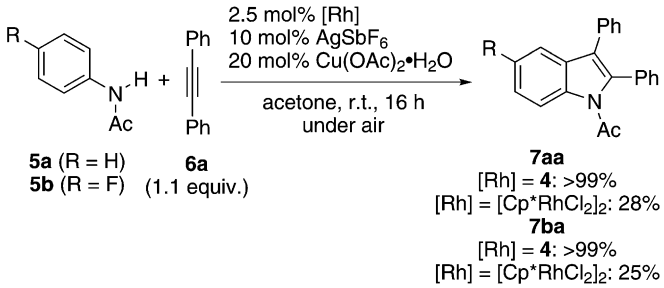
It is well known that a dicationic rhodium(III)/Cp* complex, derived from $[Cp^*RhCl_2]_2$, is a highly effective catalyst for a number of C–H bond functionalization reactions.[2] For example, Fagnou and co-workers reported the oxidative annulation of acetanilides with internal alkynes using the dicationic rhodium(III)/Cp*



Scheme 4. Fagnou's oxidative annulation of acetanilide **5a** with diphenylacetylene (**6a**) using $[Cp^*RhCl_2]_2$.[14]



Scheme 3. Plausible mechanism for the formation of **4**.



Scheme 5. Oxidative annulation of acetanilides **5a**, **b** with diphenylacetylene (**6a**) using **4** or $[Cp^*RhCl_2]_2$ under ambient conditions.[10]

complex as a catalyst.[15–17] In their initial communication, the reaction of acetanilide **5a** with diphenylacetylene (**6a**) was conducted at high temperature (120 °C, 1 h) using $[Cp^*RhCl_2]_2$ as a precatalyst and a stoichiometric amount of $Cu(OAc)_2$ as an oxidant to give the corresponding indole **7aa** in 81% yield (Scheme 4).[15a] In their subsequent article, the same reaction proceeded under mild conditions (60 °C, 16 h) in improved product yield (90%) by using an isolated dicationic rhodium(III)/Cp* complex, $[Cp^*Rh(MeCN)_3][SbF_6]_2$, as a catalyst and O_2/a catalytic amount of $Cu(OAc)_2$ as oxidants (Scheme 4).[15b]

