

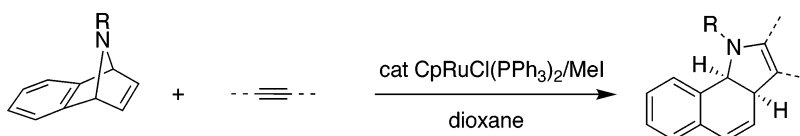
# Ruthenium-Catalyzed Cross-Coupling of 7-Azabenzonorbornadienes with Alkynes. An Entry to 3a,9b-Dihydrobenzo[g]indoles

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Electron-rich half-sandwich ruthenium complex  $\text{CpRuI}(\text{PPh}_3)_2$ , generated in situ, catalyzed the coupling reaction of 7-azabenzonorbornadienes with alkynes to form 3a,9b-dihydrobenzo[g]indoles. This transformation involves the cleavage of one C–N bond of the bicyclic alkene and formation of two (C–C and C–N) bonds at the acetylenic carbons. The scope and limitations of the reaction are addressed according to the substitution patterns of the alkyne and of the substituent at the nitrogen atom of the azabenzonorbornadiene.

## Introduction

The widespread indole nucleus present in natural products,<sup>1</sup> as well as in therapeutic agents,<sup>2</sup> still remains one of the most attractive targets in heterocyclic synthesis. Besides traditional synthetic routes,<sup>3</sup> transition-metal-catalyzed methods<sup>4</sup> provided remarkable improvements regarding efficiency, structural variations, and functional group compatibility to this important class of heterocycles. Hydroindoles have received less attention,

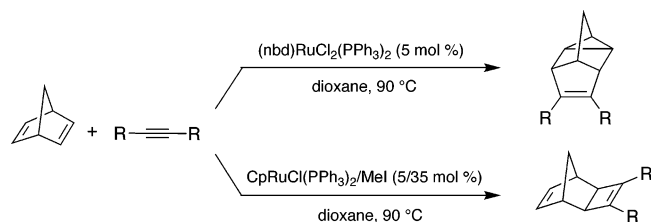
although these structures are interesting precursors of indoles through mild oxidative processes. For instance, the unusual 3a,7a-dihydroindole framework (as a substructure of dihydrocarbazoles) has been available by *stoichiometric* transition-metal-mediated processes such as the intramolecular amination of tricarbonyl( $\eta^4$ -cyclohexa-1,3-diene)iron complexes<sup>5</sup> or the dicarbonyl( $\eta^5$ -cyclopentadienyl)cobalt-mediated intermolecular [2 + 2 + 2] cycloaddition of alkynes to the pyrrole 2,3-double

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**SCHEME 1. Ruthenium-Catalyzed Cycloaddition of Norbornadiene with Alkynes**


bond.<sup>6</sup> The oxidative demetalation of the resulting complexes provided free 3a,7a-dihydroindoles or indoles depending on the reaction conditions. The formation of 3a,9b-dihydrobenzo[g]-indoles through the thermal, uncatalyzed reaction of 7-azabenzonorbornadienes with alkynes was sporadically reported. These reactions suffered from limitation to electron-deficient alkynes such as DMAD.<sup>7</sup> In this paper, we report the ruthenium-catalyzed coupling of 7-azabenzonorbornadienes **1** with alkynes **2** to produce the 3a,9b-dihydrobenzo[g]indole framework<sup>8</sup> using CpRuI(PPh<sub>3</sub>)<sub>2</sub> as a catalyst generated in situ.<sup>9</sup> The scope and limitations of the reaction are addressed according to the substitution patterns of the alkyne and the substitution at the nitrogen atom of the bicyclic alkene **1**.<sup>10</sup> In addition, the synthetic utility of the reaction is illustrated with the mild oxidative conversion of 3a,9b-dihydrobenzo[g]indoles to benzo[g]indoles.

