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Aza-Claisen Rearrangement in the Cyclization Reactions of Nitrogen-Containing Enynes via Ruthenium Vinylidene Complexes

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The cyclization reaction of several diallyl aromatic amine molecules, each containing an ethynyl group at the ortho position of the aromatic ring, is accompanied by an aza-Claisen rearrangement, causing an allyl group migration to give substituted indole compounds. This cyclization is catalyzed by ruthenium triphenylphosphine and diphenylphosphinoethane (dppe) complexes as well as gold complexes with silver reagent. The less sterically crowded dppe complex is a more efficient catalyst. The mechanism involving a vinylidene intermediate is proposed on the basis of isolation of several intermediates in the ruthenium-catalyzed system. Single crystals of a metal complex with the cyclized ligand were obtained, and the structure was determined by an X-ray diffraction analysis.

Introduction

During the past decade, metal-catalyzed reactions of enynes have become the focus of many explorations, because of their rich and versatile reactivity.[1,2] The chemistry of complexes containing vinylidene ligands, which are considered important key intermediates, reveals mechanistic insight into these reactions of enyne. Particularly, readily isolable ruthenium vinylidene complexes have attracted a great deal of attention in stoichiometric[3] as well as catalytic reactions involving enyne.[4] The indole nucleus, an important component in today's pharmaceuticals and bioactive products, is a widely distributed heterocycle found in nature. New and straightforward methods to access these substrates are thus always highly desirable.[5] Recently, alkynes become attractive starting materials for the synthesis of a variety of indole derivatives using transition-metal catalysts.[6] However, reactions of nitrogen-containing enynes aiming at substituted indole have been much less explored.

Various metals, such as zirconium,[7a] titanium,[7b−e] and zinc,[7f] are known to catalyze the intermolecular hydroamination of alkynes with arylhydrazines. The synthesis of indoles from *o*-haloaniline with alkynes via a heteroannulation process is an attractive method. The Larock heteroannulation and other palladium-catalyzed indolizations with alkynes are also known.[8] Cyclizations of *o*-alkynylaniline derivatives catalyzed by rhodium, palladium, and gold complexes have been reported.[9] These metal-catalyzed cyclizations proceed via intermolecular processes to produce functionalized indoles and their derivatives through external addition to the triple bond. However, a more efficient intramolecular cyclization accompanied by a migration of an unsaturated functional

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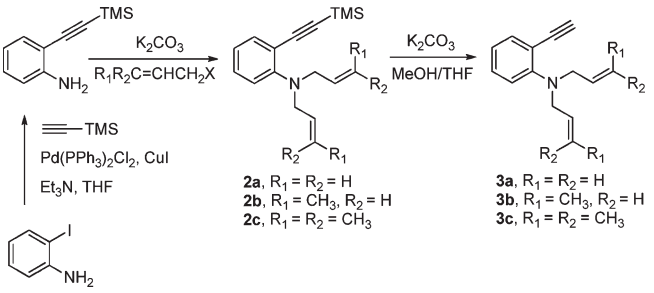
Scheme 1



group, bonded to the heteroatom, is not known. We report herein a high-yield synthesis of substituted indoles from cyclization of enynes containing nitrogen atoms accompanied by an aza-Claisen rearrangement. Mechanistic insight into the formation of substituted indoles was obtained by the isolation and characterization of several ruthenium complexes as key intermediates.

Results and Discussion

Synthesis and Catalytic Reactions of 1,7-Enynes. Synthesis of the *N*,*N*-diallyl aromatic amine **3a** was achieved first by the Sonogashira coupling reaction[10] of 2-iodoaniline with (trimethylsilyl)acetylene. This is followed by a high-yield allylation reaction using allyl iodide in acetone to give **2a**. Deprotection of **2a** in the presence of anhydrous K_2CO_3 gave **3a**, with a terminal alkynyl group (Scheme 1). The analogous compounds **3b**,**c** containing additional methyl groups were similarly prepared from a mixture of *trans*- and *cis*-crotyl bromide (6:1) via **2b** and 1-bromo-3-methyl-2-butene via **2c**, respectively. These enynes have been characterized by ^{1}H and ^{13}C NMR spectra, EI mass spectra, and elemental analysis. In the ^{1}H NMR spectrum of **3a** the olefinic terminal trans hydrogen shows a doublet peak at δ 5.18 with J = 15.5 Hz and the cis hydrogen at δ 5.14 with J = 8.7 Hz. In the ^{1}H NMR spectrum of **3c**, two methyl signals appear at δ 1.67 and 1.56. The *N*,*N*-dicrotyl aromatic amine **3b** presumably consists of a mixture of trans/trans (tt), trans/cis, (tc), and cis/cis (cc) isomers in a statistical ratio of 36:12:1. The ^{1}H NMR spectrum of the mixture of **3b** shows two singlet signals at δ 3.40 and 3.41 assigned to the proton of the terminal alkyne of tt and tc isomers, and after purification, the tt:tc ratio is about 4.7:1. The cc isomer, probably present in only a very small quantity, shows no signal. Multiplet resonances for the olefinic hydrogens of the tt and tc isomers are overlapped at δ 5.66−5.49. The doublet signal at δ 3.84 is assigned to the methylene group of the *trans*-crotyl group. The corresponding ^{1}H resonance of the *cis*-crotyl group shows a doublet resonance at δ 3.89. No attempt was made to separate the mixture.

As shown in Scheme 2, transformation of **3a** to **6a**, catalyzed by [Ru]Cl (**1**; [Ru] = $Cp(PPh_3)_2Ru$), is observed at room temperature. This process involves both a cyclization and an aza-Claisen rearrangement of one allyl group from nitrogen to the internal carbon of the triple bond. This cyclization/rearrangement reaction of **3a** could also be catalyzed with 5 mol % of $AuClPPh_3/AgSbF_6$ in CH_2Cl_2, also affording **6a**. The cyclization product **6a**, purified by chromatography, was characterized by 1D and 2D NMR spectra

