C−N and C−C Coupling Reactions: Preparation of New N-Heterocyclic Ruthenium Derivatives

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Three novel types of complexes containing heterocyclic ligands are prepared by condensation of the allenylidene ligand of [Ru(η^5-C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4 (**1**) with propargylamines. Complex **1** reacts with propargylamine to give initially [Ru(η^5-C_5H_5)-{C(CH=CPh_2)=NHCH_2C≡CH}(CO)(P^iPr_3)]BF_4 (**2**). Treatment of **2** with KOH in methanol affords the bicyclic derivative Ru(η^5-C_5H_5){4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]-hex-2-en-1-yl}(CO)(P^iPr_3) (**3**). The formation of **3** takes place via the intermediate Ru(η^5-C_5H_5){C(CH=CPh_2)=NCH_2C≡CH}(CO)(P^iPr_3) (**4**), which is isolated when the deprotonation of **2** is carried out in tetrahydrofuran as solvent. In contrast to propargylamine, the addition of 1,1-diethylpropargylamine to **1** leads to the dihydropyridiniumyl derivative [Ru(η^5-C_5H_5)-{2,2-diethyl-5-diphenylidene-2,5-dihydropyridinium-6-yl)(CO)(P^iPr_3)]BF_4 (**5**) in a one-pot synthesis. Complex **1** also reacts with *N*-methylpropargylamine. The reaction affords [Ru-(η^5-C_5H_5){C(CH=CPh_2)=N(CH_3)CH_2C≡CH}(CO)(P^iPr_3)]BF_4 (**6**). Treatment of **6** with sodium methoxide, at −78 °C, gives a 1:1 mixture of the dihydronaphthopyrrolyl diastereomers ($R_{Ru}S_C$,$S_{Ru}R_C$)-[Ru(η^5-C_5H_5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}](CO)(P^iPr_3) (**7a**) and ($R_{Ru}R_C$,$S_{Ru}S_C$)-[Ru(η^5-C_5H_5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}](CO)(P^iPr_3) (**7b**). Complexes **3** and **5** and the enantiomeric mixture **7a** have been characterized by X-ray diffraction analysis.

Introduction

Today it is rare to find a complete total synthesis that does not use a transition-metal-based reaction. In this respect, carbene complexes are one of the most useful tools.[1]

The chemistry of allenylidene compounds L_nM=C=C=CR_2, which belong to the series of unsaturated carbene derivatives L_nM=C(=C)$_n$=CR_2 ($n > 0$), has been much less studied than that of the carbene complexes. However, recent research indicates that their potential can become greater.[2] The preparation of transition-metal allenylidenes is very easy,[3] and the presence of three reactive centers (unsaturated C_3 chain) or more (unsaturated chain plus substituents) in the η^1-carbon ligand allows one to build, in one or two steps, organic skeletons (naphthofuranyl,[4] pyrazolopyrazolyl,[5] azetidine, hexahydroquinoline,[6] pyridopyridinyl, thiazinyl,[7] etc), which require multistep procedures in conventional organic synthesis.

The coordination of the π-acidic carbonyl group to the metallic fragment containing the allenylidene ligand enhances the reactivity associated with the allenylidene spine.[8] Thus, as a part of our work in the chemistry of allenylidene complexes of platinum-group metals,[4−7,8a,b,d,9] we have recently reported that the C_α−C_β double bond of the diphenylallenylidene ligand of the complex [Ru-(η^5-C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4 adds the N−H