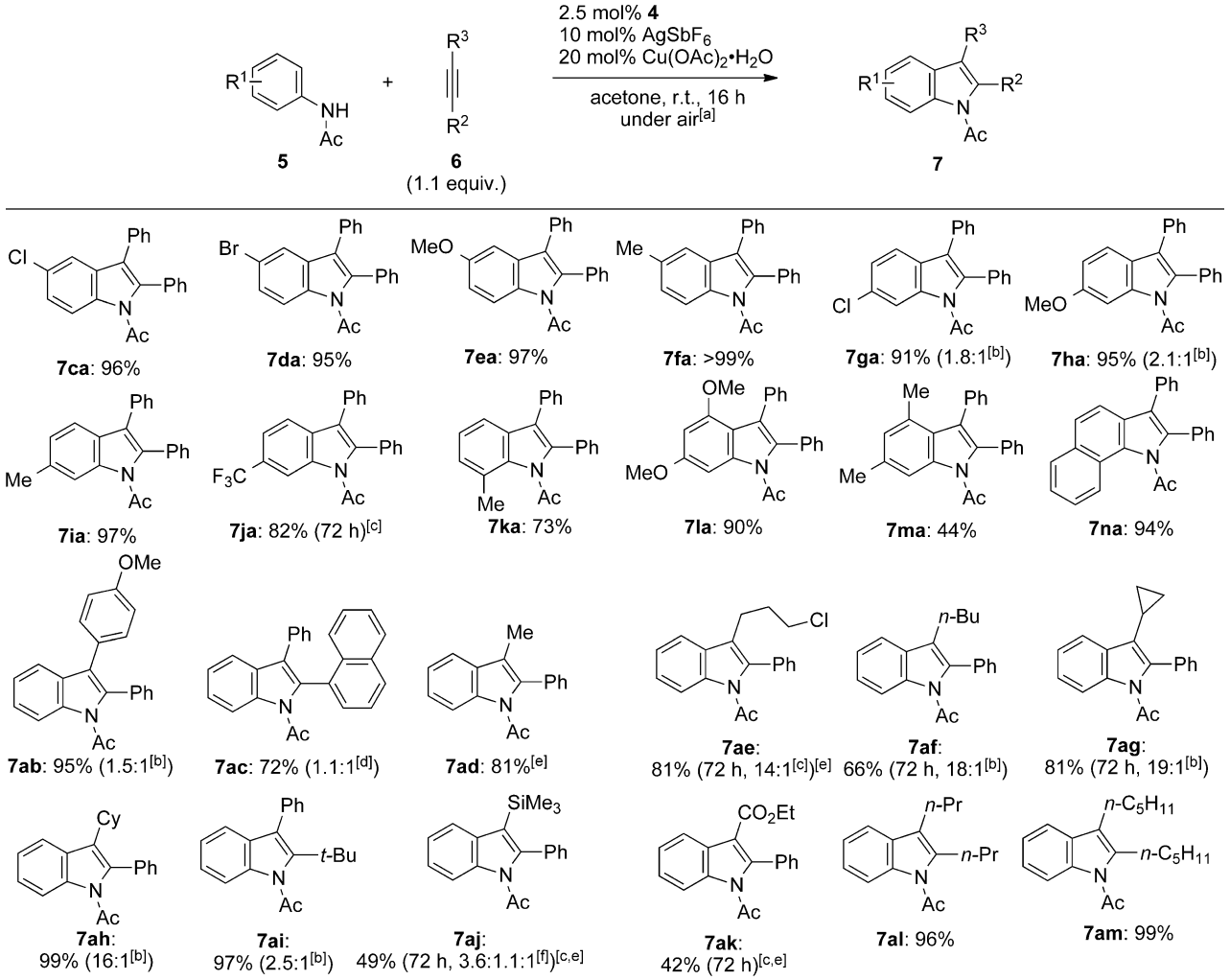
It was anticipated that an *in situ* generated electron-deficient dicationic rhodium(III) complex, derived from **4**, would show higher catalytic activity than dicationic Cp*Rh(III) complexes in the electrophilic C–H bond activation of acetanilides. Indeed, the reactions of acetanilides **5a** and **5b** with diphenylacetylene (**6a**) proceeded at room temperature under air to give the corresponding indoles **7aa** and **7ba** in quantitative yields (Scheme 5).[10] Under the same reaction conditions, the use of $[Cp^*RhCl_2]_2$ in place of **4** significantly decreased the product yields due to low substrate conversions (Scheme 5).[10]

The scope of the rhodium-catalyzed oxidative annulation of acetanilides **5** with internal alkynes **6** under ambient conditions is shown in Scheme 6. With respect to acetanilides, both electron-deficient and electron-rich acetanilides **5c–i** smoothly reacted with **6a** to give the corresponding indoles **7ca–ia** in high yields. The reactions of *meta*-substituted anilides **5g–j** provided 6-substituted indoles **7ga–ja** as the major regioisomer. 6-Methyl- and 6-trifluoromethyl-substituted indoles **7ia** and **7ja** were each obtained as a single regioisomer, while 6-chloro- and 6-methoxy-substituted indoles **7ga** and **7ha** were obtained as an about 2:1 mixture of regioisomers, presumably due to larger steric demand of the methyl and trifluoromethyl groups than the chloro and methoxy groups. Sterically demanding acetanilides **5k–n** were also able to react with **6a** to give the corresponding indoles **7ka–na** in moderate to high yields. The higher yield of **7la** than **7ma** can also be explained by the larger steric demand of the methyl group than the methoxy group. Both electronic and steric factors showed smaller impact on the product yields when using the $Cp^ERh(III)$ catalyst than using the Cp*Rh(III) catalysts.[15a,b] With respect to internal alkynes, a variety of diaryl (**6b**, **c**) and aryl-alkyl (**6d–i**) acetylenes reacted with **5a** to give the corresponding indoles **7ab–ai** in good to high yields. Trimethylsilyl-substituted alkyne **6j** and ethoxycarbonyl-substituted alkyne **6k** were also able to react with **5a**, although the product yields were moderate. The successful use of labile cyclopropyl- or trimethylsilyl-substituted alkynes **6g**, **j** and sterically demanding alkynes **6h**, **i** is worthy of note. In terms of regioselectivity, the use of monoarylacetylenes **6d–k** showed good to high regioselectivities and aryl groups are located in 2-position of the product indoles except *tert*-butyl-substituted internal alkyne **6i**. Unfortunately, poor regioselectivities were observed using unsymmetrical diarylacetylenes **6b**, **c**, possessing electronically or sterically different aryl groups. Importantly, dialkylacetylenes showed low reactivity in the Cp*Rh(III) complex-catalyzed indole synthesis, on the contrary, dialkylacetylenes **6l**, **m** were highly reactive substrates when using the $Cp^ERh(III)$ catalyst.