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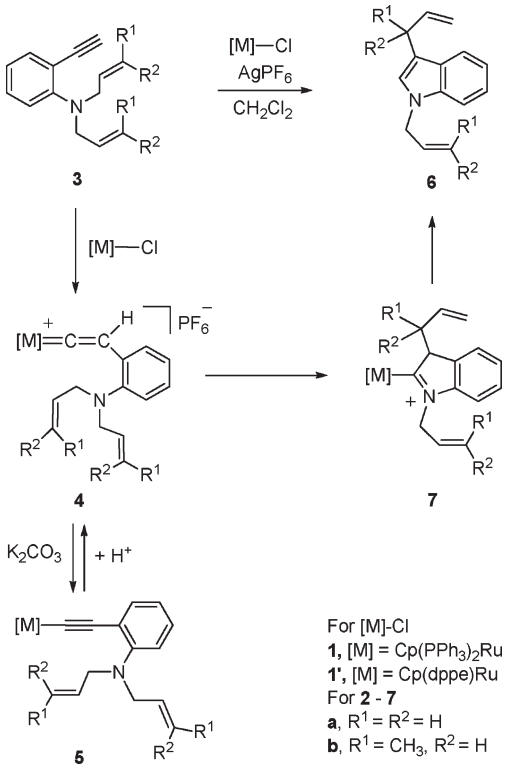
Scheme 2



and an EI mass spectrum. The single allylic pattern observed for the original *N*,*N*-diallyl groups in the ^{1}H NMR spectrum of **3a** changes to two different allylic patterns, and a new olefinic ring hydrogen peak appears at δ 6.87 as a singlet for **6a**. The singlet signal of the alkynyl hydrogen of **3a** at δ 3.36 disappears after transformation, and there is no resonance characteristic of an sp carbon in the ^{13}C NMR spectrum of **6a**. The EI mass spectrum confirms the formation of compound **6a**, showing a parent peak at m/z 197.0 and a fragmentation peak at m/z 156.1, corresponding to the cleavage of one allyl group.

In order to better understand the mechanism of the catalytic reaction, we studied the reaction of **3a** with 1 equiv of **1**. Interestingly, treatment of **3a** with **1** in the presence of $AgPF_6$ in CH_2Cl_2 afforded initially the cationic ruthenium vinylidene complex **4a**, which shows a broad singlet signal at δ 47.03 in the ^{31}P NMR spectrum, in moderate yield and other side products. Unfortunately, it is difficult to purify **4a**. From the residual solution of this reaction, the organic product **6a** and **1** were also isolated. For further characterization of **4a** we carried out the deprotonation reaction to generate the neutral acetylide complex **5a** (see Scheme 2). The singlet ^{31}P NMR resonance of **5a** at δ 51.64 is in the region of an acetylide complex. Singlet ^{31}P NMR signals are observed for both **4a** and **5a**. The solution of **4a** at room temperature and protonation of **5a** both yielded **6a**. However, no other isolable intermediate was obtained from the cyclization of **3a** in the presence of a stoichiometric amount of **1**.

Cyclization of the isomeric mixture of 1,7-enyne **3b**, which contains a terminal methyl substituent at the allyl group, was also explored. The reaction of the mixture of tt and tc isomers of **3b** with **1** in a 1:1 ratio in the presence of KPF_6 in CH_2Cl_2 for 1 day at room temperature directly afforded a mixture of **6b** in almost quantitative yield. The mixture of **6b** consists of

trans and cis isomers in a ratio of 4.5:1. A catalytic reaction could be achieved with almost quantitative yield by using 7.5 mol % of **1** at room temperature over 12 h. Using a 5 mol % $AuClPPh_3/AgSbF_6$ catalyst system, this cyclization reaction of **3b** in CH_2Cl_2 also afforded a mixture of **6b** in 85% maximum isolated yield over 7 h at room temperature. The product **6b** was characterized by ^1H, ^{13}C, 2D COSY, HSQC, and HMBC NMR spectra and an EI mass spectrum. In this transformation, migration of one linear crotyl group of **3b** to the five-membered ring to form a substituted branched but-3-en-2-yl group, a result of aza-Claisen rearrangement, is clearly observed by NMR. In the ^1H NMR spectrum of **6b**, both trans and cis isomers display identical resonances for the substituted but-3-en-2-yl group. Resonances at δ 6.10, 5.15, and 5.04 in a ratio of 1:1:1, respectively, are assigned to three olefinic hydrogens of the terminal vinyl group of the substituted but-3-en-2-yl group with the last two having $^3J_{HH}$ = 17.2 and 10.2 Hz, respectively. In addition, the singlet peak at δ 1.49 and the multiplet peak at δ 3.78, assigned to the methyl and the methyne group, respectively, on the stereogenic carbon center are identical for both isomers of **6b.** For the two isomers of **6b**, the differences on NMR data mainly appear for the *trans*- and *cis*-crotyl group on the nitrogen. A broad peak at δ 1.71 is assigned to methyl groups of the trans isomer, and for the cis isomer, the corresponding methyl doublet peak appears at δ 1.83. The characteristic broad multiplet resonance at δ 5.65 is consistent with the two olefinic protons in a trans configuration for the crotyl group. Well-separated olefinic resonances at δ 5.72 and 5.62 are observed for the cis isomer. The EI mass spectrum showing a parent peak at m/z 225.2 is consistent with the formula of **6b**. Transformation of the linear crotyl group to the branched species in the product clearly reveals that the process proceeds via the aza-Claisen rearrangement, instead of a direct allyl migration. With a stereogenic center near the but-3-en-2-yl group, identical NMR data for this group may indicate that only the *trans*-crotyl group can undergo the aza-Claisen rearrangement, thus fixing the stereochemistry of the methyl-substituted sp^3 carbon in the product. In addition, the steric effect should prohibit intramolecular approach of the double bond of the *cis*-crotyl group. Presumably the trans and cis isomeric products are obtained from the tt and tc isomers of **3b**, respectively. The tt isomer gives the trans product, and the tc isomer gives the cis product. The product distribution and the proposed mechanism discussed below most likely indicate that only the *trans*-crotyl group undergoes the aza-Claisen rearrangement. The selectivity will be discussed later on the basis of the structure determination of an intermediate.