Recently, we reported different selectivity issues of the ruthenium-catalyzed cycloaddition between norbornadiene and alkynes according to the nature of the ligands associated with the metal. For instance, electron-rich half-sandwich ruthenium complexes catalyzed the [2 + 2] cycloaddition to give cyclobutenes,<sup>9</sup> whereas norbornadiene-coordinated ruthenium complexes led exclusively to the [2 + 2 + 2] cycloaddition pathway to produce deltacyclenes (Scheme 1).<sup>11</sup>

In continuation of these studies, it was anticipated that the ruthenium-catalyzed reactions involving 7-azabenzonorbornadienes **1** were expected to afford exclusively [2 + 2] cycloadducts. Indeed, these reactions, leading to *exo*-cyclobutene derivatives, have been reported to occur with cobalt catalysts.<sup>12</sup> In the presence of nickel catalysts, [2 + 2] or [2 + 2 + 2] cycloaddition pathways are observed depending on the structural patterns of alkynes and the reaction conditions producing *exo*-

**TABLE 1. Ruthenium-Catalyzed Coupling of *N*-Boc-7-Azabenzonorbornadiene **1a** with Symmetrical Alkynes **2**<sup>a</sup>**

entry	alkyne	temp (°C)	time (h)	adduct(s) (yield) <sup>b</sup>	
				3	4
1	<b>2a</b> R = Et	60	50	<b>3aa</b> (63%)	<b>4aa</b> (12%)
2	<b>2b</b> R = Ph	60	6	—	<b>4ab</b> (97%)
3	<b>2c</b> R = CO <sub>2</sub> Me	60	20	<b>3ac</b> (53%) <sup>c</sup>	—
4	<b>2d</b> R = CH <sub>2</sub> OH	50	48	<b>3ad</b> (88%)	—
5	<b>2e</b> R = CH <sub>2</sub> OMe	60	24	<b>3ae</b> (80%)	—
6	<b>2f</b> R = CH <sub>2</sub> OBn	55	11	<b>3af</b> (98%)	—
7	<b>2g</b> R = CH <sub>2</sub> OMOM	60	22	<b>3ag</b> (82%)	—
8	<b>2h</b> R = CH <sub>2</sub> OTBDMS	60	22	<b>3ah</b> (98%)	—
9	<b>2i</b> R = CH <sub>2</sub> OAc	60	48	<b>3ai</b> (77%)	—

<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), alkyne (0.5 mmol), CpRuI(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), MeI (0.175 mmol) in dioxane (4 mL). <sup>b</sup> Isolated yields after column chromatography. <sup>c</sup> Adduct **5** (20%) was also formed (see Scheme 2).

cyclobutenes<sup>13</sup> or 1,3-cyclohexadienes,<sup>14</sup> respectively. Alkynoates reacted differently with nickel catalysts, leading to *cis*-2-alkenyl-1,2-dihydronaphthylamines, through a reductive coupling occurring with C–N bond cleavage.<sup>15</sup>

**Results and Discussion**

We initially examined the reaction of 7-azabenzonorbornadiene **1a** with hex-3-yne (**2a**) in the presence of CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (5 mol %) in dioxane at 60 °C, which afforded a complex mixture of products and a low conversion. Carrying out the reaction in the presence of methyl iodide (35 mol %) to generate in situ CpRuI(PPh<sub>3</sub>)<sub>2</sub><sup>9</sup> proved to be crucial to obtain the [2 + 2] cycloadduct **4aa** (12%) and a new unsymmetrical adduct **3aa** in 63% yield.<sup>16</sup> Interestingly, the beneficial effect of the iodo ligand<sup>17</sup> contrasted with the use of Cp\*Ru(cod)I<sup>10</sup> which turned out to be completely inactive. The structure of **3aa** was clearly established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy,<sup>18</sup> and the *cis* stereochemistry of the fused rings was established by NOESY experiment and was consistent with the H3a–H9b coupling constant of 9.5 Hz.<sup>19</sup> The yield of **3aa** slightly decreased using preformed CpRuI(PPh<sub>3</sub>)<sub>2</sub><sup>20</sup> as a catalyst. The higher efficiency of the in situ generated catalyst may be ascribed to the presence