The preparative reaction of **5a** with **6a** was conducted under low catalyst loading as shown in Scheme 7. Pleasingly, indole **7aa** was obtained in quantitative yield.

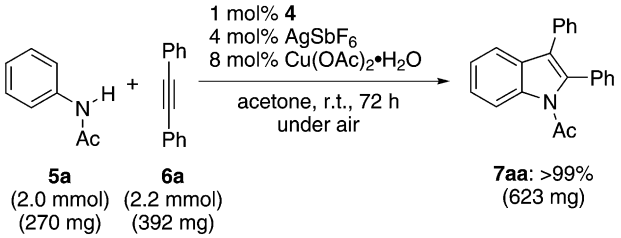
Boc-protected anilide **5o** was ineffective substrate in the Cp*Rh(III) complex-catalyzed indole synthesis presumably due to attenuated Lewis basicity at the amide oxygen.[15b] Pleasingly, **5o** was able to react with both diaryl- and dialkylacetylenes **6a**, **l** to give the corresponding indoles **7oa** and **7ol** in high yields, although high catalyst loadings (5 mol% **4**) were required (Scheme 8).

Fagnou and co-workers reported that not only anilides but also enamides are able to react with internal alkynes to give the corresponding pyrroles by using the dicationic rhodium(III)/Cp* complex, derived from $[Cp^*RhCl_2]_2$.[15b,18] They reported that enamides are more reactive than anilides, and so the reaction of enamide **8** with **6a** (Scheme 9) proceeds at room temperature to give the desired pyrrole **9a** in high yield (88%) by using the isolated dicationic rhodium(III)/Cp* complex, $[Cp^*Rh(MeCN)_3][SbF_6]_2$, as a catalyst and O_2/a catalytic amount of $Cu(OAc)_2$ as oxidants.[14b] The same reaction conditions, employed in the indole synthesis (Scheme 6), were applied to the oxidative annulation of **8** with **6a**, which revealed that the desired pyrrole **9a** was obtained in high yield (Scheme 8). Under the identical conditions, the use of $[Cp^*RhCl_2]_2$ in place of **4** significantly decreased the product yield due to low substrate conversion (Scheme 8). Not only diarylacetylene **6a** but also

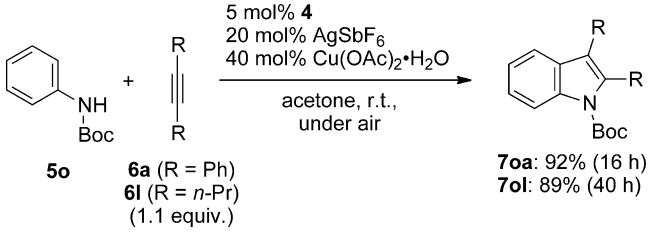


[a] **4** (0.0050 mmol), $AgSbF_6$ (0.020 mmol), $Cu(OAc)_2$·H_2O (0.040 mmol), **5** (0.20 mmol), **6** (0.22 mmol), and acetone (1.0 mL) were used. The cited yields are of the isolated products.
[b] Ratios of regioisomers. The structures of major regioisomers are shown.
[c] **4** (0.010 mmol), $AgSbF_6$ (0.040 mmol), and $Cu(OAc)_2$·H_2O (0.080 mmol) were used.
[d] The ratio of regioisomers. A major regioisomer could not be determined.
[e] **5** (0.60 mmol) and **6** (0.20 mmol) were used.
[f] The ratio of a major regioisomer/a minor regioisomer/a desilylation product. The structure of the major regioisomer is shown.