Isolation of dppe Indole Complexes. In order to better understand the mechanism, the reaction of **3b** and [Ru′]Cl (**1′**; [Ru′] = Cp(dppe)Ru) was carried out with a 1:1 ratio of two reactants, leading to the isolation of intermediates. Treatment of **1′** with an isomeric mixture of **3b** in the presence of $AgPF_6$ in CH_2Cl_2 afforded the vinylidene product **4b′**. Unfortunately, **4b′** is also unstable and displays broad resonances in its NMR spectrum. Slight heating of **4b′** in $CDCl_3$ at 50 °C yielded a mixture of **6b** and trans/cis isomers of the ruthenium complex **7b′**, containing a bicyclic indole ring. It is therefore reasonable to assume that **4b′**, like **4a**, is a cationic ruthenium vinylidene complex (see Scheme 2). Attempted deprotonation of **4b′** failed to give the desired acetylide complex. Interestingly, in MeOH, the reaction of **3b** with **1′** in the presence of KPF_6 for 4 days at room temperature

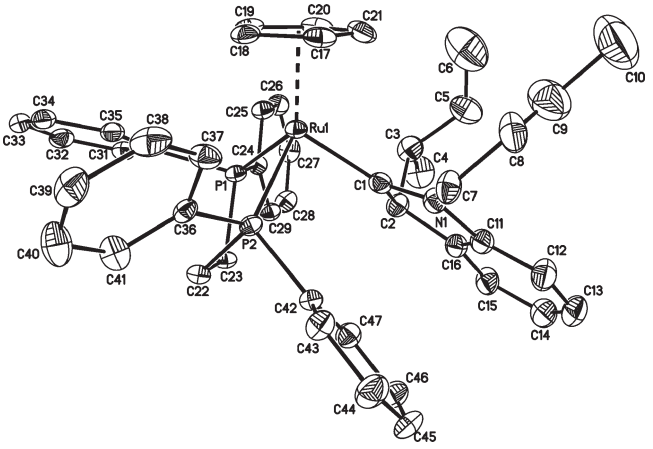


Figure 1. ORTEP drawing of *trans*-**7b′**. Phenyl groups on the chelating dppe ligand possibly control the stereochemistry of the substituted indole ring. Thermal ellipsoids are set at the 30% probability level.

directly gave **7b′** (trans:cis = 4.6:1). Further heating of **7b′** to 50 °C in a chlorinated solvent such as CH_2ClCH_2Cl, CH_2Cl_2, or $CHCl_3$ resulted in formation of **6b** and **1′** possibly proceeding via a [Ru′]H species. The lower yield of **7b′** directly from **3b** in chlorinated solvent is thus due to the rapid replacement of the cyclized ligand on the metal by the chloride to form **1′** and **6b**. Use of methanol as a solvent increases the yield of **7b′** up to 77%.

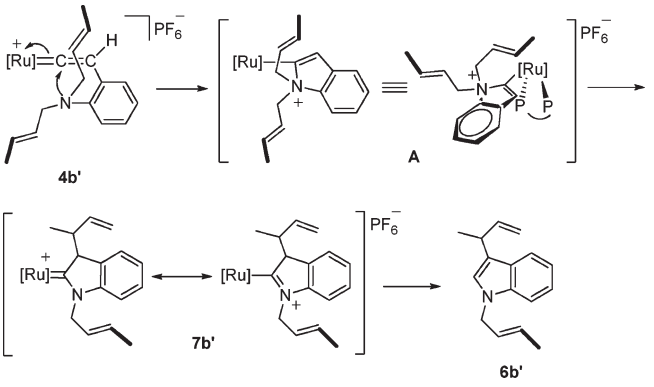
The ^{31}P NMR spectrum of the crude product of **7b′** in acetone-d_6 shows two sets of two doublet peaks at δ 76.35, 64.12 with $^2J_{PP}$ = 59.4 Hz and δ 76.82, 64.52 with $^2J_{PP}$ = 53.6 Hz in a ratio of 4.6:1. Two isomers presumably originate from the tt and tc forms, respectively, of **3b**. In order to separate two products, the mixture containing isomers of **7b′** was dissolved in CH_2Cl_2 and the solution was passed through a column packed with acidic Al_2O_3. From the second yellow band eluted with ethyl acetate, the major product *trans*-**7b′** was obtained. The ^{13}C NMR spectrum of *trans*-**7b′** was acquired at 243 K to prevent decomposition. The triplet ^{13}C NMR resonance for C_α appears at δ 263.9 with $^2J_{CP}$ = 14.7 Hz, indicating carbene character. The complex *trans*-**7b′** was also characterized by 2D COSY, HSQC, and HMBC NMR techniques at 243 K. In the $^1H,^1H$-COSY spectrum, the multiplet ^1H peak at δ 2.98, assigned to the sp^3-CH unit, shows correlations with the ^1H resonances at δ 0.35, 4.08, and 4.43, assigned to CH_3, RuCCH, and =CH, respectively. The HMBC spectrum of *trans*-**7b′** displays long-range correlation between C_α and NCH_2. The ESI mass spectrum, showing a parent peak at m/z 790.23 and fragmentation ions corresponding to dissociation of the whole indole moiety, confirms the formation of complex **7b′**.

Yellow single crystals of *trans*-**7b′** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution at −20 °C, and the solid-state crystal structure was determined by an X-ray crystallographic study. An ORTEP drawing of the cationic complex is shown in Figure 1.; selected bond distances and angles are given in Table 1. The space group is monoclinic $P2_1/c$ with unit cell dimensions a = 11.7330(1) Å, b = 20.3209(3) Å, c = 20.8087(2) Å, and β = 90.761(1)°. The final residuals of the refinement, R1 and wR2, are 0.0409 and 0.1110, respectively. The three-legged piano-stool geometry around the ruthenium center was determined by two phosphorus atoms of the chelating ligand and the bicyclic substituted

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complex *trans*-7b′

Bond Distances			
Ru1−C1	2.037(3)	N1−C1	1.343(4)
Ru1−P1	2.2871(7)	N1−C7	1.465(4)
Ru1−P2	2.3167(8)	C1−C2	1.526(4)
Bond Angles			
P1−Ru1−C1	95.99(9)	N1−C1−C2	105.0(2)
P2−Ru1−C1	90.04(8)	C1−N1−C11	113.7(2)
N1−C1−Ru1	126.4(2)	C11−N1−C7	118.8(3)

Scheme 3



indole ligand around the metal. The Ru(1)−C(1) bond length is 2.037(3) Å, typical for a Ru−C single bond. The N(1)−C(1) bond distance of 1.343(4) Å is well within the range of values for a conjugated N=C double bond.[11] The crotyl group on the nitrogen is in a trans configuration. The two atoms C(2) and C(3) are stereogenic carbon atoms.