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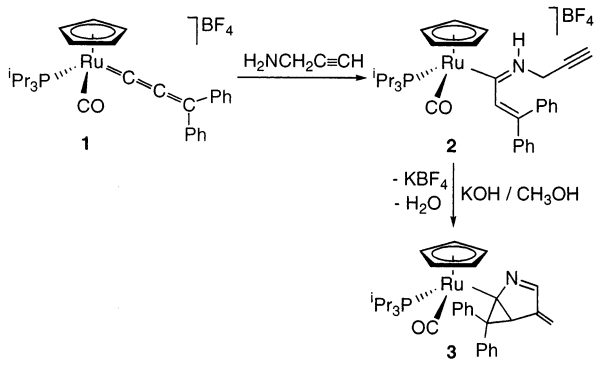
Scheme 1



bonds of primary and secondary amines to give secondary, $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N(R)H\}(CO)(P^iPr_3)]BF_4$ (R = ^{n}Pr, Ph), and tertiary, $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NR_2\}(CO)(P^iPr_3)]BF_4$ (NR_2 = NEt_2, $NCH_2(CH_2)_3CH_2$), azoniabutadienyl derivatives. In the presence of bases there is a marked difference in behavior between them. Treatment of $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N(R)H\}(CO)(P^iPr_3)]BF_4$ with sodium methoxide results in the deprotonation of the nitrogen atom and the formation of the corresponding azabutadienyl derivatives $Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NR\}(CO)(P^iPr_3)$. Under the same conditions, the deprotonation of $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NR_2\}(CO)(P^iPr_3)]BF_4$ occurs at the $CH{=}CPh_2$ group and, as a consequence, the aminoallenyl compounds $Ru(\eta^5\text{-}C_5H_5)\{C(NR_2){=}C{=}CPh_2\}(CO)(P^iPr_3)$ are formed.[10]

The hydroamination of unsaturated organic molecules in the presence of transition-metal complexes is an attractive route to prepare numerous classes of organonitrogen molecules.[11] In an effort to develop new methods of synthesis of organometallic compounds containing new types of organic nitrogen ligands, we have studied the reactivity of the allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(=C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ toward primary and secondary propargylamines.

In this paper, we report the discovery of novel reaction patterns in the chemistry of the transition-metal−allenylidene complexes and three novel types of organometallic compounds with the nitrogen-heterocyclic ligands 2-azabicyclo[3.1.0]hex-2-enyl, dihydropyridiniumyl, and dihydronaphthopyrrolyl.

Results and Discussion

1. Reaction of $[Ru(\eta^5\text{-}C_5H_5)(=C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ with Propargylamine: Formation of $Ru(\eta^5\text{-}C_5H_5)$\{4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]hex-2-en-1-yl\}$(CO)(P^iPr_3)$. Similarly to propylamine and aniline, one of the N−H bonds of propargylamine is added to the $C_\alpha{-}C_\beta$ double bond of the allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**). Thus, at room temperature, the addition of 1.1 equiv of the amine to the dichloromethane solutions of **1** leads to the secondary azoniabutadienyl derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NHCH_2C{\equiv}CH)\}(CO)(P^iPr_3)]BF_4$ (**2**). Treatment at room temperature of **2** with KOH in methanol produces its deprotonation and the formation of the bicyclic complex $Ru(\eta^5\text{-}C_5H_5)$\{4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]hex-2-en-1-yl\}$(CO)(P^iPr_3)$ (**3**) as a result of a double C−C coupling, the C_α and C_γ atoms of the allenylidene of **1** and the C_β atom of the allenylidene with the C_β atom of the propargylamine (Scheme 1).

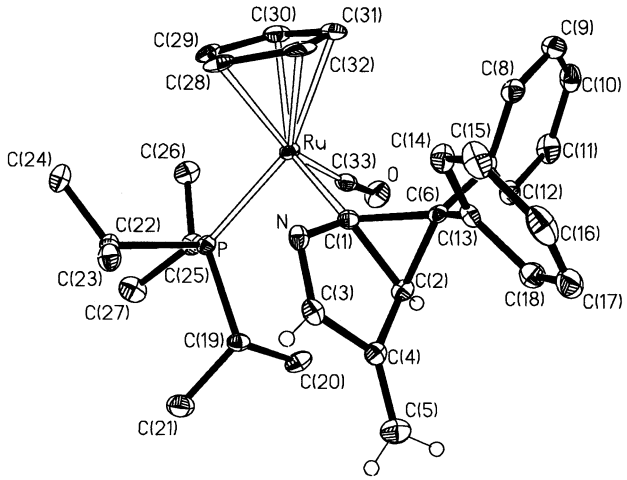


Figure 1. Molecular diagram for the complex $Ru(\eta^5\text{-}C_5H_5)$\{4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]hex-2-en-1-yl\}$(CO)(P^iPr_3)$ (**3**). Thermal ellipsoids are shown at the 50% probability level.