Scheme 6. Oxidative annulation of acetanilides **5c–n** with internal alkynes **6a–m** using **4** under ambient conditions.



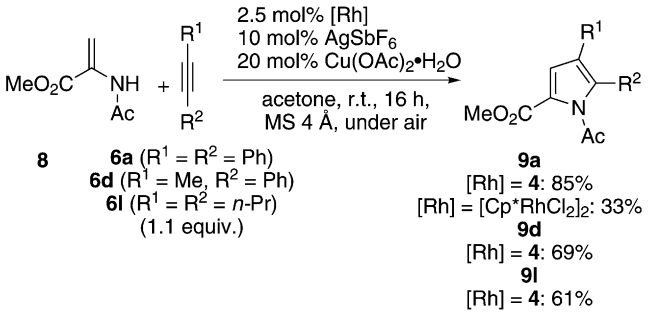
Scheme 7. Preparative scale reaction of **5a** with **6a** under low catalyst loading.



Scheme 8. Oxidative annulation of Boc-protected anilide **5o** with internal alkynes **6a**, **l** using **4** under ambient conditions.

alkylarylacetylene **6d** and dialkylacetylene **6l** could be employed for this pyrrole synthesis, although the product yields decreased (Scheme 8).

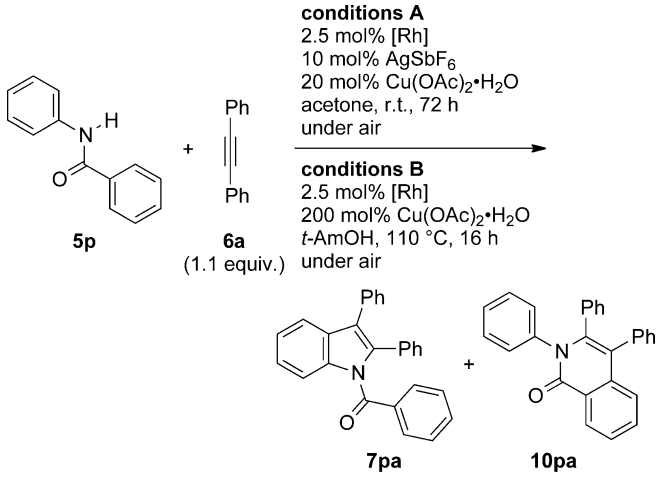
A plausible mechanism for the rhodium(III)-catalyzed indole and pyrrole synthesis, proposed by Fagnou and co-workers, is shown in Scheme 10.[14b] Rhodium(III) complex **A** undergoes C–H bond cleav-



Scheme 9. Oxidative annulation of enamide **8** with alkynes **6a**, **6d**, and **6l** using **4** or $[Cp^*RhCl_2]_2$ under ambient conditions.

