Facile Ruthenium(IV)-Catalyzed Single and Double Allylation of Indole Compounds using Alcohols as Substrates: Aspects of Ruthenium(IV) Allyl Chemistry

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The dicationic Ru(IV) salt $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(CH_3CN)_2](PF_6)_2$ is shown to be an excellent and rapid catalyst for the C-allylation of indole compounds using *allyl alcohols* as substrates. Selective, one-pot N,C-double allylation is also possible. Preliminary experiments suggest that vinyl epoxides may be used as an allyl source. Stoichiometric reactions of $CH_2{=}CHCH(OH)CH{=}CH_2$, $CH_2{=}CHCH(OAc)CH{=}CH_2$, and $CH_2{=}CHCH{=}CHCH_2Br$ with $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ afford new Ru(IV) η^3-vinyl-allyl salts, two of which, $[Ru(Cp^*)(\kappa^2\text{-}OAc)(\eta^3\text{-vinyl-allyl})](PF_6)$ (**13**) and $[Ru(Cp^*)Br(\eta^3\text{-vinyl-allyl})(CH_3CN)](PF_6)$ (**14**), have been studied by X-ray diffraction methods. In addition to the Ru(IV) η^3-vinyl-allyl bonding mode, we also find an isomer of the bromo salt **14** possessing a dynamic Ru(IV) S (rather than U)-shaped η^5-pentadienyl moiety, **20**. DFT computational results for **20** indicate that the S-shaped rather than the U-shaped form is the most stable Ru(IV) species and that the stability difference between these two forms is mainly due to interligand repulsion between the Br and pentadienyl ligands.

Introduction

The organometallic chemistry of ruthenium associated with homogeneous catalysis represents an expanding area of research.[1,2] In addition to the olefin metathesis[3] reaction, one finds new catalytic applications in oxidation,[4] reduction,[5] and C−C bond making[6–8] chemistry. The recent literature has documented renewed interest in the use of allylic substrates in the synthesis of new C−C, [9] C−N,[10] and C−O[11,12] bonds. In particular, there are an increasing number of Cp and Cp* Ru(II) complexes and salts finding applications in this catalytic area.[13]

We have become involved in studying and using Ru(IV) allyl complexes such as **1**−**3**, both as intermediates and catalyst precursors.[14–17] We were particularly interested in preparing labile Ru(IV) precursors, with the goal of accelerating the rates of existing reactions and finding new and more selective applications as a consequence of these faster reactions. A

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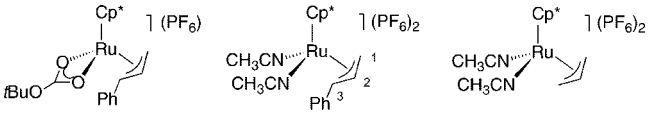


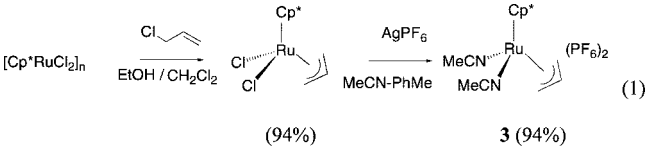
1 [14] **2** [15] **3** [16]

number of Ru(IV) allyl structures are known,[18–20] and the solid-state structure for **2** is especially useful, as it provides a clue as to why nucleophiles choose to preferentially attack the substituted terminal allyl carbon, C3, rather than the more accessible C1.[14] In our previous Ru-catalyzed reactions, concerned with allylation of phenol and indole nucleophiles, we concentrated on the use of *alcohols as substrates*,[15] at room temperature, rather than carbonate-, acetate-, or halogen-substituted substrates which waste the leaving groups. There are *no additives* required in this ruthenium chemistry, in contrast to literature reports that use alcohols but require boron[21,22] or titanium cocatalysts[23] together with the transition metal. The ability to use alcohols is related to the controlled release of a proton when the Ru(IV) catalyst is attacked.[15] This results in water as the leaving group in the oxidative addition reaction. There is still only a modest catalytic literature[24] concerned with the use of alcohols as substrates.

We report here on new C−C bond making reactions, catalyzed by **3**, using alcohols as reagents and indole and its derivatives as nucleophiles. Furthermore, we describe new preparative and structural $Ru^{IV}(Cp^*)$ organometallic chemistry derived from several diene substrates.

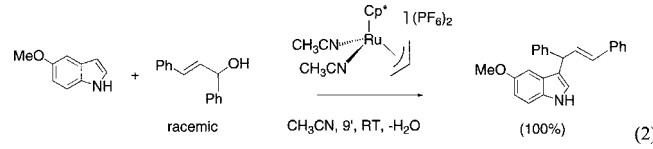
Results and Discussion

Catalytic Results. The dicationic Ru(IV) catalyst **3** was prepared in excellent yield, as shown in eq 1, and fully characterized (see the Experimental Section). We have allowed



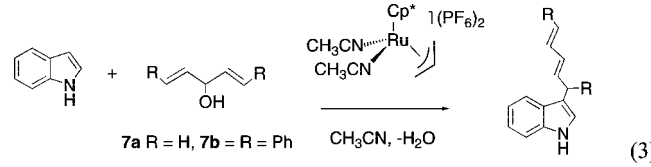
(94%) **3** (94%) (1)

indole and several indole derivatives to react with a selection of different allyl alcohols in the presence of 5 mol % of our Ru(IV) catalyst. An especially rapid example is given in eq 2. One observes 100% conversion (via ^{1}H NMR), and the C−C coupling product is formed in high yield at ambient temperature in only 9 min. The analogous reaction with indole proceeds to completion in 50 min at room temperature, and the isolated yield is 91%.



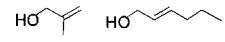
racemic CH_3CN, 9', RT, $-H_2O$ (100%) (2)

Results from the reaction of indole with a selection of alcohols are given in Scheme 1, and several points are worthy of note. Apart from allyl alcohol itself (30 min to completion), when a phenyl substituent is present in the alcohol, the reaction can be relatively rapid. In this connection, a comparison of the two dienol substrates CH_2═CHCH(OH)CH═CH_2 and PhCH═CHCH(OH)CH═CHPh is informative (see eq 3). Using the latter



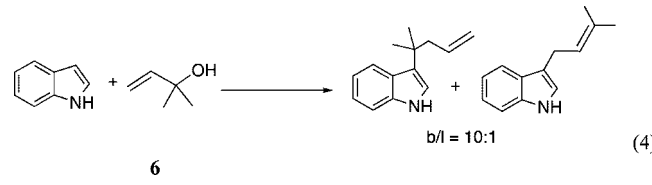
7a R = H, **7b** = R = Ph CH_3CN, $-H_2O$ (3)

substrate, the reaction is complete within 25 min (and gives an 85% isolated yield), whereas the former requires heating for several hours for complete conversion. In general, our reaction times compare very favorably with related literature reports, and a factor of 10, in time, is not unusual.[25] In the absence of a phenyl substituent, the best results are obtained when the double bond has only one substituent, i.e., a vinyl alcohol (note that the substrates **4** and **5** gave no reaction, suggesting that



4 **5**

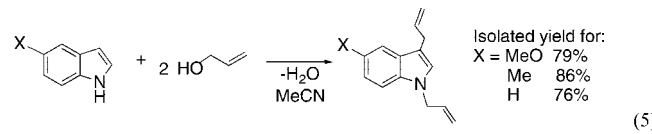
steric hindrance to olefin complexation may be important). Furthermore, the branched to linear (b/l) ratios vary considerably. The best b/l ratio was found for **6** (see eq 4). Details



6 b/l = 10:1 (4)

concerned with the b/l ratios for all of the reactions are given in the Experimental Section. It is noteworthy that CH_2═CHCH(OH)CH═CH_2 affords exclusively linear product (see eq 3), whereas PhCH(OH)CH═CH_2 gives primarily the branched isomer and we shall return to this point in connection with the stoichiometric organometallic reactions.