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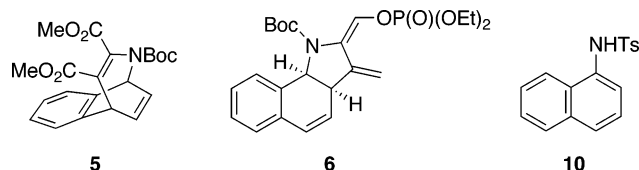
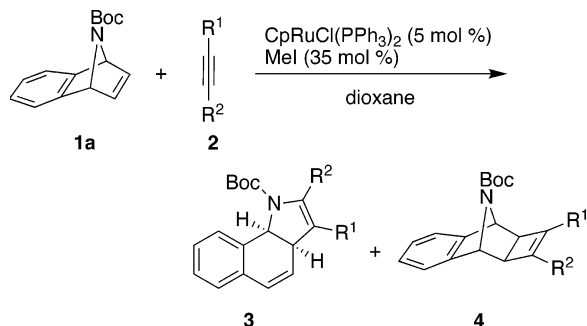
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SCHEME 2. Structure of Compounds 5, 6, and 10

TABLE 2. Ruthenium-Catalyzed Coupling of *N*-Boc-7-Azabenzonorbornadiene **1a** with Unsymmetrical Alkynes **2<sup>a</sup>**

k R<sup>1</sup> = Me, R<sup>2</sup> = CH<sub>2</sub>OH  
 l R<sup>1</sup> = Bu, R<sup>2</sup> = CH<sub>2</sub>OH  
 m R<sup>1</sup> = Et, R<sup>2</sup> = CH<sub>2</sub>OPh  
 n R<sup>1</sup> = CH<sub>2</sub>OMe, R<sup>2</sup> = CCCH<sub>2</sub>OMe  
 o R<sup>1</sup> = Ph, R<sup>2</sup> = CCHPh  
 p R<sup>1</sup> = Ph, R<sup>2</sup> = Ac  
 q R<sup>1</sup> = Ph, R<sup>2</sup> = CO<sub>2</sub>Me

entry	alkyne	temp (°C)	time (h)	adduct(s) (yield) <sup>b</sup>	
				3	4
1	2k	60	19	3ak (42%)	—
2	2l	60	48	3al (35%)	—
3	2m	60	5.5	3am (52%)	—
4	2n	60	26	3an (48%)	4an (15%)
5	2o	60	21	—	4ao (83%)
6	2p	60	15	—	4ap (98%)
7	2q	60	20	—	4aq (98%)

<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), alkyne (0.5 mmol), CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), MeI (0.175 mmol) in dioxane (4 mL). <sup>b</sup> Isolated yields after column chromatography.

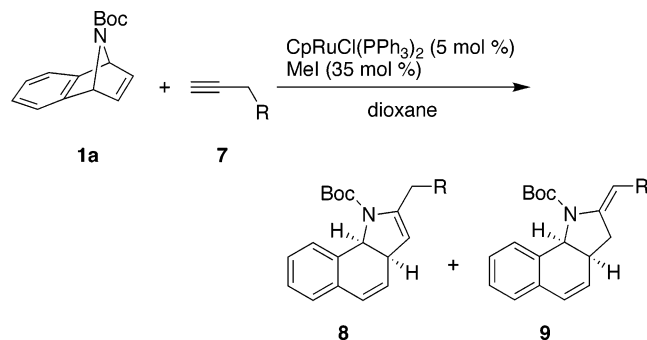
of excess MeI. Halogenoalkanes are able to coordinate the metal center of cyclopentadienylruthenium complexes via  $\sigma$ -donation of a halogen lone pair.<sup>21</sup> The resulting complexes easily undergo ligand substitution with common coordinating solvents to produce the corresponding solvento complexes which promote coordination of the reactants more easily. Therefore, the catalyst combination CpRuCl(PPh<sub>3</sub>)<sub>2</sub>/MeI was conveniently used for further studies. Under these reaction conditions, the cyclization of **1a** with various symmetrical alkynes **2c–i** afforded the expected dihydrobenzoindoles **3ac–ai** in moderate to good yields (Table 1).