Proposed Mechanism. A proposed mechanism for the formation of **7b′** is shown in Scheme 3. First, the reaction of [Ru′]Cl with the terminal alkyne gives the cationic vinylidene intermediate **4b′**, which then undergoes a 5-endodig cyclization.[12] Namely, the intramolecular nucleophilic attack of nitrogen to the electrophilic C_α forms the species **A**. This is followed by an aza-Claisen rearrangement[13] to give the cationic carbene complex **7b′**, in which the cationic charge could be delocalized either at Ru or at nitrogen. However, the solid-state structure seems to favor the form with the M−C single bond, as shown by the structure determination. This intramolecular cycloisomerization process involves the aza-Claisen rearrangement of the crotyl group from nitrogen to C_β of the vinylidene ligand. In the synthesis of furan derivatives, other types of allyl transfer have been described.[14] In their case, stabilization of the vinyl−metal intermediate via an enolate species seems necessary, since only the acetylenic esters and nitriles were reported to undergo the transfer reaction. Another type resembling allyl transfer in the presence of $PtCl_2$ or acids was reported,[15] in which the allyl group rearranges from the nitrogen to C_α of the terminal alkyne. However, in our case, the allyl group transfers to C_β, instead of C_α. In addition, the reaction of **3** to give **6** is not catalyzed by acid in the presence of silica. Other benzofuran syntheses were reported by Cacchi and Balme using $Pd(PPh_3)_3$ catalysts.[16,17]

With two stereogenic carbon centers in complex **7b′**, the stereoselectivity for its formation is discussed, even though, upon formation of **6b′**, construction of a double bond removes one stereogenic center. As shown in Scheme 3, cyclization of **4b′** possibly proceeds via intermediates **A** and **7b′** sequentially. Presumably, in **A**, the less crowded sides of the indole plane, namely that near the Cp ligand, should favor approach of the crotyl group on the nitrogen toward C_β; however, free rotation of the Ru−C bond nullifies the selectivity of the stereogenic carbon on the five-membered ring. In this aza-Claisen rearrangement, the steric effect may also inhibit the *cis*-crotyl group to approach C_β. This, along with the transition state, in either boat or chair form, in the Claisen rearrangement then determines the stereochemistry on the but-3-en-2-yl group. Hence, complex *tt*-**4b′** transforms to *trans*-**7b′** and complex *tc*-**4b′** to *cis*-**7b′**. Namely, only the *trans*-crotyl group undergoes the aza-Claisen rearrangement. Thus, the minor product of **7b′** would be the cis isomer. Notably, this cyclization reaction provides a direct approach to the substituted indole compound under mild conditions and gives a good selectivity without significant observation of the other probable isomers.

Steric Effect for the Catalytic Cyclization. As shown in Scheme 4, reactions of the TMS-protected dimethylsubstituted allylic amine **2c** were also investigated. We first carried out the reaction of **1** with **2c** in the presence of KF and KPF_6 in a MeOH/THF mixed solvent at room temperature, giving directly the acetylide complex **5c**, which shows a ^{31}P NMR singlet resonance at δ 51.30. Protonation of **5c** by HBF_4 in Et_2O generated the vinylidene complex **4c**. The ^{31}P NMR spectrum of **4c** shows a sharp singlet resonance at δ 40.80. In the ^{13}C NMR spectrum the triplet signal at δ 346.77 with J_{CP} = 11.0 Hz is assigned to C_α. Interestingly, complex **4c**, displaying normal NMR signals, is stable in $CDCl_3$. This is different from the aforementioned results of analogous vinylidene complexes **4a** and **4b**. The reaction of **1** with **3c** also stopped at the stage of the vinylidene complex **4c**, not proceeding further for cyclization and rearrangement or catalytically giving any indole product in chlorinated solvent. This can be explained by the steric hindrance between

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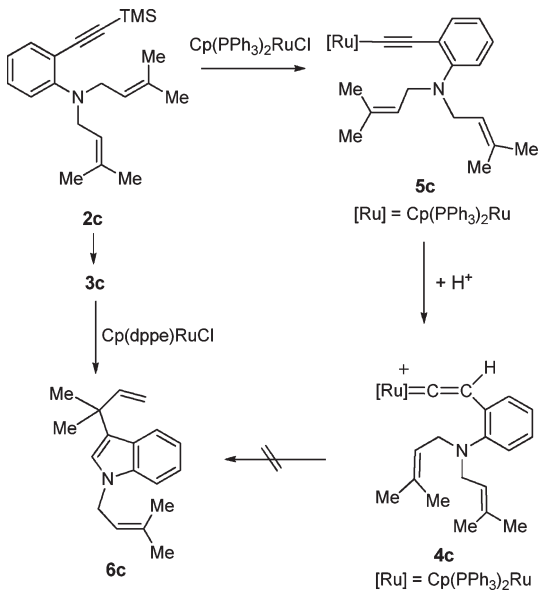
Scheme 4



PPh_3 and the slightly bulkier substituted allylic groups on the vinylidene ligand of **4c**, thus restraining the nitrogen attack.

However, the transformation of **3c** to **6c** could be catalyzed by **1′** in high yield (Scheme 4). Compound **6c** has been characterized by 1D, 2D COSY, HSQC, and HMBC NMR and EI mass techniques. The ^{1}H NMR spectrum of **6c** shows a new singlet peak at δ 1.58 assigned to two internal methyl groups. This, along with the terminal vinyl pattern at δ 5.15 and 5.08 with $^3J_{HH}$ = 17.4 and 10.6 Hz, respectively, clearly indicates the result of an aza-Claisen rearrangement. In the ^{13}C NMR spectra the 3 sp^3-carbon and 8 sp^2-carbon resonances of **3c** change to 5 sp^3-carbon and 12 sp^2-carbon resonances of **6c**. The reaction of the TMS-protected enyne **2c** with **1′** was carried out in the presence of KF in methanol/THF. The fluoride ion induces both desilylation and deprotonation to generate the resulting acetylide complex **5c′**. The ^{31}P NMR spectrum of **5c′** shows a singlet resonance at δ 92.14. Complex **5c′** is stable in solution. Interestingly, under basic conditions, the reaction of **3c** with 1 equiv of **1′** also afforded **5c′**. The ratio of **5c′** to **1′** was 2:1, as indicated from the ^{31}P NMR spectra. This is probably due to the steric bulk of **3c**, such that when it is π-coordinated to the ruthenium, the steric repulsion causes dissociation of the ligand. Further protonation of complex **5c′** by excess HBF_4 was carried out in an NMR tube, and the reaction was monitored by ^{31}P NMR spectra. Transformation of the acetylide complex into two new products was observed over a few minutes. The two ^{31}P NMR signals at δ 79.91 and 80.47 are in a ratio of 1.5:1. The former could be presumably attributed to the vinylidene intermediate,[18] and the latter could be due to a cyclization product from addition of nitrogen to C_α. After a few hours, the peak at δ 79.91 decreased but the peak at δ 80.47 increased and a set of two doublets, assigned to complex **7c′**, appeared at δ 78.44 and 66.05 with $^2J_{PP}$ = 22.5 Hz. Finally, the formation of the indole product **6c** was also observed in the ^{1}H NMR spectrum. The transformation of **3c** to **6c**, catalyzed by **1′**, clearly demonstrates that the cyclization is controlled by the steric effect. This could also imply that, for **3b**, only the *trans*-crotyl group undergoes the aza-Claisen rearrangement.