Use of an excess of allyl alcohol results in the controlled synthesis of an N,C-diallylated indole product in good yield (see eq 5). We believe this to be the first example of such a



Isolated yield for: X = MeO 79%, Me 86%, H 76% (5)

controlled one-pot double allylation.[26] This chemistry is relatively slow, 16 h, and given the fast reaction with 1 equiv of

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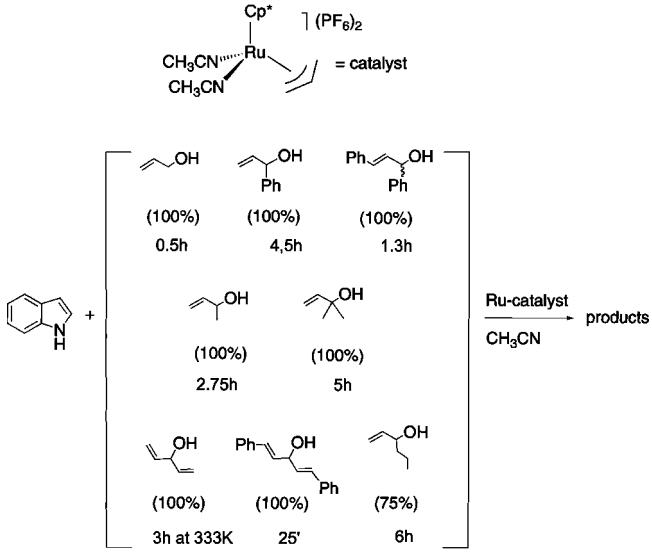
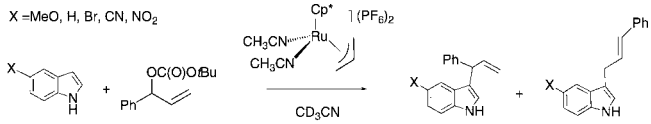
Scheme 1



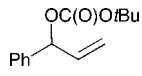
Scheme 2



X	t (in hours)	b/l ratio
MeO	0.67	3.4:1
H	3	2.6:1
Br	20	2:1
CN	19	2.1:1
NO_2	48	0.8:1
5-MeO	3	2.1:1

allyl alcohol, the N-allylation (rather than the C-allylation) is clearly much slower.

For comparison with the allyl alcohols, we have carried out related reactions for several substituted indole compounds using the allyl carbonates **8** and show these results in Scheme 2. Apart

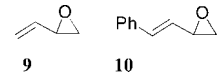


8

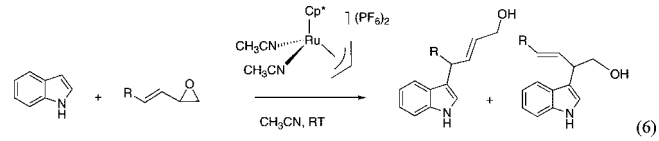
from the expected (and previously reported[15a] for allyl alcohol) marked decrease in the reaction rate with increasing electron-withdrawing capability of the substituent X, there is not much advantage[27] in using (and thus wasting) the carbonate leaving group. For X = MeO, the b/l ratio can be improved to 4.2:1 by carrying out the reaction at 273 K; however, the reaction now requires 17 h for complete conversion.

We have also conducted preliminary experiments using the vinyl epoxides **9** and **10** as substrates for the alkylation of indole. The conversion to products using **9** is complete in ca. 40 min, whereas with **10**, the reaction is complete in ca. 5 min. For both epoxides the branched to linear ratios are on the order of 2:1, and eq 6 (R = H, Ph) shows this chemistry.

(27) For indole substrates with electron-withdrawing groups, the use of carbonates affords product, albeit slowly, whereas the alcohols do not work well.



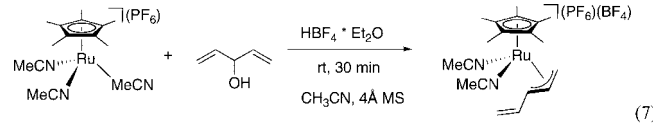
9 **10**



(6)

Preparative Organometallic Chemistry. It is usually assumed that the allyl substrate is converted into a Ru(allyl) intermediate, which is then attacked by a nucleophile. However, relatively little is known about the structure, stability, and dynamics of these Ru(IV) species (a) when they are subjected to acidic conditions and (b) when isomeric allyl complexes can form, for example, in the chemistry of $CH_2{=}CH(OH)CH{=}CH_2$. Given the exclusively linear, rather than the branched, product which develops with this alcohol as substrate, we considered it useful to study its ruthenium organometallic chemistry.

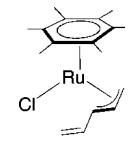
Consequently, we have allowed 1 equiv of this dienol to react with 1 equiv of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ in the presence of a strong acid and show this chemistry in eq 7. We assign the



(7)

11

structure of the isolated product to **11**, an η^3-vinyl-allyl dication, and this type of C_5 organometallic Ru species has been reported previously by Stryker and co-workers;[28] however, all of these results refer to neutral Ru^{II}(arene) compounds, e.g., **12**, whereas



12[26]

our salts contain Ru(IV). The allyl isomer with the central allyl proton remote from the Cp* is thought to be the most stable,[29] and on the basis of NOE data, this is what we observe. The ^1H NMR spectrum of **11** reveals seven nonequivalent protons in the organometallic fragment, three of which appear in the region of a noncoodinated double bond. The ^{13}C spectrum clearly reveals these two double-bond carbons at the expected high frequency as well as the two terminal allyl resonances at lower frequency. A related crystalline product can be obtained by oxidative addition of 1,4-pentadien-3-yl acetate, to afford the Ru(IV) acetate complex **13** in almost quantitative yield (see eq 8).

Two products are observed from the reaction of 5-bromo-1,3-pentadiene with $[Ru(Cp^*)(CH_3CN)_3](PF_6)$, and this chemistry is shown in Scheme 3. A few crystals of the orange-red *minor* component **14** could be isolated and were suitable for diffusion studies.

X-ray Crystallography. Crystals of complexes **13** and **14** suitable for X-ray diffraction were obtained from ether/dichlo-

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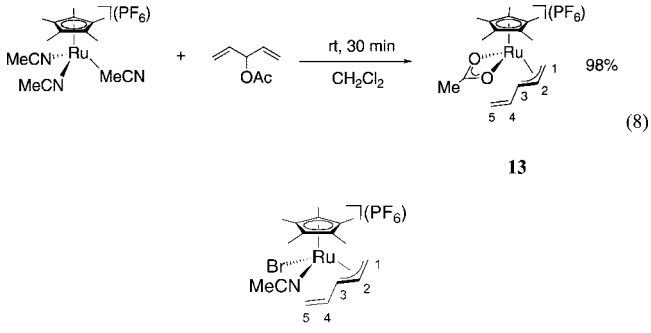


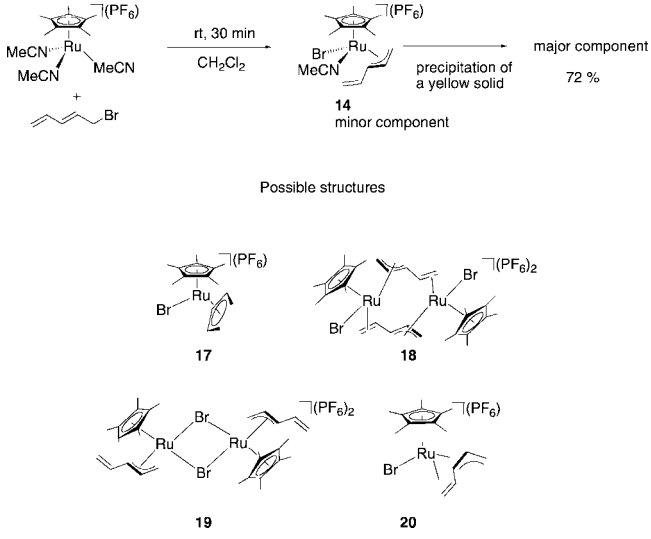
romethane solutions. Figures 1 and 2 show views of the two cations, and the captions give a selection of bond lengths and bond angles. Both species contain a Ru atom complexed to a Cp* and the η^3-vinyl-allyl ligand. Salt **13** contains a κ^2 bidentate acetate ligand, whereas in **14** a bromide and an acetonitrile complete the coordination sphere. As noted above, in both structures the allyl ligand has the central allyl proton remote from the Cp*.