The best results were observed with but-2-yn-1,4-diol (**2d**) (entry 4) and the corresponding bisethers **2e–h** (entries 5–8) and bisacetate **2i** (entry 9). The reaction of dimethylacetylene dicarboxylate (DMAD) **2c** (entry 3) afforded along with **3ac**

(19) Typical vicinal coupling constants of 5–9 Hz were observed for related cis-fused bicyclic compounds. The corresponding trans isomers exhibit *J* values of 20–24 Hz; see: Barinelli, L. S.; Nicholas, K. M. *J. Org. Chem.* **1988**, 53, 2114–2117 and references therein.

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TABLE 3. Ruthenium-Catalyzed Coupling of *N*-Boc-7-Azabenzonorbornadiene **1a** with Terminal Alkynes **7**

entry	alkyne	temp (°C)	time (h)	product(s) (yield) <sup>b</sup>	
				8	9
1	7a R = Pr	90	20	8aa (19%)	9aa (59%)
2	7b R = (CH <sub>2</sub> ) <sub>2</sub> CN	90	27	8ab (23%)	9ab (56%)
3	7c R = OPh	90	25	8ac (10%)	9ac (73%)
4	7d R = OBn	60	18	8ad (23%)	9ad (69%)
5	7e R = OAc	65	20	8ae (91%)	—
6	7f R = OCO <sub>2</sub> Et	60	20	8af (89%)	—
7	7g R = SO <sub>2</sub> Ph	90	20	—	9ag (87%)
8	7h R = CMe <sub>2</sub> OH	90	20	8ah (93%)	—

<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), alkyne (0.5 mmol), CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), MeI (0.175 mmol) in dioxane (4 mL). <sup>b</sup> Isolated yields after column chromatography.

(53%) an unexpected adduct **5** (20%) (Scheme 2). In contrast with these observations, the reaction of **1a** with diphenylethyne **2b** gave exclusively the [2 + 2] cycloadduct **4ab** in 97% yield (Table 1, entry 2). The reaction with bisphosphate **2j** (R = CH<sub>2</sub>OP(O)(OEt)<sub>2</sub> (not shown in Table 1)) required a higher temperature (90 °C) and afforded, instead of adduct **3aj** (R = OP(O)(OEt)<sub>2</sub>), the dienol phosphate **6** (38%) (Scheme 2) as a single diastereomer.

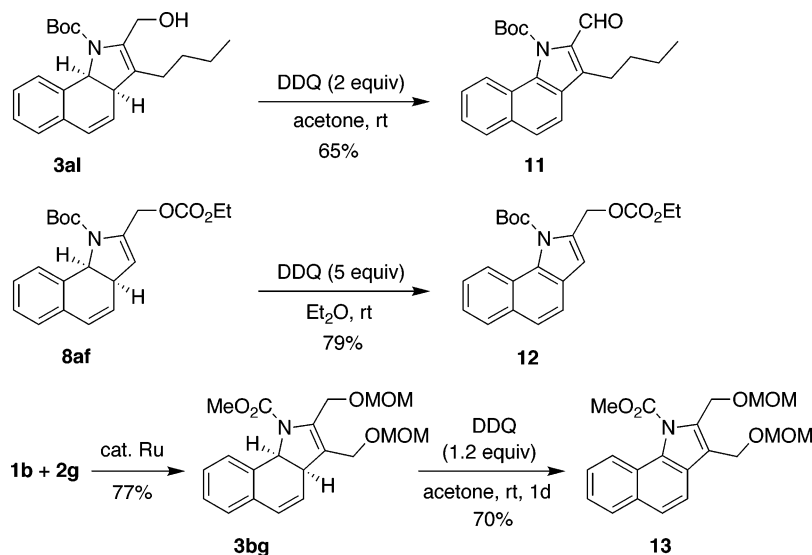
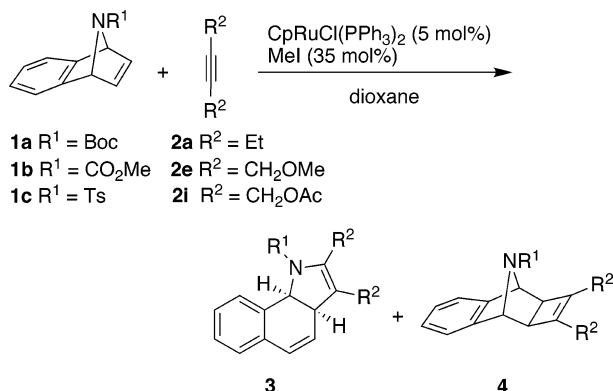
To address the selectivity issues of the coupling reactions, unsymmetrical alkynes with different electronic properties were examined in cross-coupling reactions of **1a** (Table 2).