Complex **2** was isolated as a yellow solid in 94% yield. Its spectroscopic data strongly support the formation of the secondary azoniabutadienyl ligand. The IR spectrum in Nujol shows a ν(NH) band at 3361 cm^{-1}, along with ν(≡CH), ν(C≡C), and ν(C=N) absorptions at 3256, 2120, and 1598 cm^{-1}, respectively. In the ^{1}H NMR spectrum in chloroform-*d*, the =NH resonance is observed at 9.83 ppm as a broad signal, whereas the =CH resonance appears at 6.67 ppm as a singlet. The propargylic unit gives rise to two double doublets of doublets at 4.55 and 4.42 (CH_2) ppm and a double doublet at 2.37 (CH) ppm with H−H coupling constants of 16.8 (^2J), 4.8 (^3J), and 2.1 Hz (^4J). In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C=N carbon atom appears at 247.9 ppm as a doublet with a C−P coupling constant of 10.5 Hz, whereas the $=CPh_2$ and =CH resonances are observed at 142.5 and 133.3 ppm as singlets. The propargylic carbon atoms display singlets at 75.8 (C≡), 74.0 (≡CH), and 40.1 ppm (CH_2). The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 62.4 ppm. These spectroscopic data agree with those previously reported for the complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N(R)H\}(CO)(P^iPr_3)]BF_4$ (R = ^{n}Pr, Ph).[10]

Complex **3** was isolated as a yellow solid in 51% yield. Figure 1 shows a view of the molecular geometry of this compound. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, the carbonyl, and the η^1-carbon ligand are all close to 90°. The bicycle contains an exocyclic C−C double bond (C(4)−C(5) = 1.319(3) Å), and its skeleton can be described as a cyclopropane fused with a 1-pyrroline (N−C(3) = 1.273(3) Å). The five-membered cycle is almost planar and forms a dihedral angle of 71.92(13)° with the three-membered ring. The

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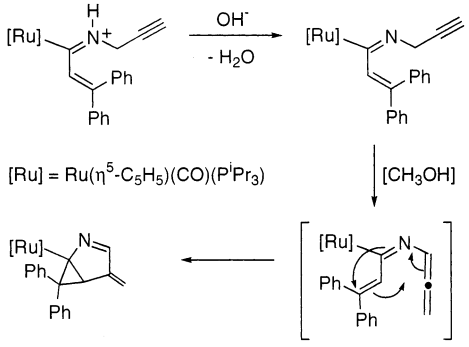
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ru(η^5-C_5H_5){4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]hex-2-en-1-yl}(CO)-(P^iPr_3) (3)

Ru−P	2.3283(6)	N−C(1)	1.470(3)
Ru−C(1)	2.118(2)	N−C(3)	1.273(3)
Ru−C(28)	2.260(2)	C(1)−C(2)	1.530(3)
Ru−C(29)	2.266(2)	C(1)−C(6)	1.551(3)
Ru−C(30)	2.267(2)	C(2)−C(6)	1.532(3)
Ru−C(31)	2.252(2)	C(2)−C(4)	1.477(3)
Ru−C(32)	2.251(2)	C(3)−C(4)	1.473(3)
Ru−C(33)	1.828(2)	C(4)−C(5)	1.319(3)
M[a]−Ru−P	127.95(7)	N−C(1)−C(6)	109.63(17)
M−Ru−C(1)	118.57(9)	N−C(3)−C(4)	115.8(2)
M−Ru−C(33)	124.75(10)	C(1)−N−C(3)	109.16(18)
P−Ru−C(1)	93.55(6)	C(1)−C(2)−C(6)	60.84(14)
P−Ru−C(33)	88.14(7)	C(1)−C(6)−C(2)	59.52(14)
C(1)−Ru-C(33)	94.84(9)	C(2)−C(1)−C(6)	59.64(14)
Ru−C(1)−N	112.34(14)	C(2)−C(4)−C(3)	103.30(18)
Ru−C(1)−C(2)	132.15(15)	C(2)−C(4)−C(5)	130.2(2)
Ru−C(1)−C(6)	127.36(14)	C(3)−C(4)−C(5)	126.4(2)
N−C(1)−C(2)	105.30(17)		

[a] M represents the midpoint of the C(28)−C(32) Cp ligand.