Table 1 shows the three Ru−C(allyl) distances for **13** and **14** plus the analogous data from two literature salts, carbonate **15**[14] and the chloro analogue of **14**, salt **16**.[20] Whereas the C1 and C2 bond lengths do not vary drastically within this series, the separations for C3 vary quite markedly. The long 2.351(2) Å distance has been discussed previously,[14,20] and we assume that the smaller value of 2.299(4) Å for **14** reflects the difference in size between the vinyl and phenyl substituents. A similar decrease in the length of Ru−C3 is observed on going from **15** to **13**. Clearly, the distortions in allyl bonding for the vinyl-allyl salts are not quite so marked as in those for related $Ru^{IV}(\eta^3$-$PhCHCHCH_2)$ complexes. Assuming that such a distortion favors attack at the branched carbon, these results partly rationalize the observation that the allyl intermediate from $CH_2{=}CHCH(OH)CH{=}CH_2$ affords only linear products.

In both **13** and **14** there is a considerable spread in the Ru−C(Cp*) separations, ca. 2.18−2.27 Å; however, these are not unusual bond lengths.[30] The Ru−N(acetonitrile), Ru−Br, and Ru−O(acetate) distances are in keeping with the literature data.[31]

***η*^{5}-C$_5$ Pentadienyl Salts.** The nature of the complex from the major fraction of the chemistry of Scheme 3 was not

Scheme 3



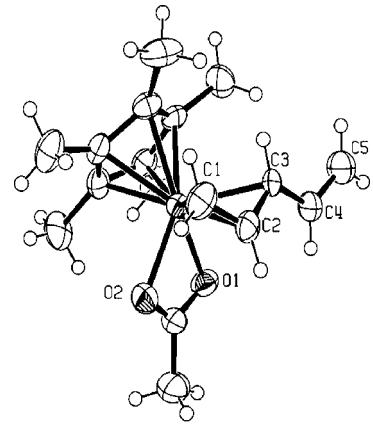


Figure 1. ORTEP view of complex **13** showing the η^3-allyl coordination as well as the bidentate coordination of the acetate ligand. Selected bond lengths (Å) and bond angles (deg): Ru1−C1, 2.195(8); Ru1−C2, 2.123(6); Ru1−C3, 2.260(7); Ru1−O2, 2.139(4); Ru1−O1, 2.147(3); Ru1−C10, 2.205(5); Ru1−C20, 2.243(5); Ru1−C30, 2.236(7); Ru1−C40, 2.223(5); Ru1−C50, 2.183(4); Ru1−C60, 2.511(5); C1−C2, 1.409(12); C2−C3, 1.397(12); C3−C4, 1.500(9); C4−C5, 1.338(9); O2−Ru1−O1, 61.29(19).

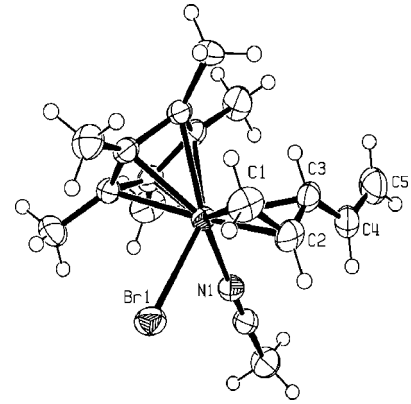


Figure 2. ORTEP view of the cation of salt **14** showing the η^3-allyl coordination as well as the acetonitrile and bromide ligands. Selected bond lengths (Å) and bond angles (deg): Ru1−Br1, 2.5522(5); Ru1−N1, 2.080(3); Ru1−C1, 2.220(4); Ru1−C2, 2.159(4); Ru1−C3, 2.299(4); Ru1−C10, 2.250(3); Ru1−C20, 2.273(3); Ru1−C30, 2.237(3); Ru1−C40, 2.209(3); Ru1−C50, 2.182(3); C1−C2, 1.404(6), C2−C3, 1.404(6); C3−C4, 1.455(6); C4−C5, 1.315(7); N1−Ru1−Br1, 82.45(9); C6−N1−Ru1, 177.2(3).

immediately obvious. We considered the possible structures **17**−**20** indicated in the scheme. The dinuclear species **19**, containing an η^3-vinyl-allyl ligand, was dismissed on the basis of its ^{1}H and ^{13}C NMR properties, since all five carbons (and the seven associated protons) show marked high-frequency shifts. PGSE diffusion studies, which are useful in connection with distinguishing salts and compounds of differing molecular volumes,[32−35] suggest[36] that this unknown is a mononuclear

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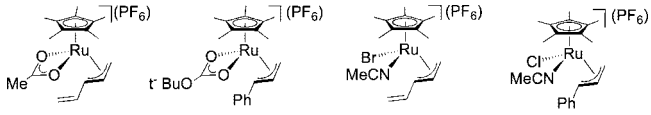
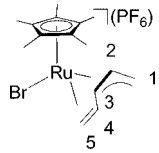
Table 1. Comparison of the Ru−C(allyl) Bond Lengths (Å)



	13	**15**	**14**	**16**
C1	2.195(8)	2.162(5)	2.220(4)	2.192(3)
C2	2.123(6)	2.137(5)	2.159(4)	2.162(3)
C3	2.260(7)	2.303(5)	2.299(4)	2.351(2)

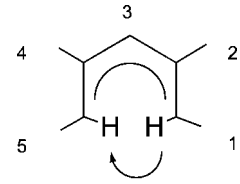
species, thereby eliminating **18** (and **19**). Structure **17**, in which the U-shaped η^5-C_5 pentadienyl is rotated in order to account for the observed lack of symmetry, could eventually be eliminated due to the observed Overhauser effects.

A number of Ru(η^5-pentadienyl) complexes are known from the early studies of Ernst and co-workers,[37] among others;[38] however, these are Ru(II) complexes and do not show an asymmetric arrangement. However, there are several reports[39] on Mo(II) η^5-C_5 S-shaped (rather than U-shaped) pentadienyl species.



20

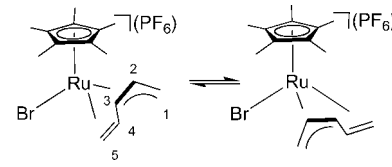
This type of η^5-pentadienyl moiety results when the vinyl group in a U orientation is rotated around the C3−C4 bond and then complexed. The five carbon atoms are not coplanar. Figure 3 shows a slice through the 2-D NOESY spectrum for this species at 243 K, in which the contacts to the Cp* methyl groups are given. In contrast to the observations for **14**, for example, the central allyl proton H2 now reveals a strong cross-peak to the methyl groups. Further, the presence of strong contacts to H1(syn) and H3 and the absence of significant contacts to H1(anti) and H4 confirm that the vinyl group is now in an anti position, relative to H2. Although not shown, the absence of a strong NOE between the two anti protons of the possible U-shaped form, associated with a structure such as **21**, definitively eliminates this possibility. Consequently, we assign



21 not observed

the major component of this reaction to structure **20**, as this proposal fits all of the observed NMR data.

Given structure **20**, it is not surprising that the room-temperature NOESY reveals a selective exchange process (see Figure 4). The observed pairwise exchange of H2 with H4, $H1_{anti}$ with Hb and $H1_{syn}$ with Ha is consistent with the equilibrium (the S-shaped allyl-ene moiety can twist back and forth,



exchanging carbons 1 and 5 and 2 and 4).

Computational Aspects. DFT calculations[40] were performed in order to evaluate the relative stability of the differing structures observed for the two isomers of the cation [Ru(Cp*)-(η^5-C_5H_7)Br]$^+$. We were especially interested in understanding the driving force for the observation of the S- vs the U-shaped conformations of the pentadienyl ligand: that is, molecules with structures **20** and **21**, respectively. The geometries calculated for both isomers are represented in Figure 5.