Conclusion

In conclusion, cyclopentadienyl ruthenium chloride complexes with phosphine ligands catalyze the transformation of diallylarylamine with a terminal alkynyl group on the aromatic ring to give the substituted-indole product. The reaction proceeds by the formation of the vinylidene intermediate from the terminal alkyne followed by a cyclization reaction to give the indole product. Subsequent aza-Claisen rearrangement under mild conditions results in migration of the substituted or nonsubstituted allyl group to the indole ring. The catalytic reaction is influenced by the steric bulk of the phosphine ligands. All transformations of **3a**−**c** to **6a**−**c** can be catalyzed smoothly by the less bulky CpRu(dppe)Cl complex. However, transformation of **3c** could not be catalyzed by $CpRu(PPh_3)_2Cl$ because of the steric hindrance between the bulkier phosphine ligand and the substituted allylic groups. Several intermediates were observed, and one of them was fully characterized by single-crystal X-ray diffraction analysis.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line, drybox, and standard Schlenk techniques unless mentioned otherwise. Hexanes and CH_2Cl_2 were distilled from CaH_2, diethyl ether and THF were distilled from sodium benzophenone ketyl, and methanol was distilled from Mg/I_2. All other solvents and reagents were of reagent grade and were used as received. NMR spectra were recorded on Bruker AM-300, Avance-400, and DMX-500 FT-NMR spectrometers at room temperature unless stated otherwise and were reported in units of δ with residual protons in the solvent as a standard ($CDCl_3$, δ 7.24; C_6D_6, δ 7.16; d_6-acetone, δ 2.04). FT-IR spectra were carried out on a Bruker Tensor 27 spectrometer. Mass spectrometry, elemental analyses, and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University. All reagents were obtained from commercial suppliers. The complexes $Cp(PPh_3)_2RuCl$[19a] and Cp(dppe)RuCl[19b] were prepared using literature methods.

Synthesis of 2a and 3a. Excess allyl iodide (2.40 mL, 26.15 mmol) was added to a solution of 2-[(trimethylsilyl)ethynyl]aniline (1.00 g, 5.28 mmol) and K_2CO_3 (2.92 g, 21.13 mmol) in 40 mL of dried acetone. The mixture was stirred at 55 °C overnight. The resulting solution was filtered through Celite, and the solvent of the filtrate was evaporated to give the crude product, which was purified by flash chromatography on silica gel with *n*-hexane/CH_2Cl_2 (8.5/1.5) as eluent to afford a yellow band. The solvent was removed under vacuum to give the pure liquid **2a** (1.27 g, 89% yield). Spectroscopic data of **2a** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40, 7.16, 6.86, 6.79 (m, 4H, Ph), 5.86 (m, 2H, =CH), 5.20 (d, J = 16.9 Hz, 2H, =CHH *trans*), 5.14 (d, J = 10.1 Hz, 2H, =CHH *cis*), 3.91 (d, J = 5.4 Hz, 4H, CH_2), 0.22 (s, 9H, TMS). Then K_2CO_3 (14.11 g, 102.09 mmol) was added to a solution of **2a** (1.27 g, 4.72 mmol) in MeOH/THF (1:1). The mixture was stirred at room temperature for 5 h. The resulting solution was filtered through Celite and was dried by rotary evaporation to give yellow liquid **3a** (0.90 g, 97% yield). Spectroscopic data of **3a** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ

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7.45−6.84 (m, 4H, Ph), 5.84 (m, 2H, =CH), 5.18 (d, J = 15.5 Hz, 2H, =CHH *trans*), 5.14 (d, J = 8.7 Hz, 2H, =CHH *cis*), 3.89 (d, J = 4.6 Hz, 4H, CH_2), 3.36 (s, 1H, ≡CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1 (=CN), 135.1, 135.0, 129.3, 120.6, and 119.6 (Ph), 117.3, 114.9 (C=C), 83.0, 82.2 (C≡C), 54.5 (CH_2). EI-MS: m/z 197.00 (M^+). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.08; H, 7.53; N, 7.01.