Scheme 2

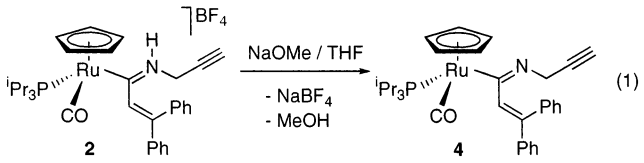


bicycle is bonded to the ruthenium by a single bond through one of the ring junction carbon atoms (Ru−C(1) = 2.118(2) Å).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** are consistent with the formation of the bicycle. In the ^{1}H NMR spectrum in benzene-d_6, the resonances corresponding to the vinylic proton of the pyrroline unit, the protons of the exocyclic CH_2 group, and the proton bonded to the ring junction C(2) atom are observed as singlets at 6.80, 5.20 and 4.91, and 3.14 ppm, respectively. In the ^{13}C{^{1}H} NMR spectrum, the Ru−C carbon atom gives rise to a doublet at 62.8 ppm with a C−P coupling constant of 10.1 Hz. The C(2), C(3), C(4), C(5), and C(6) atoms of the bicycle display singlets at 42.7, 157.8, 156.5, 108.5, and 57.8 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 64.5 ppm.

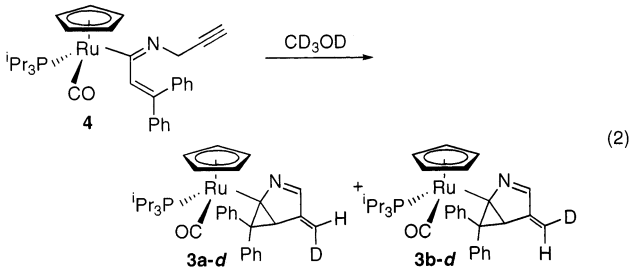
The formation of the bicycle from the unsaturated η^1-carbon donor ligand of **2** is a three-elemental-step reaction involving: (i) deprotonation of the nitrogen atom, (ii) propargylic to allenic isomerization catalyzed by the solvent (methanol), and (iii) double intramolecular C−C coupling (Scheme 2).

In agreement with this proposal, we have observed that the treatment at room temperature of **2** with sodium methoxide in tetrahydrofuran affords Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NCH$_2$C≡CH)}(CO)(P^iPr_3) (**4**), as a result of the deprotonation of the nitrogen atom of **2** (eq 1), and that in methanol at room temperature complex **4** isomerizes into **3** in quantitative yield after 4 h.



Complex **4** was isolated as a white solid in 75% yield. In the ^{1}H NMR spectrum of this compound in dichloromethane-d_2, the most noticeable feature is the absence of any NH resonance. The presence of a propargylic unit is strongly supported by the CH_2 and ≡CH resonances, which are observed as an AB spin system (δ 4.26, $\Delta\nu$ = 33.2 Hz, J_{A-B} = 16.5 Hz) and a singlet (δ 2.26), respectively. The =CH resonance appears at 6.63 ppm, as a singlet. In the ^{13}C{^{1}H} NMR spectrum, the propargylic unit displays three singlets at 83.0 (C≡), 70.6 (≡CH), and 45.8 (CH_2) ppm, whereas the Ru−C carbon atom gives rise to a doublet at 204.2 ppm, with a C−P coupling constant of 12.1 Hz. The resonances corresponding to the =CH and =CPh$_2$ carbon atoms appear as singlets at 140.3 and 133.1 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 66.0 ppm.