The calculations indicate that the most stable isomer (by 5.8 kcal/mol) corresponds to the complex with the S-shaped pentadienyl ligand (**20**), in agreement with the conclusions based on the NMR results. In this cation, the pentadienyl ligand adopts an allyl-ene coordination mode with the coordinated C4−C5 double bond making a 55° angle with the plane of the C1−C2−C3 allyl moiety. The C2−H bond is directed toward the Cp* ligand, corroborating the data from the NOESY spectrum.

Despite several attempted initial geometries with an asymmetric coordination of the pentadienyl ligand (such as **17**), the structure obtained for the complex with a U-shaped pentadienyl ligand, **21**, has a symmetric coordination geometry with the central C atom pointing toward the Cp* ligand. In the optimized structure **21**, the pentadienyl ligand presents a planar coordina-

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(36) The diffusion coefficient (D value) and hydrodynamic radius (r_H) for a 2 mmol solution of the acetate complex **13** (D = 12.20, r_H = 5.2 Å) is similar to that found for a 2 mmol solution of **20** (D = 11.80, r_H = 5.3 Å), suggesting that these are both mononuclear complexes. We note that the $r_{X\text{-}ray}$ value for **13**, calculated from the crystallographic data, is ca. 4.9 Å.

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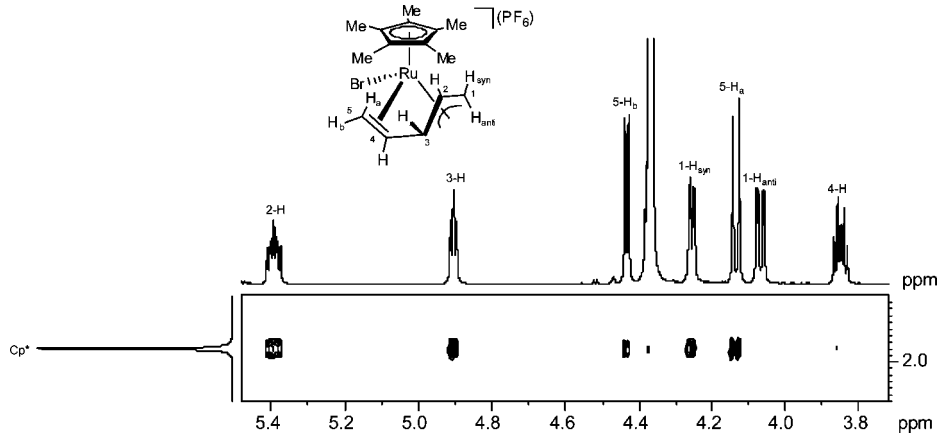

Figure 3. Section of the 2-D NOESY spectrum for salt **20** showing the contacts from the Cp* methyl groups to the various C_5H_7 protons. Note that H4 and $H1_{anti}$ show no and very weak contacts, respectively (243 K, 700 MHz, CD_2Cl_2).

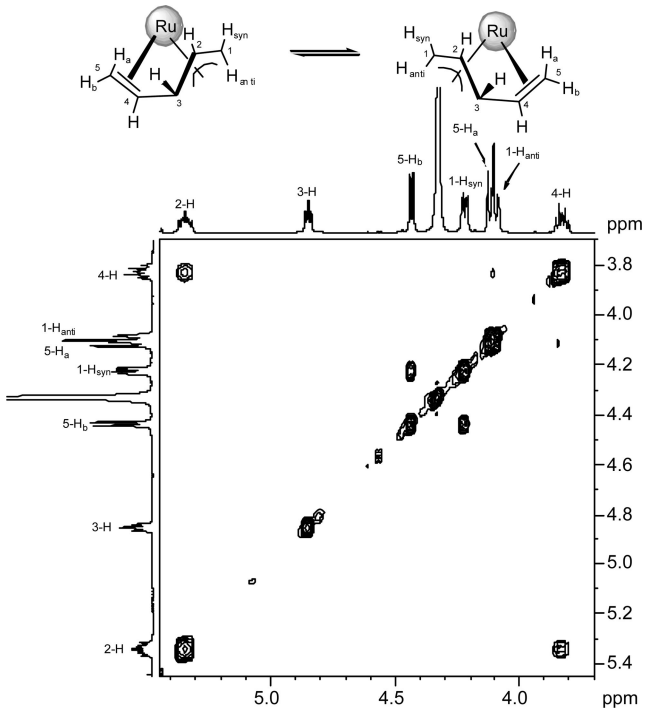

Figure 4. Section of the 2-D NOESY spectrum for salt **20** showing the selective exchange cross-peaks between H2 and H4 as well as between $H1_{syn}$ and $H5_b$. The exchange between $H1_{anti}$ and $H5_a$ is present but is not well-resolved (ambient temperature, 500 MHz, CD_2Cl_2).

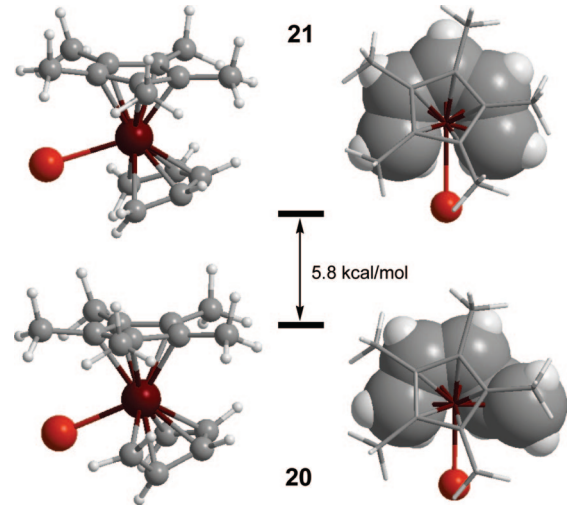

Figure 5. Optimized geometry of $[Ru(Cp^*)(\eta^5\text{-}C_5H_7)Br]^+$ with two conformations of the pentadienyl ligand: (a) the U-shaped ligand (structure **21**, top); (b) the S-shaped ligand (structure **20**, bottom). Side views of the optimized structures are given on the left, and top views of the molecules with space-filling representations of the pentadienyl ligand are given on the right. The energy difference (kcal/mol) is indicated.

tion geometry with the five carbon atoms within bonding distances from the metal (2.21−2.31 Å) and a Ru−C mean distance of 2.26 Å. This value is 0.03 Å longer than the Ru−C(pentadienyl) mean distance in **20**. Although a slightly shorter Ru−C mean distance suggests a stronger coordination of the pentadienyl moiety in complex **20**, no clear electronic reason could be found to explain the stability difference calculated for the two isomers. The metal charge, obtained by means of a natural population analysis (NPA),[41] is within 0.01 in both species,[42] indicating similar electron densities at both metal centers.

From a structural point of view, the main difference between the two isomeric species is the Ru−Br distance, which is considerably longer in complex **21**, 2.59 Å (assuming a symmetric pentadienyl), compared with the isomer **20**, 2.55 Å (with an "S" shaped conformation). In addition, the X_{Cp^*}−Ru−Br angle (X_{Cp^*} being the Cp* ring centroid) is significantly smaller in the case of complex **21**, 109°, than in **20**, 114°. In other words, the Br ligand is somewhat more remote from the pentadienyl fragment in **21**, relative to **20**. When the pentadienyl adopts a symmetric U-shaped arrangement, there is less space left for the Br in the metal coordination sphere, as illustrated by the space-filling representations in Figure 5 and shown by the closest Br−C(pentadienyl) distances in both complexes: 2.99/3.02 Å in **21** and 3.10/3.22 Å in **20**. Taken together, these computational results indicate that the stability difference between both isomers is mainly due to interligand repulsion between the Br and pentadienyl ligands.