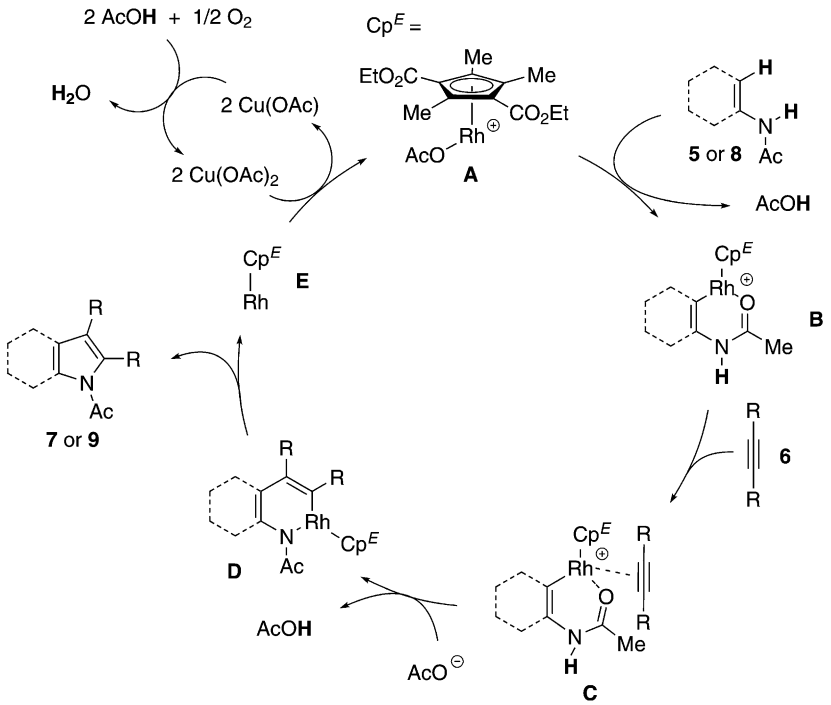
age of anilide **5** or enamide **8** producing amide oxygen-coordinated rhodium(III) complex **B**. Coordination of internal alkyne **6** forms intermediate **C**, followed by migratory insertion of **6** to afford azarhodacyle **D**. C–N bond reductive elimination affords the desired indole **7** or pyrrole **9** along with rhodium(I) complex **E**. This rhodium(I) complex **E** is then oxidized back to the active rhodium(III) complex **A** with copper(II) acetate which is then reoxidized by the combination of molecular oxygen and acetic acid.

We anticipated that highly electrophilic nature of rhodium(III) complex **A** would facilitate the C–H bond cleavage of electron-rich substrates over electron-deficient substrates. Indeed, the reaction of *N*-phenylbenzamide (**5p**) with **6a** under the same conditions (conditions A), employed in Scheme 6, exclusively afforded indole **7pa** through the anilide C–H bond cleavage (Scheme 11). Under these reaction conditions, electron-deficient complex **4** showed significantly higher catalytic activity than electron-rich $[Cp^*RhCl_2]_2$. On the contrary, the reaction of **5p** with **6a** in the absence of a silver salt (conditions B), re-

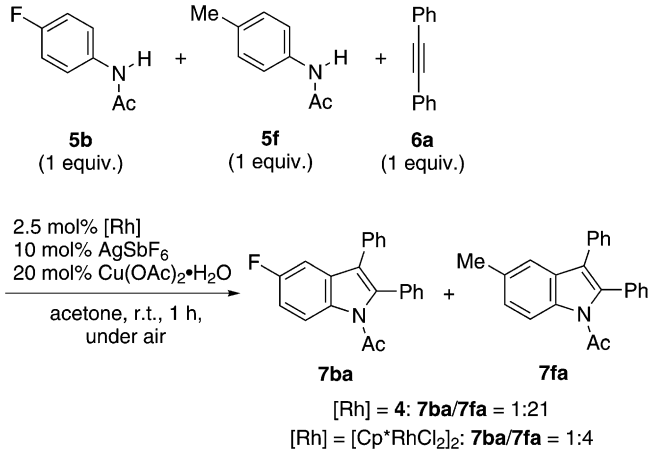


	[Rh]	conv. of **5p**	**7pa**	**10pa**
conditions A	**4**	70%	61%	<5%
	$[Cp^*RhCl_2]_2$	44%	6%	<5%
conditions B	**4**	67%	0%	30%
	$[Cp^*RhCl_2]_2$	77%	0%	52%

Scheme 11. Chemoselectivity between anilide and benzamide C–H bonds in *N*-phenylbenzamide (**5p**).



Scheme 10. Plausible mechanism for the formation of **7** and **9**.