The ring-opening adducts **3** were exclusively observed with propargylic alcohols **2k,l** and propargylic phenyl ether **2m** although obtained in moderate yields (Table 2, entries 1–3) from complex reaction mixtures. Even the 1,3-diyne **2n** is incorporated satisfactorily, affording **3an** (48%) and the cyclobutene **4an** (15%) (Table 2, entry 4). Dihydrobenzoindoles **3** were formed as single regio- and stereoisomers with the most polar group located at the carbon atom vicinal to the nitrogen group (entries 1–3). Phenyl-substituted alkynes afforded exclusively (Table 2, entries 5–7) the [2 + 2] cycloadducts. The same trend was observed with diphenylethyne **2b** (see Table 1, entry 2).

The successful application of internal alkynes in the ruthenium-catalyzed coupling reaction prompted us to examine the reaction with terminal alkynes (Table 3). So far, ruthenium-catalyzed intermolecular [2 + 2] cycloadditions of norbornadienes with terminal alkynes are less efficient with respect to internal alkynes and give aromatic compounds as byproducts.<sup>22</sup> In our hand, ruthenium-catalyzed intermolecular [2 + 2] cycloadditions of norbornadienes failed when terminal alkynes were involved.<sup>23</sup> We were pleased to observe that the coupling of **1a** with terminal alkynes **7** afforded the dihydrobenzoindoles **8** and/or isomers **9**

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SCHEME 3. DDQ-Promoted Oxidation of 3a,9b-Dihydrobenzo[g]indoles to Benzo[g]indoles

TABLE 4. Effect of the Substitution at the Nitrogen of 7-Azabenzonornbornadienes **1** on the Ru-Catalyzed Coupling with Alkynes **2**<sup>a</sup>

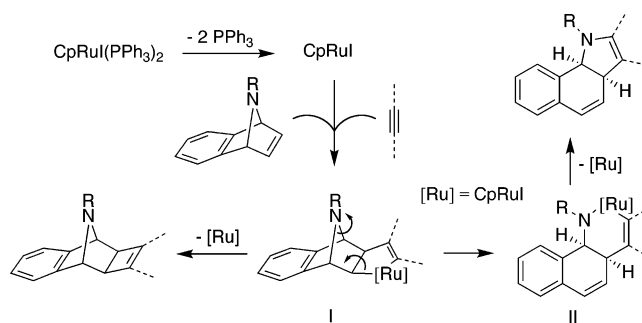
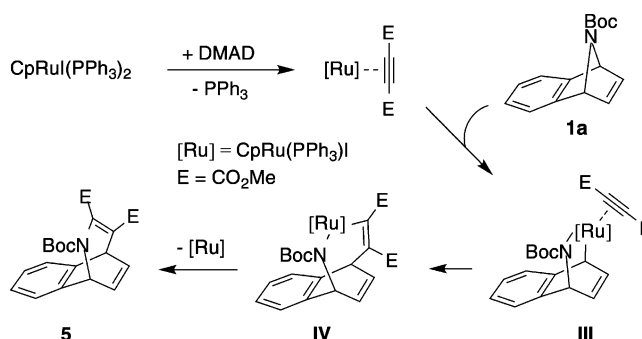
entry	alkene	alkyne	temp (°C)	time (h)	adduct(s), yield <sup>b</sup>	
					3	4
1	<b>1a</b>	<b>2a</b>	60	50	<b>3aa</b> (63%)	<b>4aa</b> (12%)
2 <sup>c</sup>	<b>1b</b>	<b>2a</b>	90	8	<b>3ba</b> (5%) <sup>d</sup>	<b>4ba</b> (63%)
3	<b>1a</b>	<b>2e</b>	50	65	<b>3ae</b> (84%)	—
4	<b>1b</b>	<b>2e</b>	60	22	<b>3be</b> (79%)	—
5	<b>1a</b>	<b>2i</b>	90	6	<b>3ai</b> (77%)	—
6	<b>1b</b>	<b>2i</b>	90	6	<b>3bi</b> (86%)	—