Conclusions

The dicationic Ru(IV) salt $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(CH_3CN)_2](PF_6)_2$ is an excellent catalyst for the C-allylation of indole compounds using allyl alcohols as substrates. Addition of an

(42) The calculated Ru NPA charges are 0.23 and 0.24 for the complexes **20** and **21**, respectively.

excess of alcohol results in N,C-double-allylation in good yield. Further, preliminary experiments suggest that selected vinyl epoxides may be used as the allyl source. Stoichiometric oxidative addition reactions of CH_2═$CHCH(OH)CH$═CH_2, CH_2═$CHCH(OAc)CH$═CH_2, or CH_2═$CHCH$═$CHCH_2Br$ with $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ afford new Ru(IV) η^3-vinyl-allyl salts, two of which have been studied by X-ray diffraction methods. In these two salts, the distortions in allyl bonding are not quite so marked as in those for related $Ru^{IV}(\eta^3$-PhCHCHCH$_2)$ complexes. In addition to the Ru(IV) η^3-vinyl-allyl bonding mode, we also find an isomer of **14**, structure **20**, which reveals a dynamic Ru(IV) S-shaped (rather than U-shaped) η^5-pentadienyl moiety. DFT computational results indicate that the S form rather than the U form is the most stable Ru(IV) species and that the stability difference between both isomers is mainly due to interligand repulsion between the Br and pentadienyl ligands.

Experimental Section

General Comments. All air-sensitive manipulations were carried out under a nitrogen atmosphere. All solvents were dried over an appropriate drying agent and then distilled under nitrogen. Deuterated acetonitrile and nitromethane were dried over molecular sieves and stored under nitrogen. Acetone-d_6 and CD_2Cl_2 were distilled over $CaSO_4$ and CaH_2, respectively, and stored under nitrogen. All commercially available starting materials were purchased from commercial sources and used as received. $[Ru(Cp^*)(CH_3CN)_3](PF_6)$,[43] $[Ru(Cp^*)(\eta^3$-$C_3H_5)Cl_2]$,[44] (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-ol,[45] 1,4-pentadien-3-yl acetate,[46] and 5-bromopenta-1,3-diene[47] were synthesized according to known literature procedures. ^{1}H, ^{13}C, and 2D NMR spectra were recorded with Bruker DPX-250, 300, 400, 500, and 700 MHz spectrometers at room temperature. Chemical shifts are given in ppm and referenced to TMS for ^{1}H. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

$[Ru(Cp^*)(\eta^3$-$C_3H_5)(MeCN)_2](PF_6)_2$ (3). Toluene (110 mL) was added to an acetonitrile (110 mL) solution of $[Ru(\eta^3$-$C_3H_5)$-$(Cp^*)Cl_2]$ (0.565 g, 1.62 mmol) and $AgPF_6$ (1.640 g, 6.49 mmol). The reaction mixture was stirred at room temperature for 20 h, after which time the solution was evaporated under vacuum. The resulting residue was dissolved in acetone (5 mL) and filtered through Celite. After evaporation of the solvent the resulting solid was washed with acetone (2 × 5 mL). The filtrate was evaporated under vacuum and the residue washed with water (3 × 5 mL) to remove the remaining $AgPF_6$. After the mixture was dried under vacuum, the crude product was again dissolved in acetone (5 mL), filtered through Celite, evaporated, and dried under vacuum to afford a brown solid (0.990 g, 94%). ^{1}H NMR (400 MHz, acetone-d_6): δ 5.98 (m, 1H, C−$H_{central}$), 4.80 (d, 2H, J = 6 Hz, C−H_{syn}), 3.33 (d, 2H, J = 11 Hz, C−H_{anti}), 2.72 (s, 6H, *Me*CN), 2.02 (s,15H, C_5*Me*$_5$). ^{13}C NMR: δ 135.23 (Me*C*N), 111.7 (C_5Me$_5$), 101.4 ($C_{central}$), 73.6 ($C_{terminal}$), 10.5 (C_5*Me*$_5$), 5.3 (*Me*CN). Anal. Calcd for $C_{17}H_{26}F_{12}N_2P_2Ru$: C, 31.44; H, 4.04; N, 4.31. Found: C, 31.61; H, 3.95; N, 4.12.

$[Ru(OAc)(\eta^3$-$CH_2CHCHCH$═$CH_2)(Cp^*)](PF_6)$ (13). 1,4-Pentadien-3-yl acetate (28.8 μL, 0.228 mmol) was added to a solution of $[Ru(Cp^*)(MeCN)_3](PF_6)$ (0.100 g, 0.198 mmol) in CH_2Cl_2 (8 mL). The resulting reddish solution was stirred at room temperature for 30 min. The solution volume was reduced under vacuum, and hexane was added, precipitating a brown-yellow powder. The solid was washed with hexane (2 × 3 mL) and dried under vacuum to yield a yellow solid (0.105, 98%). A dichloromethane solution of this solid was then layered with diethyl ether and stored at −32 °C, to afford crystals of **13** suitable for X-ray diffraction. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.08 (dt, 1H, J_1 = 17 Hz, J_2 = 10 Hz, C4−*H*), 5.75 (d, 1H, J = 10, C5−H_b), 5.71 (d, 1H, J = 17 Hz, C5−H_a), 5.47 (dt, 1H, J_1 = 10 Hz, J_2 = 6 Hz, C2−*H*), 4.46 (d, 1H, J = 6 Hz, C1−H_{syn}), 4.05 (t, 1H, J = 10 Hz, C3−*H*), 3.01 (d, 1H, J = 10 Hz, C1−H_{anti}), 1.92 (s, 3H, κ^2-O_2C*Me*), 1.55 (s, 15H, C_5*Me*$_5$). ^{13}C NMR: δ 194.5 (κ^2-O_2CMe), 135.6 (*C4*), 124.1 (*C5*), 107.1 (C_5Me$_5$), 103.6 (*C2*), 88.5 (*C3*), 66.7 (*C1*), 25.6 (κ^2-O_2C*Me*), 9.0 (C_5*Me*$_5$). Anal. Calcd for $C_{17}H_{25}O_2F_6PRu$: C, 40.24; H, 4.97. Found: C, 40.19; H, 5.09. HR MALDI-MS: calcd for $[C_{17}H_{25}$-$O_2Ru^+]$ 363.0893, found 363.0893 ($[(M - PF_6)^+]$).

$[Ru(\eta^5$-"S"-$CH_2CHCHCH$═$CH_2)Br(Cp^*)](PF_6)$ (20). 5-Bromopenta-1,3-diene (0.0525 g, 0.357 mmol) was added to a solution of $[Ru(Cp^*)(MeCN)_3](PF_6)$ (0.150 g, 0.297 mmol) in CH_2Cl_2 (8 mL). The resulting red-brown solution was stirred at room temperature for 30 min, after which time the solution was filtered and then slowly concentrated under vacuum. The brown crude solid was washed with hexane (2 × 3 mL) and dissolved in CH_2Cl_2 (9 mL). Addition of hexane (4.5 mL) afforded a yellow precipitate, which was collected by filtration and dried under vacuum to yield a yellow solid (0.113 g, 72%). ^{1}H NMR (CD_3NO_2, 243 K, 700 MHz): δ 5.39 (ddd, 1H, J_1 = 12 Hz, J_2 = 8 Hz, J_3 = 6 Hz, C2−*H*), 4.90 (t, 1H, J = 7 Hz, C3−*H*), 4.43 (d, 1H, J = 7 Hz, C5−H_b), 4.26 (dd, 1H, J_1 = 8 Hz, J_2 = 3 Hz, C1−H_{syn}), 4.13 (d, 1H, J = 12 Hz, C5−H_a), 4.07 (dd, 1H, J_1 = 12 Hz, J_2 = 3 Hz, C1−H_{anti}), 3.86 (dt, 1H, J_1 = 12 Hz, J_2 = 7 Hz, C4−*H*), 1.98 (s, 15H, C_5*Me*$_5$). ^{13}C NMR: δ 109.4 (C_5Me$_5$), 107.4 (*C2*), 100.6 (*C4*), 90.9 (*C3*), 78.0 (*C5*), 68.6 (*C1*), 9.3 (C_5*Me*$_5$). Anal. Calcd for $C_{15}H_{22}BrF_6PRu$: C, 34.10; H, 4.20; Br, 15.13. Found: C, 34.41; H, 4.29; Br, 15.01.