The direct participation of methanol in the formation of **3**, catalyzing the propargylic-allenic isomerization is strongly supported by the formation of a 1:1 isomeric mixture of **3a-*d*** and **3b-*d*** (eq 2) when complex **4** is stirred in methanol-d_4 over 4 h.



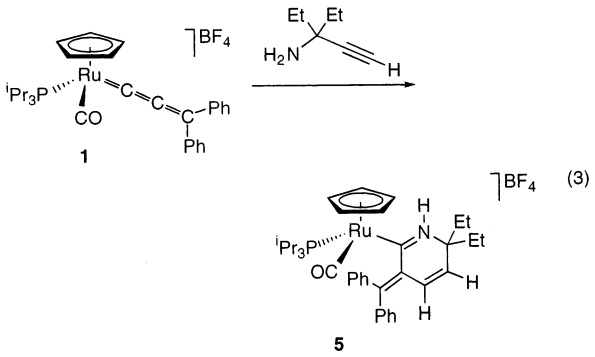
The presence of a deuterium atom at each side of the exocyclic C−C double bond is inferred from the ^{1}H and ^{2}H NMR spectra of the isomeric mixture. The ^{1}H NMR spectrum shows two singlets at 5.20 and 4.90 ppm with a 0.5:0.5 intensity ratio, whereas the ^{2}H NMR spectrum contains two broad singlets at 5.22 and 4.98 ppm.

The deprotonation of **2** and the double intramolecular C−C coupling are the fast steps in the formation of **3**, while the propargylic to allenic rearrangement appears to be the slow step of the reaction. In agreement with this, all attempts to isolate the allenic intermediate were unsuccessful.

In addition, it should be noted that the formation of the three-membered ring of **3** involves a novel intramolecular cyclopropanation, which has no precedent in the allenylidene chemistry. The fact that the propargyl−azabutadienyl derivative **4** is stable in the absence of methanol suggests that the cyclopropanation process is induced by the allenic unit and involves the initial nucleophilic attack of the central carbon atom of the unsaturated Ru−C_3 chain at the central carbon atom of the allenic unit (Scheme 2).

Intermolecular cyclopropanation reactions have received predominant attention in the chemistry of carbene complexes.[12] The intramolecular formation of three-membered rings from vinylidene starting compounds has been also observed. Thus, we note that the addition of $[N^nBu_4]OH$ to cationic vinylidene compounds of the type $[Ru(\eta^5\text{-}C_5H_5)\{=C=C(R)CH_2R'\}(PPh_3)_2]^+$ affords cyclopropenyl derivatives, where, in contrast to **3**, the three-membered ring is unsaturated.[13]

2. Reaction of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ with 1,1-Diethylpropargylamine: Formation of $[Ru(\eta^5\text{-}C_5H_5)$(2,2-diethyl-5-diphenylidene-2,5-dihydropyridinium-6-yl)$(CO)(P^iPr_3)]BF_4$. The propargylic−allenic isomerization involves a 1,3-hydrogen shift within the substituent of the amine. To block this process, we have carried out the reaction of **1** with 1,1-diethylpropargylamine, which does not contain hydrogen atoms in α-positions with regard to the nitrogen atom. Unexpectedly, the treatment at room temperature of **1** with 1.2 equiv of 1,1-diethylpropargylamine in dichloromethane led to the dihydropyridiniumyl derivative $[Ru(\eta^5\text{-}C_5H_5)$(2,2-diethyl-5-diphenylidene-2,5-dihydropyridinium-6-yl)$(CO)(P^iPr_3)]BF_4$ (**5**). This reaction, without precedent in the organometallic chemistry, involves the selective N,C_γ addition of the amine to the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of **1** (eq 3).



Complex **5** was isolated as a yellow solid in 65% yield and characterized by elemental analysis, IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and X-ray diffraction analysis. Figure 2 shows a view of the cation of this compound. Selected bond distances and angles are listed in Table 2.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, the carbonyl, and the heterocycle are all close to 90°.