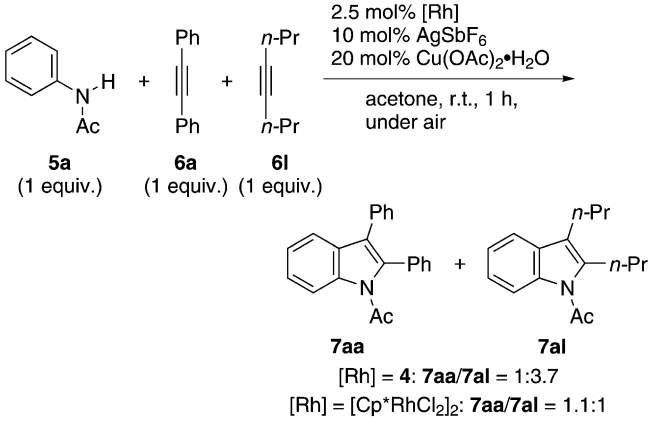


Scheme 12. Competition experiments between electron-deficient and electron-rich anilides (**5b** and **5f**).

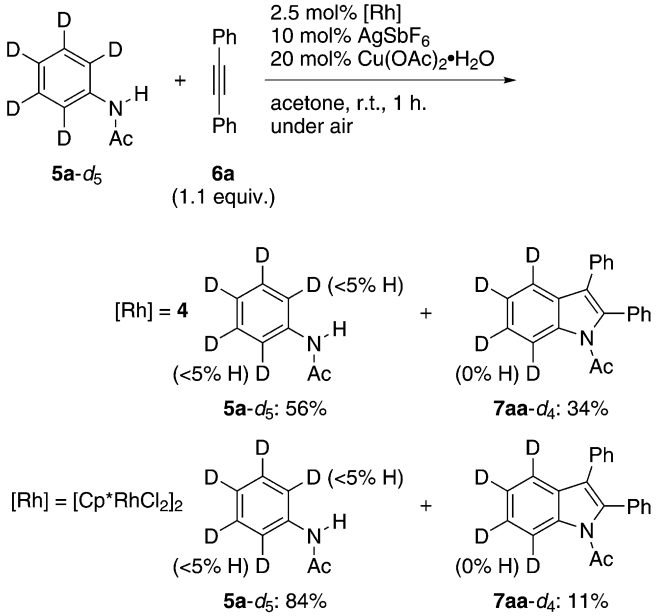
ported in the oxidative annulation of benzamide with alkynes,[19] exclusively afforded isoquinolone **10pa** through the benzamide C–H bond cleavage (Scheme 11). Under these reaction conditions, electron-rich $[Cp^*RhCl_2]_2$ showed higher catalytic activity than electron-deficient complex **4**.

Similarly, the intermolecular competition experiments between electron-deficient and electron-rich anilides **5b** and **5f** with **6a** revealed that the preference for annulation across electron-rich anilide **5f** over electron-deficient anilide **5b** is more significant on using electron-deficient complex **4** than electron-rich $[Cp^*RhCl_2]_2$ (Scheme 12).

We anticipated that highly electrophilic nature of rhodium(III) complex **B** would also facilitate migratory insertion of electron-rich internal alkynes over electron-deficient internal alkynes. Thus, the intermolecular competition experiments between electron-deficient diarylacetylene **6a** and electron-rich dialkylacetylene **6l** with **5a** were conducted (Scheme 13).



Scheme 13. Competition experiments between diaryl- and dialkylacetylenes (**6a** and **6l**).

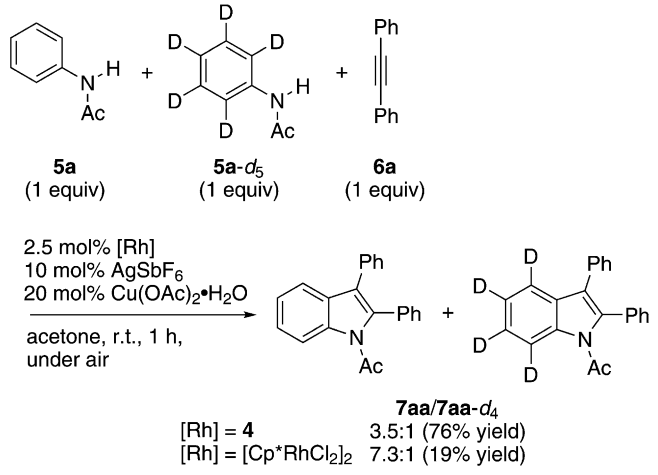


Scheme 14. Reaction of **5a**-d_5 and **6a** using **4** and $[Cp^*RhCl_2]_2$ as the precatalyst under ambient conditions.