<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), alkyne (0.5 mmol), CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (5 mol %), MeI (0.175 mmol) in dioxane (4 mL). <sup>b</sup> Isolated yields after column chromatography. <sup>c</sup> No reaction occurred at 60 °C. <sup>d</sup> Yield determined by <sup>1</sup>H NMR.

as single diastereomers in good overall yields (78–92%). The reactions proceeded with complete regioselectivity giving adducts with the alkyl and/or alkenyl substituent at the C-2 position. Interestingly, the competitive [2 + 2] cycloaddition reaction observed so far was totally suppressed.

Alkyl-substituted alkynes **7a,b** (Table 3, entries 1 and 2) and propargylic ethers **7c,d** (Table 3, entries 3 and 4) gave the adducts **8aa–ad** as minor products, and the *E*-exocyclic double

SCHEME 4. Proposed Mechanism for the Ru-Catalyzed Formation of Dihydrobenzo[g]indoles

SCHEME 5. Proposed Mechanism for the Ru-Catalyzed Formation of Adduct **5**

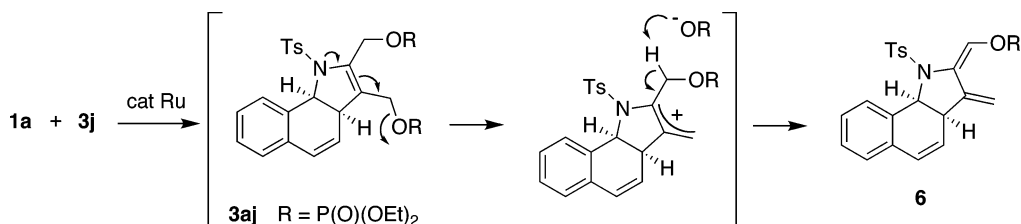
bond isomers **9aa–ad** as single regio- and stereoisomers. Propargylic acetate **7e** (Table 3, entry 5) or mixed carbonate **7f** (Table 3, entry 6) afforded exclusively **8ae** (91%) or **8af** (89%), respectively. In contrast, the propargylic phenylsulfone **7g** provided only the vinyl sulfone **9ag** (87%) (Table 3, entry 7). An X-ray crystallographic analysis secured both the structure and the stereochemistry of **9ag**.<sup>24</sup> Tertiary propargylic alcohol **7h** proved to be stable under the reactions conditions,<sup>25</sup> providing exclusively **8ah** in 93% yield (entry 8).

Variation in the substitution of the nitrogen atom of 7-azabenzonornbornadienes was also examined in these reactions (Table 4). The reactions of **1a** or **1b**, bearing the tertiary carbamate at the bridgehead position, with alkynes **2e** and **2i**, afforded the dihydroindoles in good yields (Table 4, entries

(23) A notable exception was recently reported in the case of the ruthenium-catalyzed vinylcyclopropanation of norbornadienes using tertiary propargylic carboxylates. See: Tenaglia, A.; Marc, S. *J. Org. Chem.* **2006**, *71*, 3569–3575.



## SCHEME 6. Proposed Mechanism for the Ru-Catalyzed Formation of Adduct 6



3–6). Unexpectedly, an inversion of selectivity between the dihydroindole and the [2 + 2] adduct was observed for reactions of **1a** or **1b** with hex-3-yne (**2a**) (entries 1 and 2). All of the reactions carried out with **1c** bearing the tosyl group at the nitrogen atom afforded only 4-methyl-*N*-naphthalen-1-ylbenzenesulfonamide (**10**) (Scheme 2), resulting from the isomerization of **1c**.