$[Ru(\eta^3$-$CH_2CHCHCH$═$CH_2)(Cp^*)(CH_3CN)_2](BF_4)(PF_6)$ (11). 1,4-Pentadien-3-ol (0.010 g, 0.119 mmol) and $HBF_4 \cdot Et_2O$ (0.016 g, 0.099 mmol) was added to a solution of $[Ru(Cp^*)(MeCN)_3](PF_6)$ (0.050 g, 0.099 mmol) in CH_3CN (6 mL) over 4 Å molecular sieves. The resulting red solution was stirred at room temperature for 30 min, after which time the solution was filtered and then slowly concentrated under vacuum. The crude red solid was washed with Et_2O (2 × 2 mL) and dried under vacuum to afford the mixture (0.050 g, 82%, 2:1 ratio of the Cp* signals) as an orange solid. The major product was identified as **11**. ^{1}H NMR (CD_3CN, 500 MHz): δ 6.39 (dt, 1H, J_1 = 17 Hz, J_2 = 10 Hz, C4−*H*), 6.04 (d, 1H, J = 10 Hz, C5−H_b), 5.99 (d, 1H, J = 17 Hz, C5-H_a), 5.86 (dt, 1H, J_1 = 11 Hz, J_2 = 7 Hz, C2−*H*), 4.54 (d, 1H, J = 7 Hz, C1−H_{syn}), 4.29 (t, 1H, J = 11 Hz, C3−*H*), 2.94 (d, 1H, J = 11 Hz, C1−H_{anti}), 1.75 (s, 15H, C_5*Me*$_5$), MeCN not detectable because of the exchange with CD_3CN. ^{13}C NMR: δ 135.7 (*C4*), 129.1 (*C5*), 108.9 (C_5Me$_5$), 98.6 (*C3*), 97.0 (*C2*), 67.4 (*C1*), 9.1 (C_5*Me*$_5$).

The second component (not completely characterized) was shown to contain an η^5-C_5H_7 fragment with seven protons in the ratio 2:2:2:1 and is reasonably a U-shaped fragment. ^{1}H NMR (CD_3CN, 500 MHz): δ 4.90 (m, 2H, C2−*H*), 4.40 (t, 1H, J = 12, C3−*H*), 4.03 (d, 2H, J = 7 Hz, C1−H_{syn}), 3.13 (d, 2H, J = 16 Hz, C1−H_{anti}), 1.71 (s, 30H, C_5*Me*$_5$), MeCN not detectable because of the exchange with CD_3CN. ^{13}C NMR: δ 129.0 (*C3*), 99.8 (C_5Me$_5$), 61.5 (*C1*), 9.2 (C_5*Me*$_5$), C2 not detectable.

$[Ru(\eta^3$-$CH_2CHCHCH$═$CH_2)Br(Cp^*)(CH_3CN)](PF_6)$ (14). 5-Bromopenta-1,3-diene (0.0525 g, 0.357 mmol) was added to a solution of $[Ru(Cp^*)(MeCN)_3](PF_6)$ (0.150 g, 0.297 mmol) in CH_2Cl_2 (8 mL). The resulting red-brown solution was stirred at room temperature for 30 min, after which time the solution was filtered and then slowly concentrated under vacuum. The brown crude solid was washed with hexane (2 × 3 mL) and dissolved in CH_2Cl_2 (9 mL). Addition of hexane (4.5 mL) afforded a yellow

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precipitate, which was collected by filtration. The filtrate was evaporated, and the remaining brown solid was dissolved in CH_2Cl_2 and layered with Et_2O at −32 °C to get crystals suitable for X-ray diffraction. ^{1}H NMR ($MeNO_2$-d_3, 300 MHz): δ 6.27 (dt, 1H, J_1 = 17 Hz, J_2 = 10 Hz, C4−*H*), 5.79 (d, 1H, J = 17 Hz, C5−H_a), 5.82 (d, 1H, J = 10 Hz, C5−H_b), 5.43 (dt, 1H, J_1 = 10 Hz, J_2 = 6 Hz, C2−*H*), 4.54 (d, 1H, J = 6 Hz, C5−H_{syn}), 3.82 (t, 1H, J = 10 Hz, C3−H_i), 2.56−2.54 (m, 4H, *Me*CN and C1−H_{anti}), 1.73 (s, 15H, C_5*Me*$_5$). ^{13}C NMR: δ, 136.2 (*C4*), 124.3 (*C5*), 106.1 (C_5Me$_5$), 95.8 (*C2*), 87.4 (*C3*), 65.8 (*C1*), 8.3 (C_5*Me*$_5$), 3.1 (*Me*CN), $C_{nitrile}$ not detectable. If one redissolves the crystals of **14**, a mixture of **14** and **20** is obtained.

Typical Procedure for NMR-Monitored Allylation of Indoles. Indole (0.07 mmol) was added to a CD_3CN (0.5 mL) solution of allylic alcohol (0.07 mmol) and [Ru(η^3-C_3H_5)(Cp*)(MeCN)$_2$](PF$_6$)$_2$ (**3**); 0.0023 g, 0.035 mmol) in an oven-dried NMR tube, and the mixture was monitored at ambient temperature. The 1,3-diphenyl allyl indole compounds have been described by Cheung et al.,[48] the alkyl allyl indole derivatives by Kimura et al.,[21b] and the isomeric monophenyl allyl compounds by Westermaier and Mayr.[49]

3-(But-3-en-2-yl)-1*H*-indole and (*E*)-3-(But-2-enyl)-1*H*-indole. Full conversion of but-3-en-2-ol in its reaction with indole was achieved after 1.75 h; l/b ratio = 1:1. 3-(But-3-en-2-yl)-1*H*-indole: ^{1}H NMR (CD_3CN, 250 MHz) δ 3.84−3.72 (m, 1H). (*E*)-3-(but-2-enyl)-1*H*-indole: ^{1}H NMR (CD_3CN, 250 MHz) δ 3.45 (d, 2H, J = 6 Hz).

3-(Hex-1-en-3-yl)-1*H*-indole and (*E*)-3-(Hex-2-enyl)-1*H*-indole. Full conversion of hex-1-en-3-ol in its reaction with indole was achieved after 6 h; l/b ratio = 1:0.43. 3-(Hex-1-en-3-yl)-1*H*-indole: ^{1}H NMR (CD_3CN, 300 MHz) δ 3.64−3.57 (m, 1H). (*E*)-3-(Hex-2-enyl)-1*H*-indole: ^{1}H NMR (CD_3CN, 300 MHz) δ 3.45 (d, 2H, J = 6 Hz).

Typical Preparative Procedure for 3-Allylation of Indoles. Indole (1 mmol) was added to an acetonitrile (5 mL) solution of allylic alcohol (1 mmol) and [Ru(η^3-C_3H_5)(Cp*)-(MeCN)$_2$](PF$_6$)$_2$ (**3**; 0.0325 g, 0.05 mmol). After it was stirred at room temperature, the reaction mixture was evaporated at 40 °C under vacuum and separated by column chromatography on SiO_2.

3-((2*E*,4*E*)-1,5-Diphenylpenta-2,4-dienyl)-1*H*-indole: hexane/DCM = 1:1; 85% yield, very viscous oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (br s, 1H), 7.49 (d, 1H, J = 8 Hz), 7.44−7.23 (m, 12H), 7.11 (t, 1H, J = 8 Hz), 6.93 (s, 1H), 6.92 (dd, 1H, J_1 = 12 Hz, J_2 = 14 Hz), 6.51 (d, 1H, J = 16 Hz), 6.41 (dd, 1H, J_1 = 7 Hz, J_2 = 16 Hz), 6.31 (dd, 1H, J_1 = 11 Hz, J_2 = 15 Hz), 5.13 (d, 1H, J = 8 Hz); ^{13}C NMR δ 143.7, 137.8, 137.3, 137.0, 131.7, 131.5, 129.3, 128.91, 128.86, 128.80, 128.76, 127.6, 126.7, 126.6, 122.9, 122.5, 120.2, 119.8, 199.0, 111.4, 46.4; HR EI-MS *m*/*z* calcd for [$C_{25}H_{21}N^{\bullet+}$] 335.1669, found 335.1667.