The preference for the migratory insertion across electron-rich alkyne **6l** over electron-deficient alkyne **6a** was observed using electron-deficient complex **4**. On the contrary, the slight preference for the migratory insertion across electron-deficient alkyne **6a** over electron-rich alkyne **6l** was observed using electron-rich $[Cp^*RhCl_2]_2$.[20]

Reversibility of the acetanilide cyclorhodation was examined under ambient conditions by using **4** and and $[Cp^*RhCl_2]_2$ (Scheme 14). The metalation of acetanilide was found to be irreversible using both **4** and and $[Cp^*RhCl_2]_2$ as the precatalysts, with almost no loss in deuterium from both **5a**-d_5 and **7aa**-d_4.

Thus, deuterium kinetic isotope effects (DKIE) were investigated in the reactions of **5a**, **5a**-d_5, and **6a**



Scheme 15. Reaction of **5a**, **5a**-d_5, and **6a** using **4** and $[Cp^*RhCl_2]_2$ as the precatalyst under ambient conditions.

(1:1:1) using **4** and $[Cp^*RhCl_2]_2$ as the precatalyst under ambient conditions (Scheme 15). The study revealed that DKIE using **4** is significantly smaller than that using $[Cp^*RhCl_2]_2$. Therefore, the electron-deficient catalyst **4** would facilitate the C–H bond activation step in the catalytic cycle.

Conclusions

In conclusion, a dinuclear (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex was synthesized on a preparative scale *via* the rhodium-catalyzed cross [2+2+1] cyclotrimerization of silylacetylenes and two alkynyl esters, leading to substituted silylfulvenes, followed by reductive complexation with $RhCl_3$ in EtOH. The thus obtained dinuclear (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex is a highly active precatalyst for the oxidative annulation of anilides with internal alkynes under ambient conditions (at room temperature under air). Employing air as a terminal oxidant in acetone at room temperature is operationally more convenient than the previously reported Fagnou system (employing O_2 as a terminal oxidant in *tert*-amyl alcohol at 60 °C). Our new Cp^ERhX_2 precatalyst **4** is more active for the directed C–H bond functionalization of electron-rich arenes than the conventional Cp^*RhX_2 precatalyst. The preference for annulation across electron-rich substrates over electron-deficient substrates was observed using this electron-deficient rhodium(III) complex. The study of deuterium kinetic isotope effects revealed that the electron-deficient catalyst **4** would facilitate the C–H bond activation step in the catalytic cycle.

Experimental Section

Preparative Scale Synthesis of Silylfulvene 3

To a 1,4-dioxane (2.0 mL) suspension of $[Rh(cod)_2]BF_4$ (0.102 g, 0.250 mmol) was added a 1,4-dioxane (8.0 mL) solution of **1** (0.912 g, 5.00 mmol) and **2** (1.121 g, 10.00 mmol), and the mixture was stirred at 80 °C for 24 h. The resulting solution was concentrated under reduced pressure and purified by a silica gel column chromatography (hexane/EtOAc = 5:1) to give **3** as a red oil; yield: 1.55 g (3.81 mmol, 76%); *E*/*Z* = 78:22.

2,4-Dimethyl-5-[(triisopropylsilanyl)methylene]cyclopenta-1,3-diene-1,3-dicarboxylic acid diethyl ester (3, *E*/*Z* = 78:22): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.86 (s, 1H), 4.32 (q, J = 7.2 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H), 1.39–1.28 (m, 3H), 1.37 (t, J = 7.2 Hz, 6H), 1.11 (d, J = 7.4 Hz, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.5, 165.1, 156.9, 151.9, 147.3, 144.8, 133.9, 120.9, 60.3, 59.8, 19.1, 15.2, 14.4, 14.2, 13.6, 13.2.