The heterocycle contains endocyclic N−C(1) (1.313(4) Å) and C(3)−C(4) (1.316 (4) Å) double bonds and a

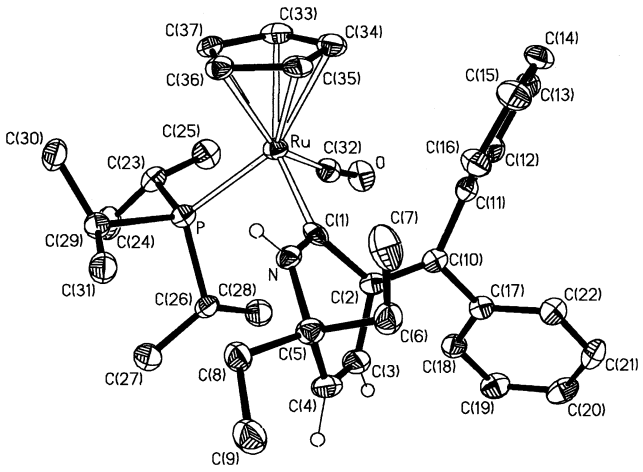


Figure 2. Molecular diagram of the cation of $[Ru(\eta^5\text{-}C_5H_5)$(2,2-diethyl-5-diphenylidene-2,5-dihydropyridinium-6-yl)$(CO)(P^iPr_3)]BF_4$ (**5**). Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ru(\eta^5\text{-}C_5H_5)$(2,2-diethyl-5-diphenylidene-2,5-dihydropiridinium-6-yl)$(CO)(P^iPr_3)]BF_4$ (5)′

Ru−P	2.3560(10)	N−C(1)	1.313(4)
Ru−C(1)	2.033(3)	N−C(5)	1.504(4)
Ru−C(32)	1.829(3)	C(1)−C(2)	1.502(4)
Ru−C(33)	2.250(3)	C(2)−C(3)	1.475(4)
Ru−C(34)	2.234(3)	C(2)−C(10)	1.351(4)
Ru−C(35)	2.230(3)	C(3)−C(4)	1.316(4)
Ru−C(36)	2.262(3)	C(4)−C(5)	1.511(4)
Ru−C(37)	2.261(3)		
M[a]−Ru−P	125.18(10)	N−C(1)−C(2)	111.6(3)
M−Ru−C(1)	124.41(13)	N−C(5)−C(4)	105.8(3)
M−Ru−C(32)	121.65(15)	C(1)−C(2)−C(3)	112.9(3)
P−Ru−C(1)	92.18(9)	C(1)−C(2)−C(10)	123.6(3)
P−Ru−C(32)	91.24(10)	C(2)−C(3)−C(4)	118.6(3)
C(1)−Ru−C(32)	92.89(13)	C(3)−C(4)−C(5)	120.4(3
Ru−C(1)−N	123.2(2)	C(3)−C(2)−C(10)	123.2(3)
Ru−C(1)−C(2)	125.0(2)		

[a] M represents the midpoint of the C(33)−C(37) Cp ligand.

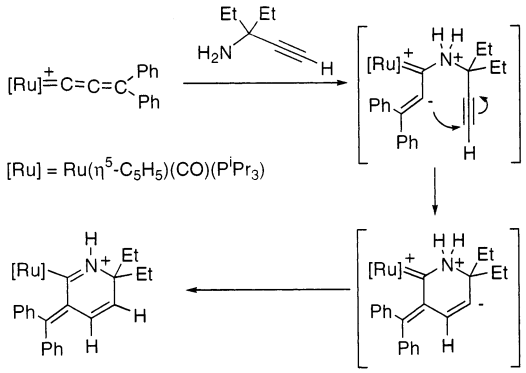
C(2)−C(10) (1.351(4) Å) exocyclic double bond. The latter is disposed in a para position with regard to the disubstituted C(5) carbon atom and in an ortho position with regard to the Ru−C(1) bond (2.033(3) Å), which is in a position α to the nitrogen atom. The N−C(1) bond length compares well with the N−C double-bond length found in $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NEt_2\}(CO)(P^iPr_3)]BF_4$ (1.306(7) Å), Schiff bases, hydrazones, and related compounds.[10] The Ru−C(1) distance lies between those reported for the allenyl derivatives $Ru(\eta^5\text{-}C_5H_5)\{C(C\equiv CPh)=C=CPh_2\}(CO)(P^iPr_3)$ (2.004(5) Å)[8b] and $[Ru(\eta^5\text{-}C_5H_5)\{C(PHPh_2)=C=CPh_2\}(CO)(P^iPr_3)]BF_4$ (2.139(5) Å),[8e] where a Ru−C(sp^2) single bond is proposed to exit.