(*E*)-3-(Penta-2,4-dienyl)-1*H*-indole: pentane/DCM = 10:1; 45% yield, viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95 (br s, 1H), 7.61 (d, 1H, J = 8 Hz), 7.38 (d, 1H, J = 8 Hz), 7.22 (t, 1H, J = 7 Hz), 7.16 (t, 1H, J = 8 Hz), 7.01 (s, 1H), 6.47−6.34 (m, 1H), 6.28−6.20 (m, 1H), 6.05−5.95 (m, 1H), 5.13 (d, 1H, J = 17 Hz), 5.00 (d, 1H, J = 10 Hz), 3.59 (d, 2H, J = 7 Hz); ^{13}C NMR δ 137.1, 136.4, 133.5, 131.6, 127.4, 122.1, 121.7, 119.3, 119.1, 115.3, 114.5, 111.1, 28.5; HR EI-MS *m*/*z* calcd for [$C_{13}H_{13}N^{\bullet+}$] 183.1043, found 183.1037.

3-(1-Phenylallyl)-1*H*-indole and 3-cinnamyl-1*H*-indole: pentane/DCM, gradient from 10:1 to 2:1; 64 and 26% yields, respectively.

3-(1-Phenylallyl)-1*H*-indole: transparent oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (br s, 1H), 7.56 (d, 1H, J = 8 Hz), 7.44−7.34 (m, 6H), 7.31 (t, 1H, J = 8 Hz), 7.18 (t, 1H, 8 Hz), 6.91 (s, 1H), 6.50 (m, 1H), 5.35 (d, 1H, J = 10 Hz), 5.23 (d, 1H, J = 18 Hz), 5.11 (d, 1H, J = 7 Hz); ^{13}C NMR δ 143.5, 140.8, 136.9, 128.73, 128.65, 127.1, 126.6, 122.8, 122.3, 120.1, 119.6, 118.7, 115.8, 111.4, 47.3.

3-Cinnamyl-1*H*-indole: solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (br s, 1H), 7.68 (d, 1H, J = 8 Hz), 7.41−7.13 (m, 8H), 7.06 (s, 1H), 6.61−6.50 (m, 2H), 3.72 (d, 2H, J = 6 Hz); ^{13}C NMR δ 29.1, 111.2, 114.8, 119.3, 119.5, 121.9, 122.2, 126.3, 127.1, 127.6, 128.6, 129.4, 130.6, 136.6, 137.9.

(*E*)-3-(1,3-diphenylallyl)-1*H*-indole: DCM; 91% yield, white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (br s, 1H), 7.48 (d, 1H, J = 8 Hz), 7.42−7.19 (m, 12H), 7.07 (t, 1H, J = 8 Hz), 6.94 (s, 1H), 6.78 (dd, 1H, J_1 = 7 Hz, J_2 = 16 Hz), 6.49 (d, 1H, J = 16 Hz), 5.17 (d, 1H, J = 8 Hz); ^{13}C NMR:143.7, 137.9, 137.0, 132.9, 130.9, 128.83, 128.82, 128.76, 127.5, 127.2, 126.72, 126.67, 122.9, 122.4, 120.2, 119.8, 119.1, 111.4, 46.5.

Mixture of 3-(1,1-dimethylallyl)-1*H*-indole and 3-(3-methylbut-2-enyl)-1*H*-indole: pentane/DCM, gradient from 10:1 to 2:1; 75% yield, mixture ratio 13:1, viscous oil.

3-(1,1-Dimethylallyl)-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (br s, 1H), 7.76 (d, 1H, J = 8 Hz), 7.34 (d, 1H, J = 8 Hz), 7.19 (t, 1H, J = 8 Hz), 7.10 (t, 1H, J = 8 Hz), 6.96 (s, 1H), 6.17 (dd, 1H, J_1 = 10 Hz, J_2 = 17 Hz), 5.11 (d, 1H, J = 17 Hz), 5.06 (d, 1H, J = 10 Hz), 1.55 (s, 6H); ^{13}C NMR δ 147.9, 137.2, 126.1, 124.0, 121.7, 121.5, 120.2, 119.0, 111.3, 110.8, 37.6, 28.2.

3-(3-Methylbut-2-enyl)-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, 1H, J = 9 Hz), 6.89 (s, 1H), 5.43 (t, 1H, J = 8 Hz), 3.47 (d, 2H, J = 7 Hz), 1.79 (s, 6H).

2-(1*H*-Indol-3-yl)but-3-en-1-ol and 4-(1*H*-Indol-3-yl)but-2-en-1-ol: hexane/EE, gradient from 10:1 to 2:1; 34 and 16% yields, respectively.

2-(1*H*-Indol-3-yl)but-3-en-1-ol: viscous oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (br s, 1H), 7.70 (d, 1H, J = 8 Hz), 7.37 (d, 1H, J = 8 Hz), 7.26 (t, 1H, J = 8 Hz), 7.18 (t, 1H, J = 8 Hz), 7.02 (s, 1H), 6.18−6.10 (m, 1H), 5.31 (d, 1H, J = 17 Hz), 5.27 (d, 1H, J = 10 Hz), 4.04−3.87 (m, 3H), 2.02 (br s, 1H); ^{13}C NMR δ 138.3, 136.6, 126.7, 122.3, 121.9, 119.5, 119.4, 116.7, 114.7, 111.5, 65.3, 44.1; HR EI-MS *m*/*z* calcd for [$C_{12}H_{13}NO^{\bullet+}$] 187.0992, found 187.0992.

Table 2. Crystal Data and Structure Refinement Details for 13

empirical formula	$C_{17}H_{25}F_6O_2PRu$
formula wt	507.41
temp	233(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1$
unit cell dimens	
a	9.0768(7) Å
b	8.3752(6) Å
c	13.2634(9) Å
α	90°
β	95.8600(10)°
γ	90°
V	1003.01(13) Å^3
Z	2
calcd density	1.680 Mg m^{-3}
abs coeff	0.924 mm^{-1}
F(000)	512
cryst size	0.40 × 0.34 × 0.05 mm^3
θ range for data collecn	1.54−33.57°
index ranges	$-13 \le h \le 13$, $-12 \le k \le 13$, $-20 \le l \le 20$
no. of rflns collected	7597
no. of indep rflns	3582 (R(int) = 0.0247)
completeness to θ = 33.57°	47.1%
max, min transmissn	0.9552, 0.7088
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3582/1/250
goodness of fit on F^2	1.018
final R indices ($I > 2\sigma(I)$)	R1 = 0.0350, wR2 = 0.0690
R indices (all data)	R1 = 0.0558, wR2 = 0.0744
absolute structure param	−0.06(4)
largest diff peak, hole	0.304, −0.317 e Å^{-3}

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4-(1*H*-Indol-3-yl)but-2-en-1-ol: viscous oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (br s, 1H), 7.62 (d, 1H, J = 8 Hz), 7.38 (d, 1H, J = 8 Hz), 7.22 (t, 1H, J = 8 Hz), 7.14 (t, 1H, J = 8 Hz), 7.00 (s, 1H), 6.00−5.94 (m, 1H), 5.84−5.78 (m, 1H), 4.15 (d, 1H, J = 6 Hz), 3.55 (d, 1H, J = 6 Hz), 1.63 (br s, 1H); ^{13}C NMR δ 136.4, 131.6, 129.7, 127.3, 122.0, 121.6, 119.3, 119.0, 114.4, 111.1, 63.6, 28.2; HR EI-MS m/z calcd for [$C_{12}H_{13}NO^{\bullet+}$] 187.0992, found 187.0991.

(*E*)-4-(1*H*-Indol-3-yl)-4-phenylbut-2-en-1-ol and 4-(1*H*-indol-3-yl)but-2-en-1-ol: hexane/EE, gradient from 10:1 to 2:1; 44 and 24% yields, respectively.