Preparative Scale Synthesis of Rhodium(III) Complex 4

To an ethanol (4.0 mL) solution of $RhCl_3 \cdot n H_2O$ (38.16 wt% Rh, 1.00 g, 3.81 mmol Rh) was added an ethanol (6.0 mL) solution of **3** (1.55 mg, 3.81 mmol), and the mixture was stirred at 80 °C for 16 h. The resulting solution was concentrated under reduced pressure. The residue was diluted with CH_2Cl_2 (40 mL) and filtered. The filtrate was poured into hexane (200 mL). The resulting precipitates were collected, washed with Et_2O (20 mL) twice, and dried under vacuum to give **4** as a red powder; yield: 1.30 g (1.53 mmol, 80%).

Dichloro[1,3-di(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl]rhodium(III) dimer (4): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.45–4.33 (m, 8H), 2.23 (s, 6H), 1.96 (s, 12H), 1.36 (t, J = 6.9 Hz, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 163.9, 110.5 (d, J = 7.2 Hz), 102.4 (d, J = 7.2 Hz), 77.2 (d, J = 9.6 Hz), 62.6, 14.1, 12.5, 11.2.

Typical Procedure for Rhodium-Catalyzed Oxidative Annulation Under Ambient Conditions (7ca, Scheme 6)

To a 13.5-mL screw-cap vial bottle was added $AgSbF_6$ (6.9 mg, 0.020 mmol), Rh(III) complex **4** (4.3 mg, 0.0050 mmol), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 0.040 mmol), 4′-chloroacetanilide (**5c**, 33.9 mg, 0.200 mmol), diphenylacetylene (**6a**, 39.2 mg, 0.220 mmol), and acetone (1.0 mL) under air in this order. The mixture was sealed and stirred at room temperature under air for 16 h. The resulting mixture was diluted with ether, filtered through a silica gel pad, and washed with EtOAc. The solvent was concentrated under reduced pressure and the residue was purified by a preparative TLC (hexane/toluene/CH_2Cl_2 = 1:2:1) to give **7ca**; yield: 66.3 mg (0.192 mmol, 96%).

1-(5-Chloro-2,3-diphenylindol-1-yl)ethanone (7ca): Colorless solid; mp 204.2–205.0 °C; IR (KBr): ν = 3084, 3061, 3029, 1702, 1447 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.41 (d, J = 8.5 Hz, 1H), 7.54–7.50 (m, 1H), 7.41–7.23 (m, 9H), 7.22–7.16 (m, 2H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.5, 136.3, 135.2, 132.6, 132.5, 130.8, 130.7, 130.0, 129.5, 129.0, 128.8, 128.5, 127.3, 125.6, 122.8, 119.2, 117.6, 27.9; HR-MS (ESI): m/z = 368.0816, calcd. for $C_{22}H_{16}NONaCl$ $[M+Na]^+$: 368.0813.

Rhodium-Catalyzed Oxidative Annulation Under Ambient Conditions on a Preparative Scale (7aa, Scheme 7)

To a 50-mL round-bottom flask was added $AgSbF_6$ (27.5 mg, 0.080 mmol), Rh(III) complex **4** (17.0 mg, 0.020 mmol), $Cu(OAc)_2 \cdot H_2O$ (31.9 mg, 0.160 mmol), acetanilide (**5a**, 270.3 mg, 2.00 mmol), diphenylacetylene (**6a**, 392.1 mg, 2.20 mmol), and acetone (10 mL) under air in this order. The flask was sealed and the mixture stirred at room temperature under air for 72 h. The resulting mixture was diluted with ether, filtered through a silica gel pad, and washed with EtOAc. The solvent was concentrated under reduced pressure and the residue was purified by a silica gel

column chromatography (hexane/EtOAc = 5:1) to give **7aa**;[10] yield: 622.8 mg (2.00 mmol, >99%).

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