Synthesis of 2b and 3b. An aliquot of *trans*- and *cis*-crotyl bromide (6:1, 5.50 mL, 52.83 mmol) was added to a suspension of 2-[(trimethylsilyl)ethynyl]aniline (2.01 g, 10.57 mmol) and K_2CO_3 (4.38 g, 31.69 mmol) in 50 mL of dried acetone. The mixture was stirred at 55 °C overnight. The resulting solution was filtered through Celite and evaporated to give the crude product, which was purified by flash chromatography on silica gel with *n*-hexane/CH_2Cl_2 (9:1) as eluent to afford a yellow band. Solvent was then removed under vacuum to give the liquid product **2b** (2.64 g, 84% yield). The ratio of trans/trans (tt) to trans/cis (tc) product is 4.7:1. Spectroscopic data of **2b** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): tt isomer, δ 7.39−6.73 (m, 4H, Ph), 5.61−5.48 (m, 4H, =CH), 3.82 (d, $^3J_{HH}$ = 5.4 Hz, 4H, CH_2), 1.67 (d, $^3J_{HH}$ = 5.9 Hz, 6H, CH_3), 0.23 (s, 9H, TMS); tc isomer, δ 7.39−6.73 (m, 4H, Ph), 5.61−5.48 (m, 4H, =CH), 3.89 (d, $^3J_{HH}$ = 5.7 Hz, 4H, CH_2), 1.63 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 0.22 (s, 9H, TMS). ^{13}C NMR (125 MHz, $CDCl_3$): tt isomer, δ 153.29 (=CN), 135.06, 129.04, 119.47, and 118.71 (Ph), 128.25, 127.86 (C=C), 104.92, 98.84 (C≡C), 52.86 (CH_2), 17.77 (CH_3), 0.04 (TMS); tc isomer, 153.11 (=CN), 134.94−118.91 (Ph), 127.98, 126.20 (C=C), 104.76, 98.99 (C≡C), 47.32 (CH_2), 13.13 (CH_3), 0.32 (TMS). Then K_2CO_3 (0.48 g, 3.47 mmol) was added to a solution of **2b** (2.64 g, 8.88 mmol) in MeOH/THF (1:1). The mixture was stirred at room temperature for 5 h. The resulting solution was filtered through Celite, and the filtrate was dried by rotary evaporation to give yellow liquid product **3b** (1.96 g, 98% yield). The ratio of tt to tc product remained the same. Spectroscopic data of **3b** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): tt isomer, δ 7.48−6.82 (m, 4H, Ph), 5.66−5.49 (m, 4H, =CH), 3.84 (d, $^3J_{HH}$ = 5.9 Hz, 4H, CH_2), 3.40 (s, 1H, ≡CH), 1.69 (d, $^3J_{HH}$ = 5.4 Hz, 6H, CH_3); tc isomer, δ 7.48−6.82 (m, 4H, Ph), 5.66−5.49 (m, 4H, =CH), 3.89 (d, $^3J_{HH}$ = 6.1 Hz, 4H, CH_2), 3.41 (s, 1H, ≡CH), 1.63 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): tt isomer, δ 153.38 (=CN), 134.94, 129.10−114.72 (Ph), 128.19, 127.79 (C=C), 83.18, 81.98 (≡C), 53.38 (CH_2), 17.72 (CH_3); tc isomer, δ 153.47 (=CN), 134.90−115.17 (Ph), 127.94, 127.79 (C=C), 83.06, 82.08 (C≡C), 47.77 (CH_2), 13.07 (CH_3). EI-MS: m/z 225.00 (M^+). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22.

Synthesis of 2c and 3c. 1-Bromo-3-methyl-2-butene (1.00 mL, 8.52 mmol) was added to a suspension of 2-[(trimethylsilyl)-ethynyl]aniline (0.51 g, 2.69 mmol) and K_2CO_3 (1.12 g, 8.07 mmol) in 20 mL of dried acetone. The mixture was stirred at 50 °C overnight. The resulting solution was filtered through Celite and evaporated to give the crude product, which was purified by flash chromatography on silica gel with *n*-hexane/CH_2Cl_2 (8:2) as eluent to afford a yellow band. Solvent was then removed under vacuum to give the yellow liquid **2c** (0.76 g, 87% yield). Spectroscopic data of **2c** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−6.72 (m, 4H, Ph), 5.26 (t, $^3J_{HH}$ = 6.3 Hz, 2H, =CH), 3.82 (d, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2), 1.69 (s, 6H, CH_3), 1.61 (s, 6H, CH_3), 0.22 (s, 9H, TMS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.62 (CNH_2), 133.99−115.23 (Ph), 134.91, 122.46 (C=C), 104.85, 99.05 (C≡), 49.30 (CH_2), 25.77, 17.89 (CH_3), 0.03 (TMS). Then K_2CO_3 (0.65 g, 4.68 mmol) was added to a solution of **2c** (0.76 g, 2.34 mmol) in MeOH/THF (1:1). The mixture was stirred at room temperature for 4.5 h. The procedure for the preparation of **3c** (0.57 g, 97% yield) is similar to that for **3b**. Spectroscopic data of yellow liquid **3c** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−6.82 (m, 4H, Ph), 5.21 (t, $^3J_{HH}$ = 6.4 Hz, 2H, =CH), 3.80 (d, $^3J_{HH}$ = 6.4 Hz, 4H, CH_2), 3.37 (s, 1H, ≡CH), 1.67 (s, 6H, CH_3), 1.56 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.38 (C−NH_2), 133.79−114.08 (Ph), 135.01, 121.57 (C=C), 83.18, 81.98 (C≡C), 48.79 (CH_2), 24.91, 18.20 (CH_3). EI-MS: m/z 253.20 (M^+). Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.72; H, 9.04; N, 5.48.

Synthesis of Complexes 5c and 5c′. To a Schlenk flask containing [Ru]Cl (**1**; 100 mg, 0.137 mmol), **2c** (70 mg, 0.215 mmol), KF (24 mg, 0.411 mmol), and KPF_6 (50 mg, 0.274 mmol) were added 20 mL of MeOH and 10 mL of THF. Then the solution was stirred overnight under nitrogen at room temperature. The solvent was removed in vacuo, and diethyl ether was used to extract the crude product. The ether solution was filtered through the Celite. Removal of the solvent under vacuum gave the desired product, characterized as **5c** (103 mg, 80% yield). Spectroscopic data of **5c** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60−6.70 (m, 34H, Ph), 5.43 (t, 2H, =CH), 4.40 (s, 5H, Cp), 4.16 (d, 4H, CH_2), 1.79 (s, 3H, CH_3), 1.71 (s, 3H, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 51.30. MS (FAB+): m/z 943.30 $(M + 1)^+$. Anal. Calcd for $C_{59}H_{57}NP_2Ru$: C, 75.14; H, 6.09; N, 1.49. Found: C, 75.09; H, 6.21; N, 1.32. Complex **5c′** (110 mg, 0.134 mmol, 81% yield) was similarly prepared from the reaction of [Ru']Cl (**1′**; 100 mg, 0.166 mmol), **2c** (69 mg, 0.212 mmol), KF (25 mg, 0.428 mmol), and KPF_6 (48 mg, 0.263 mmol) in 20 mL of methanol and 10 mL of THF. Spectroscopic data of **5c′** are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.92−6.58 (m, 24H, Ph), 5.25 (t, $^3J_{HH}$ = 6.4 Hz, 1H, =CH), 4.68 (s, 5H, Cp), 3.84 (d, $^3J_{HH}$ = 6.4 Hz, 2H, CH_2), 2.25 (m, 2H, dppe), 2.09 (m, 2H, dppe), 1.71 (s, 3H, CH_3), 1.64 (s, 3H, CH_3). MS (FAB+): m/z 817.20 $(M + 1)^+$. ^{31}P NMR (162 MHz, acetone-d_6): δ 92.14. Anal. Calcd for $C_{49}H_{51}NP_2Ru$: C, 72.04; H, 6.29; N, 1.71. Found: C, 72.22; H, 6.36; N, 1.59.