(*E*)-4-(1*H*-Indol-3-yl)-4-phenylbut-2-en-1-ol: viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.03 (br s, 1H), 7.42−7.17 (m, 8H), 7.05 (t, 1H, J = 8 Hz), 6.91 (s, 1H), 5.73 (dt, 1H, J_1 = 15 Hz, J_2 = 6 Hz), 6.26 (dd, 1H, J_1 = 15 Hz, J_2 = 8 Hz), 5.00 (d, 1H, J = 8 Hz), 4.20 (d, 2H, J = 6 Hz), 1.40 (br s, 1H); ^{13}C NMR δ 143.2, 136.7, 134.4, 130.0, 128.4, 128.3, 126.7, 126.4, 122.4, 122.1, 119.7, 119.4, 118.5, 111.1, 63.5, 45.6; HR EI-MS m/z calcd for [$C_{18}H_{17}NO^{\bullet+}$] 263.1305, found 263.1303.

(*E*)-2-(1*H*-indol-3-yl)-4-phenylbut-3-en-1-ol: viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (br s, 1H), 7.71 (d, 1H, J = 8 Hz), 7.43−7.12 (m, 9H), 6.64 (d, 1H, J = 16 Hz), 6.53 (dd, 1H, J_1 = 16 Hz, J_2 = 6 Hz), 4.01−3.99 (m, 3H), 1.70 (br s, 1H); ^{13}C NMR δ 137.5, 136.7, 131.8, 129.8, 128.5, 127.4, 126.6, 126.3, 122.4, 121.8, 119.6, 119.4, 114.9, 111.4, 65.7, 65.7; HR EI-MS m/z calcd for [$C_{18}H_{17}NO^{\bullet+}$] 263.1305, found 263.1305.

Typical Preparative Procedure for 1,3-Diallylation of Indoles. Indole (0.35 mmol) was added to an acetonitrile (2.5 mL) solution of allylic alcohol (1.4 mmol) and [Ru(η^3-C_3H_5)(Cp*)(MeCN)$_2$]-(PF_6)$_2$ (**3**; 0.0114 g, 0.018 mmol). After it was stirred at room temperature, the reaction mixture was evaporated at 40 °C under vacuum and separated by column chromatography on SiO_2.

1,3-Diallyl-1*H*-indole: pentane/DCM = 5:1; 76% yield, transparent liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, 1H, J = 8 Hz), 7.37 (d, 1H, J = 8 Hz), 7.29 (t, 1H, J = 8 Hz), 7.19 (t, 1H, J = 8 Hz), 6.96 (s, 1H), 6.22−6.12 (m, 1H), 6.11−6.01 (m, 1H), 5.28−5.15 (m, 4H), 4.74 (m, 2H), 3.61 (d, 2H, J = 6 Hz); ^{13}C NMR δ 137.7, 136.9, 134.0, 128.4, 125.8, 121.9, 119.6, 119.2, 117.4, 115.4, 113.7, 109.8, 49.0, 30.1; HR EI-MS m/z calcd for [$C_{14}H_{15}N^{\bullet+}$] 197.1199, found 197.1199.

1,3-Diallyl-5-methyl-1*H*-indole: DCM; 86% yield, yellowish liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39 (s, 1H), 7.20 (d, 1H, J = 8 Hz), 7.05 (d, 1H, J = 8 Hz), 6.87 (s, 1H), 6.16−5.93 (m, 2H), 5.21−5.07 (m, 4H), 4.67 (d, 2H, J = 5 Hz), 3.51 (d, 2H, J = 6 Hz), 2.48 (s, 3H); ^{13}C NMR δ 137.9, 135.4, 134.1, 128.6, 128.4, 125.9, 123.5, 119.2, 117.3, 115.3, 113.1, 109.6, 49.0, 30.1, 21.8; HR EI-MS m/z calcd for [$C_{15}H_{17}N^{\bullet+}$] 211.1356, found 211.1356.

1,3-Diallyl-5-methoxy-1*H*-indole. DCM; 79% yield, transparent liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24 (d, 1H, J = 9 Hz), 7.10 (s, 1H), 6.94 (d, 1H, J = 8 Hz), 6.92 (s, 1H), 6.20−5.96 (m, 2H), 5.26−5.12 (m, 4H), 4.68 (d, 2H, J = 5 Hz), 3.92 (s, 3H), 3.55 (d, 2H, J = 6 Hz); ^{13}C NMR δ 154.0, 137.7, 134.1, 132.3, 128.6, 126.4, 117.3, 115.3, 113.0, 112.0, 110.6, 101.5, 56.2, 49.1, 30.1; HR EI-MS m/z calcd for [$C_{15}H_{17}NO^{\bullet+}$] 227.1305, found 227.1305.

X-ray Crystallography. Data sets were obtained using a Bruker SMART Platform diffractometer equipped with a CCD detector (graphite-monochromated Mo Kα radiation, λ = 0.7107 Å) at 233 K (**13**) and 223 K (**14**), respectively. The structures were solved by Patterson and direct methods,[50] respectively. The crystallographic data, R values of the full-matrix least-squares refinements,[51] and interatomic distances and angles are given in the Supporting Information. All atoms except hydrogen atoms and atoms of disordered molecules were refined anisotropically. H atoms were placed at calculated positions on the basis of stereochemical considerations and refined according to the riding model. The relevant experimental parameters for **13** and **14** are given in Tables 2 and 3, respectively.

Table 3. Crystal Data and Structure Refinement Details for 14

empirical formula	$C_{20.60}H_{25}BrF_6NPRu$
formula wt	612.51
temp	223(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a	8.2925(10) Å
b	15.354(2) Å
c	17.775(2) Å
α	90°
β	94.660(10)°
γ	90°
V	2255.8(5) Å^3
Z	4
calcd density	1.804 Mg m^{-3}
abs coeff	2.594 mm^{-1}
F(000)	1214
cryst size	0.44 × 0.30 × 0.25 mm^3
θ range for data collecn	1.76−33.75°
Iindex ranges	$-12 \le h \le 12$, $-23 \le k \le 22$, $-26 \le l \le 27$
no. of rflns collected	33 139
no. of indep rflns	8250 (R(int) = 0.0335)
completeness to θ = 33.75°	91.4%
max, min transmissn	0.5632, 0.3948
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	8250/0/267
goodness of fit on F^2	1.023
final R indices ($I > 2\sigma(I)$)	R1 = 0.0467, wR2 = 0.1190
R indices (all data)	R1 = 0.0753, wR2 = 0.1346
largest diff peak, hole	1.479 and −0.972 e Å^{-3}

Computational Details. The calculations were performed using the Gaussian 03 software package,[52] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25% mixture of Hartree−Fock[53] exchange with DFT[40] exchange correlation, given by the Perdew, Burke, and Ernzerhof functional (PBE).[54] The optimized geometries were obtained with the LanL2DZ basis set[55] augmented with an f-polarization function[56] for Ru, the same basis set augmented with a d-polarization function[57] for Br, and a standard 6-31G(d,p) basis set[58] for the remaining elements (basis b1). Frequency calculations were performed, yielding no imaginary frequency modes and confirming the nature of the stationary points

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as minima. Atomic charges were obtained using natural population analysis (NPA).[41]

The energy difference reported was obtained from single-point energy calculations using a VTZP basis set (basis b2) and the geometries optimized at the PBE1PBE/b1 level. Basis b2 consisted of a Stuttgart/Dresden ECP with valence triple-ζ (SDD)[59] for Ru and Br with added f-[56] and d-polarization functions,[57] respectively, and standard 6-311++G(d,p)[60] for the remaining elements (C and H). Solvent (dichloromethane) effects were considered in the PBE1PBE/b2//PBE1PBE/b1 energy calculations using the polarizable continuum model (PCM) initially devised by Tomasi and coworkers[61] as implemented in Gaussian 03,[62] and thus, the calculated energy difference can be taken as free energy.[63] The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level.

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Supporting Information Available: Tables of atomic coordinates for the DFT calculations and CIF files giving structural data for **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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