In agreement with the structure shown in Figure 2, the IR spectrum shows a ν(NH) band at 3323 cm^{-1}. In the ^1H NMR spectrum at room temperature in chloroform-*d*, the NH resonance is observed at 9.61 ppm, as a broad signal. In addition, we should mention two doublets with a H−H coupling constant of 9.6 Hz, at 6.30 and 5.75 ppm, corresponding to the olefinic protons of the endocyclic C(3)−C(4) double bond. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to C(1) appears at 237.4 ppm, as a doublet with a C−P coupling constant of 9.8 Hz, whereas the C(sp^2) atoms C(2), C(3), C(4), and C(10) display singlets at 147.7, 136.4, 131.5, and 142.8

(12) For example: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5. (d) Buchert, M.; Reissig, H.-U. *Chem. Ber.* **1992**, *125*, 2723. (e) Doyle, M. D.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (f) Barluenga, J.; López, S.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **2000**, *122*, 8145. (g) Che, C.-M.; Huang, J.-S.; Lee, F.-W.; Li, Y.; Lai, T.-S.; Kwong, H.-L.; Teng, P.-F.; Lee, W.-S.; Lo, W.-C.; Peng, S.-M.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 4119. (h) Li, Y.; Huang, J.-S.; Zou, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843.

(13) Ting, P. C.; Lin, Y.-C.; Lee, G.-H.; Cheng, M.-C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433.

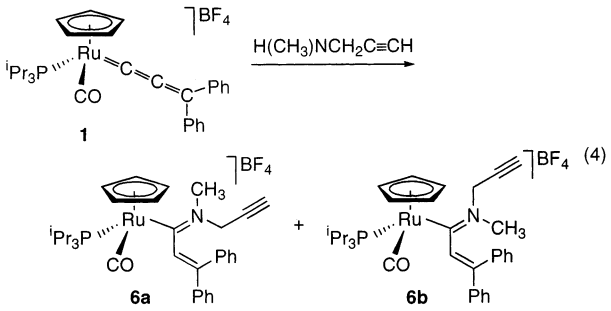
Scheme 3



ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 60.4 ppm.

The formation of **5** can be rationalized according to Scheme 3. Because EHT-MO calculations on transition-metal allenylidene complexes indicate that the C_α and C_β atoms are electrophilic and nucleophilic centers, respectively,[8b,9a,14] it has been proposed that the addition of amines to the allenylidene ligand of **1** requires an initial N−C_α interaction, which labilizes the N−H bond.[10] In accordance with this, the coordination of the nitrogen atom of the amine to the C_α atom of the allenylidene of **1**, followed by the nucleophilic attack of the C_β atom at the terminal carbon atom of the propargylic unit, and the subsequent 1,3-hydrogen shift of one of the NH-hydrogen atoms should give **5**.

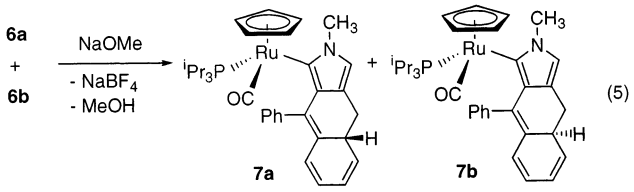
3. Reaction of [Ru(η5-C5H5)(=C=C=CPh2)(CO)(PiPr3)]BF4 with *N*-Methylpropargylamine: Formation of [Ru(η5-C5H5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}(CO)(PiPr3)]BF4. In contrast to 1,1-diethylpropargylamine but in agreement with propargylamine, the N−H bond of *N*-methylpropargylamine is added to the C_α−C_β double bond of the allenylidene ligand of **1**. Thus, at room temperature, the addition of 1.1 equiv of the amine to dichloromethane solutions of **1** affords the tertiary azoniabutadienyl derivative [Ru(η5-C_5H_5){C(CH=Ph_2)=N(CH_3)CH_2C≡CH}(CO)(P^iPr_3)]BF_4 (**6**), which was isolated as a yellow solid in 93% yield. The solid is formed by the isomers **6a** and **6b** shown in eq 4, in a 7:3 molar ratio.