Synthesis of Complex 4c. A dilute solution of $HBF_4 \cdot Et_2O$ in diethyl ether was added dropwise at 0 °C to a stirred solution of complex **5c** (100 mg, 0.122 mmol) in 20 mL of diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted, and the pink solid was washed with diethyl ether and dried in vacuo to give **4c** (100 mg, 79% yield). Spectroscopic data of **4c** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87−6.56 (m, 34H, Ph), 5.95 (s, 1H, Hβ), 5.20 (7H, Cp and =CH), 4.38 (d, $^3J_{HH}$ = 6.7 Hz, 4H, CH_2), 1.53 (s, 3H, CH_3), 1.52 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 346.77 (t, $^2J_{CP}$ = 11.0 Hz, C_α), 145.26−111.89 (m, Ph), 134.29 (=C), 129.04 (=CH), 123.07 (C_β), 95.72 (Cp), 57.76 (CH_2), 26.03, 18.21 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.80. MS (FAB+): m/z 944.29 $(M + 1)^+$. Anal. Calcd for $C_{59}H_{58}BF_4NP_2Ru$: C, 68.74; H, 5.67; N, 1.36. Found: C, 68.79; H, 5.77; N, 1.51.

Synthesis of 7b′. To a Schlenk flask containing [Ru']Cl, (**1′**; 110 mg, 0.183 mmol) and KPF_6 (70 mg, 0.38 mmol) was added methanol (25 mL) under nitrogen. Then to the solution was added 2.1 equiv of **3b** (78 mg, 0.39 mmol) in methanol (5 mL), and the solution was stirred at room temperature for 4 days. The solvent was removed in vacuo, and CH_2Cl_2 was used to extract the product. After filtration through Celite the solution was concentrated to ca. 5 mL and was added to a stirred diethyl ether (50 mL) solution to produce the yellow precipitates. The powder was collected, washed with diethyl ether, and dried under vacuum to give the crude product. ^{31}P NMR of the crude product (162 MHz, acetone-d_6): δ 76.35, 64.12 (2 d, $^2J_{PP}$ = 59.4 Hz); δ 76.82, 64.52 (2 d, $^2J_{PP}$ = 53.6 Hz) in a ratio of 4.6:1. The mixture was redissolved in EtOAc and chromatographed over acidic Al_2O_3 with EtOAc as eluent. A yellow band was collected and dried to give the major product *trans*-**7b′** (132 mg, 77% yield). Spectroscopic data of *t*-**7b′** are as follows. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.10−6.54 (m, 24H, Ph), 5.63 (m, 1H, =CH), 5.43 (m, 1H, =CH), 5.23 (s, 5H, Cp), 4.73 (d, $^3J_{HH}$ = 17.2 Hz, 1H, trans =CH_2), 4.63 (d, $^3J_{HH}$ = 10.5 Hz, 1H, cis =CH_2), 4.43 (m, 1H, =CH), 4.08 (d, $^3J_{HH}$ = 2.4 Hz, 1H, CH), 3,13−2.38 (m, 4H, dppe), 2.98 (m, 1H, CH), 2.66 (d, $^3J_{HH}$ = 4.3 Hz, 2H, CH_2), 1.61 (d, $^3J_{HH}$ = 6.4 Hz, 3H, =CCH_3), 0.35 (d,

$^3J_{HH}$ = 7.0 Hz, 3H, HCCH_3). ^{13}C NMR (125 MHz, acetone-d_6): δ 263.9 (dd, $^2J_{PC}$ = 14.7 Hz, C$_\alpha$), 147.2−112.5 (Ph), 138.2, 130.2, 124.6, and 116.2 (=C), 85.0 (Cp), 71.8 and 42.5 (CH), 55.0 (CH_2), 19.4 and 17.9 (CH_3). ^{31}P NMR (162 MHz, acetone-d_6): δ 76.35, 64.12 (2 d, $^2J_{PP}$ = 59.4 Hz). MS (ESI): m/z 790.23 (M^+). Anal. Calcd for $C_{49}H_{53}Cl_4F_6NP_3Ru$ (with solvent molecule obtained from recrystallization): C, 53.22; H, 4.83; N, 1.27. Found: C, 52.98; H, 4.77; N, 1.18. The reaction of [Ru']Cl, (**1′**; 100 mg, 0.166 mmol) and **3b** (66 mg, 0.332 mmol) was also carried out in CH_2Cl_2 (4 mL) in the presence of $AgPF_6$ (43 mg, 0.170 mmol) under nitrogen for 5 min. The resulting solution was filtered through Celite, concentrated to ca. 3 mL, and added to stirred diethyl ether (40 mL) to produce precipitates. The powder (79 mg) was collected by filtration, washed with diethyl ether, and dried under vacuum. Spectroscopic data are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (br, 1H, H$_\beta$), 4.88 (br, 5H, Cp). ^{31}P NMR (162 MHz, $CDCl_3$): δ 80.61 (br). Thermolysis of this powder considered as the vinylidene intermediate at 50 °C also gave **7b′**.