The usefulness of this ruthenium-catalyzed coupling was demonstrated through the facile conversion of 3a,9b-dihydrobenzo[*g*]indoles **3al**, **8af**, and **3bg** to the corresponding benzo[*g*]indoles **11**, **12**, and **13**, respectively, under mild oxidative conditions in the presence of DDQ (Scheme 3). Under these conditions, allylic alcohol **3al** reacted smoothly at room temperature in the presence of 2 equiv of DDQ to give the 2-formylbenzo[*g*]indole **11**, whereas **8af** proved to be reluctant to oxidation and required 5 equiv of DDQ for completion of the reaction affording the benzo[*g*]indole **12** in 79% yield.

A mechanistic rationale accounting for the formation of the dihydrobenzoindoles is proposed in Scheme 4. The catalytic cycle starts with the formation of the coordinatively unsaturated CpRuI by dissociation of the phosphine ligands from CpRuI-(PPh<sub>3</sub>)<sub>2</sub>. The oxidative coupling of the reactants to the metal center would give the ruthenacyclopentene **I**. Reductive elimination of the metal species would form the [2 + 2] adduct, while  $\beta$ (N)-elimination would allow the formation of ruthenadehydropiperidine **II**, which upon reductive elimination might release the dihydrobenzoindole and the active species CpRuI. The cross-coupling regioselectivity observed with unsymmetrical alkynes, including terminal ones, is worth being mentioned. The presence of a propargylic oxygen substituent able to coordinate to the metal center favors carbon–carbon bond formation to the distal acetylenic carbon in ruthenacyclopentene **I**.<sup>26</sup> Interestingly, in the couplings of **1a** with terminal alkynes (Table 3), the orientation of the alkyne in the coupling step is not affected by the absence of such a substituent.

The observation of azabicyclic adduct **5** (Table 1, entry 3 and Scheme 2) when **1a** reacted with DMAD **2c** suggested that the insertion of **2c** into the bridgehead C–N bond of **1a** occurred during its formation. A plausible mechanism may involve the coordination of this highly electron-deficient alkyne to the electron-rich ruthenium center. This species would undergo oxidative addition with the benzylic and allylic bridgehead C–N

bond to form complex **III**. Insertion of the alkyne into the metal–carbon bond<sup>27</sup> would give the ruthenacycle **IV** which upon reductive elimination would release **5** (Scheme 5).

The formation of adduct **6**, depicted in Scheme 6, presumably arose through a regio- and stereoselective 1,4-elimination of diethyl phosphonate from the putative intermediate **3aj** under the reaction conditions.

In summary, we have developed the ruthenium-catalyzed cross-coupling reactions of azabenzonorbornadienes and alkynes that resulted in a formal [3 + 2] annulation reaction to afford 3a,9b-dihydrobenzo[*g*]indoles. The competitive ruthenium-catalyzed [2 + 2] cycloaddition is suppressed in reactions involving terminal alkynes. The synthetic utility of the reaction was demonstrated by the conversion of the 3a,9b-dihydrobenzo[*g*]indoles into benzo[*g*]indoles functionalized on the heterocyclic ring for further structural modifications.

## Experimental Section

**Typical Procedure for the Coupling of 1a with 2h as a Representative Example:** CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (18.2 mg, 0.025 mmol) and dioxane (2 mL) were placed in a flame-dried Schlenk flask. A solution of **1a** (121.7 mg, 0.5 mmol) and **2h** (157.3 mg, 0.5 mmol) in dioxane (2 mL) and MeI (11.7  $\mu$ L, 0.175 mmol) were added at once, and the mixture was stirred at 60 °C for 22 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (AcOEt/hexanes 1/19) to give 273 mg (98% yield) of **3ah** as a colorless oil.