Catalytic Synthesis of 6a−c by Ruthenium Complexes. To a Schlenk flask containing **1** (100 mg, 0.137 mmol) and $AgPF_6$ (41.6 mg, 0.164 mmol) was added CH_2Cl_2 (3 mL) under nitrogen. Then to the solution was added 2.0 equiv of **3a** (54.0 mg, 0.274 mmol) in CH_2Cl_2 (4 mL), and the mixture was stirred for 5 min. The resulting solution was filtered through Celite, concentrated to ca. 3.0 mL, and added to stirred diethyl ether (40 mL) to produce a yellowish brown precipitate and a yellow solution. After filtration, the solvent of the filtrate was removed under vacuum to afford the yellow product **6a** (48.6 mg, 90% yield). Spectroscopic data of **6a** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ph), 7.27 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ph), 7.18 (t, 1H, Ph), 7.08 (t, 1H, Ph), 6.87 (s, 1H, =CH), 6.05 (m, 1H, =CH), 5.96 (m, 1H, =CH), 5.18−5.03 (m, 4H, =CH_2), 4.66 (ddd, ^3J = 5.4 Hz, ^4J = 1.6 Hz, 2H, N−CH_2), 3.50 (dd, ^3J = 6.5 Hz, ^4J = 0.8 Hz, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 133.7, 125.4 (=*C*H), 136.6 (=C), 117.1, 115.1 (=CH_2), 128.0, 121.6, 119.2, 118.8, 113.4, 109.5 (6C, Ph), 48.7, 29.8 (CH_2). EI-MS: m/z 197.0 (M^+). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.21; H, 7.70; N, 7.03.

Similarly, treatment of **3b** (100 mg, 0.444 mmol) in CH_2Cl_2 in the presence of a catalytic amount of [Ru]Cl (**1**; 48.7 mg, 0.067 mmol) and KPF_6 (24.5 mg, 0.13 mmol) at room temperature for 7 h afforded the yellow indole product **6b** (100 mg, 99%, trans:cis ratio 4.5:1) in almost quantitative isolated yield. Spectroscopic data of **6b** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): trans isomer, δ 7.65, 7.31, 7.21, 7.10 (4H, Ph), 6.88 (s, 1H, =CH), 6.10 (m, $^3J_{HH}$ = 17.2, 10.2 Hz, 1H, =CH), 5.65 (m, 2H, HC=CH), 5.15 (d, $^3J_{HH}$ = 17.2 Hz, 1H, =CH_2), 5.04 (d, $^3J_{HH}$ = 10.2 Hz, 1H, =CH_2), 4.62 (br, 2H, CH_2), 3.78 (m, 1H, CH), 1.71 (br, 3H, CH_3), 1.49 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3); cis isomer, δ 7.65−7.10 (4H, Ph), 6.89 (s, 1H, =CH), 6.10 (m, $^3J_{HH}$ = 17.2, 10.2 Hz, 1H, =CH), 5.72 (m, 1H, =CH), 5.62 (m, 1H, =CH), 5.15 (d, $^3J_{HH}$ = 17.2 Hz, 1H, =CH_2), 5.04 (d, $^3J_{HH}$ = 10.2 Hz, 1H, =CH_2), 4.72 (d, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2), 3.78 (m, 1H, CH), 1.83 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 1.49 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): trans isomer, δ 143.45−109.57 (Ph, =C), 48.08 (CH_2), 34.85 (CH), 20.30, 17.06 (CH_3); cis isomer, δ 143.45−109.42 (Ph, =C), 42.82 (CH_2), 34.85 (CH), 20.30, 13.06 (CH_3). EI-MS: m/z 225.2 (M^+). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.21; H, 8.51; N, 6.17.

Compound **6c** (68 mg, 97% yield) was obtained from **3c** (70 mg, 0.276 mmol) by a similar catalytic process using **1′**. Spectroscopic data of **6c** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ph), 7.34 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ph), 7.21 (t, 1H, Ph), 7.11 (t, 1H, Ph), 6.92 (s, 1H, =CH), 6.20 (dd, $^3J_{HH}$ = 17.4 and 10.6 Hz, 1H, =CH), 5.43 (t, $^3J_{HH}$ = 6.7 Hz, 1H, =CH), 5.15 (d, $^3J_{HH}$ = 17.4 Hz, 1H, =CH_2), 5.08 (d, $^3J_{HH}$ = 10.6 Hz, 1H, =CH_2), 4.69 (d, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2), 1.88 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.58 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.90−109.51 (Ph, =C), 44.01 (CH_2), 37.47 (C), 28.11, 25.62, and 17.99 (CH_3). EI-MS: m/z 253.18 (M^+). Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53.

Catalytic Synthesis of 6a and 6b by a Gold Complex. Treatment of **3a** (330 mg, 1.67 mmol) in CH_2Cl_2 in the presence of a catalytic amount of $AuClPPh_3$ (42.0 mg, 0.084 mmol) and $AgSbF_6$ (28.6 mg, 0.084 mmol) at room temperature for 6 h afforded the yellow indole product **6a** (287 mg, 87% yield). Treatment of **3b** (300 mg, 1.33 mmol) in CH_2Cl_2 in the presence of a catalytic amount of $AuClPPh_3$ (33.0 mg, 0.066 mmol) and $AgSbF_6$ (22.5 mg, 0.066 mmol) at room temperature for 5 h also afforded the yellow indole product **6b** (255 mg, 85% yield, trans:cis = 4.5:1).

Single-Crystal X-ray Diffraction Analysis of *trans*-7b′. Single crystals suitable for an X-ray diffraction study were grown via slow diffusion of diethyl ether into a CH_2Cl_2 solution of **7b′** at −20 °C. A single crystal of dimensions 0.20 × 0.15 × 0.10 mm^3 was glued to a glass fiber and mounted on a Nonius Kappa CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube molybdenum Kα radiation (T = 100(2) K). The exposure time was 5 s per frame. Multiscan absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL program.[20] The structure was solved using direct methods and confirmed by Patterson methods refined on intensities of all data (31 671 reflections) to give R1 = 0.0409 and wR2 = 0.1110 for 11 375 unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogen. Crystal data for *trans*-**7b′**: $C_{47}H_{48}NF_6P_3Ru \cdot 2CHCl_3$; M_r = 1174.59; 0.20 × 0.15 × 0.10 mm; monoclinic, space group $P2_1/c$; a = 11.7330(1) Å, b = 20.3209(3) Å, c = 20.8078(2) Å; β = 90.761(1)°; V = 4960.5(1) Å^3; Z = 4; ρ_{calcd} = 1.573 g cm^{-3}; μ = 0.795 mm^{-1}; $F(000)$ = 2388; T = 100(2) K; R1 = 0.0409; wR2 = 0.1110; 11 375 independent reflections.

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Supporting Information Available: A CIF file giving crystallographic data for *trans*-**7b′**. This material is available free of charge via the Internet at http://pubs.acs.org.

(20) *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc., Madison, WI, 1995.