(**3aR**\*,**9bS**\*)-*tert*-Butyl 2,3-bis[(*tert*-butyldimethylsilyloxy)-methyl]-3a,9b-dihydro-1*H*-benzo[*g*]indole-1-carboxylate (**3ah**): *R*<sub>f</sub> (AcOEt/hexanes 1/19) 0.48; IR (neat)  $\nu$  3038, 2955, 2857, 1702, 1671, 1472, 1365, 1250, 1169, 1059, 836, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (m, 1H), 7.15 (m, 2H), 6.97 (m, 1H), 6.40 (d, *J* = 9.8 Hz, 1H), 5.97 (dd, *J* = 6.1, 9.7 Hz, 1H), 5.61 (d, *J* = 9.7 Hz, 1H), 4.62 (br d, *J* = 13.1 Hz, 1H), 4.50 (br d, *J* = 13.3 Hz, 1H), 4.47 (d, *J* = 12.3 Hz, 1H), 4.09 (d, *J* = 12.3 Hz, 1H), 3.88 (m, 1H), 1.55 (s, 9H), 0.91 (s, 9H), 0.75 (s, 9H), 0.07 (s, 6H), -0.16 (s, 3H), -0.23 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  153.8 (s), 136.8 (s), 133.7 (s), 132 (s), 127.9 (2  $\times$  d), 127.4 (2  $\times$  d), 126.0 (d), 124.4 (d), 123.7 (s), 80.5 (s), 60.3 (d), 58.1 (t), 57.0 (t), 41.5 (d), 28.4 (3  $\times$  q), 25.9 (3  $\times$  q), 25.7 (3  $\times$  q), 18.3 (s), 18.1 (s), -5.3 (q), -5.4 (q), -5.6 (q), -5.7 (q). Anal. Calcd for C<sub>31</sub>H<sub>51</sub>NO<sub>4</sub>Si<sub>2</sub>: C, 66.74; H, 9.21; N, 2.51. Found: C, 66.83; H, 9.21; N, 2.57.

**Typical Procedure for the Oxidation of Dihydrobenzo[*g*]indole to Benzo[*g*]indole:** DDQ (1–5 equiv) was added to a solution of 3a,9b-dihydrobenzo[*g*]indole (1 equiv) in dry Et<sub>2</sub>O. The mixture was stirred at room temperature until complete conversion (monitored by TLC) and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding benzo[*g*]indole.

(24) CCDC-655677 contains the supplementary crystallographic data. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. See also the Supporting Information.

(25) The propensity of tertiary propargylic alcohols to form ruthenium allenylidene complexes is known. See: Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **2004**, *248*, 1585–1601.

(26) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615–623.

(27) For insertion of DMAD into a Pd–heteroatom bond, see: (a) Yagyu, K.; Osakada, K.; Brookhart, M. *Organometallics* **2000**, *19*, 2125–2129. (b) Sugoh, K.; Kuniyasu, H.; Kurosawa, H. *Chem. Lett.* **2002**, 106–107.

***tert*-Butyl 3-butyl-2-formyl-1*H*-benzo[*g*]indole-1-carboxylate (11)** was obtained as a colorless oil:  $R_f$  (hexanes/AcOEt 9/1) 0.35;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  10.12 (s, 1H), 8.43 (m, 1H), 7.92 (m, 1H), 7.63 (m, 2H), 7.54 (m, 2H), 3.11 (t,  $J = 7.5$  Hz, 2H), 1.74 (s, 9H), 1.72 (m, 2H), 1.46 (m, 2H), 0.97 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  179.8 (d), 152.0 (s), 134.1 (s), 133.3 (s), 132.8 (s), 131.7 (s), 129.2 (d), 126.4 (d), 126.0 (d), 124.7 (s), 124.0 (d), 122.8 (d), 122.2 (s), 118.8 (d), 86.1 (s), 33.8 (t), 27.5 (3 x q), 23.6 (t), 22.7 (t), 13.8 (q). Anal. Calcd for  $\text{C}_{22}\text{H}_{25}\text{NO}_3$ : C, 75.19; H, 7.17; N, 3.99. Found: C, 75.31; H, 7.13; N, 3.75.

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**Supporting Information Available:** Experimental procedures, cif file for compound **9ag**, and characterization data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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