(4)

The formation of both isomeric azoniabutadienyl ligands is strongly supported by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **6** in chloroform-*d* at room temperature. In the ^1H NMR spectrum the HC= resonances appear at 6.70 (**6b**) and 6.60 ppm (**6a**) as singlets, whereas the *N*-methylpropargyl units display a doublet (CH_2, $^4J_{H-H}$ = 2.1 Hz) at 5.01 ppm (**6a** and **6b**), two singlets (CH_3) at 3.80 (**6b**) and 3.72 ppm (**6a**), and a triplet (≡CH) at 2.64 ppm (**6a** and **6b**). In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the Ru−C_α atoms are observed at 244.0 (**6a**) and 243.6 ppm (**6b**), as doublets with C−P coupling constants between 9 and 10 Hz, whereas the =CH and =CPh_2 resonances appear at 138.3 (**6a**) and 137.1 ppm (**6b**) and at 141.4 (**6a**) and 140.6 (**6b**), respectively, as singlets. The propargylic units display singlets, for **6a** at 77.1 (≡CH), 75.7 (C≡), and 53.8 ppm (CH_2) and for **6b** at 76.8 (≡CH), 74.8 (C≡) and 43.6 ppm (CH_2). The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 63.1 (**6a**) and 62.6 ppm (**6b**).

Treatment at −78 °C of the tetrahydrofuran solutions of the isomeric mixture of **6** with 2.0 equiv of sodium methoxide affords after 40 min a 1:1 mixture of the dihydronaphthopyrrolyl diastereomers ($R_{Ru}S_C$,$S_{Ru}R_C$)-[Ru(η5-C_5H_5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}(CO)(P^iPr_3) (**7a**) and ($R_{Ru}R_C$,$S_{Ru}S_C$)-[Ru(η5-C_5H_5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}(CO)(P^iPr_3) (**7b**) according to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the crude reaction product. The isomeric mixture was isolated as a yellow solid in 85% yield (eq 5).



(5)

Microcrystals of **7a** were obtained by slow diffusion of pentane into a concentrated solution of the diastereomeric mixture in toluene and characterized by X-ray diffraction analysis. The asymmetric unit contains the enantiomers as two crystallographically independent molecules. A drawing of both optic isomers is shown in Figure 3. Selected bond distances and angles are listed in Table 3.

The geometry around the ruthenium center is like those of **3** and **5**: i.e., close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, the carbonyl group, and the polycyclic ligand are all close to 90°. The polycycle is coordinated to the ruthenium atom with Ru−C distances of 2.133(2) Å (Ru(1)−C(1)) and 2.107(3) Å (Ru(51)−C(51)), which compare well with those found in **3** and **5** and support the Ru−C(sp^2) single-bond formulation.

The five-membered rings N(1)−C(4)−C(3)−C(2)−C(1) (R_{Ru},S_C) and N(51)−C(51)−C(52)−C(53)−C(54) (S_{Ru},R_C) are almost planar and aromatic. The aromaticity, which is the result of the overlap of the filled orbital containing the lone pair of the nitrogen with the p orbitals of the adjacent C(sp^2) atoms, is strongly supported by the structural parameters within the rings. The C(3)−C(4) (1.344(3) Å) and C(53)−C(54) (1.339(4) Å) distances are in agreement with the sample mean of carbon−carbon bond length for double bonds (1.32(1)

(14) (a) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch.* **1981**, *36B*, 1277. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J., González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

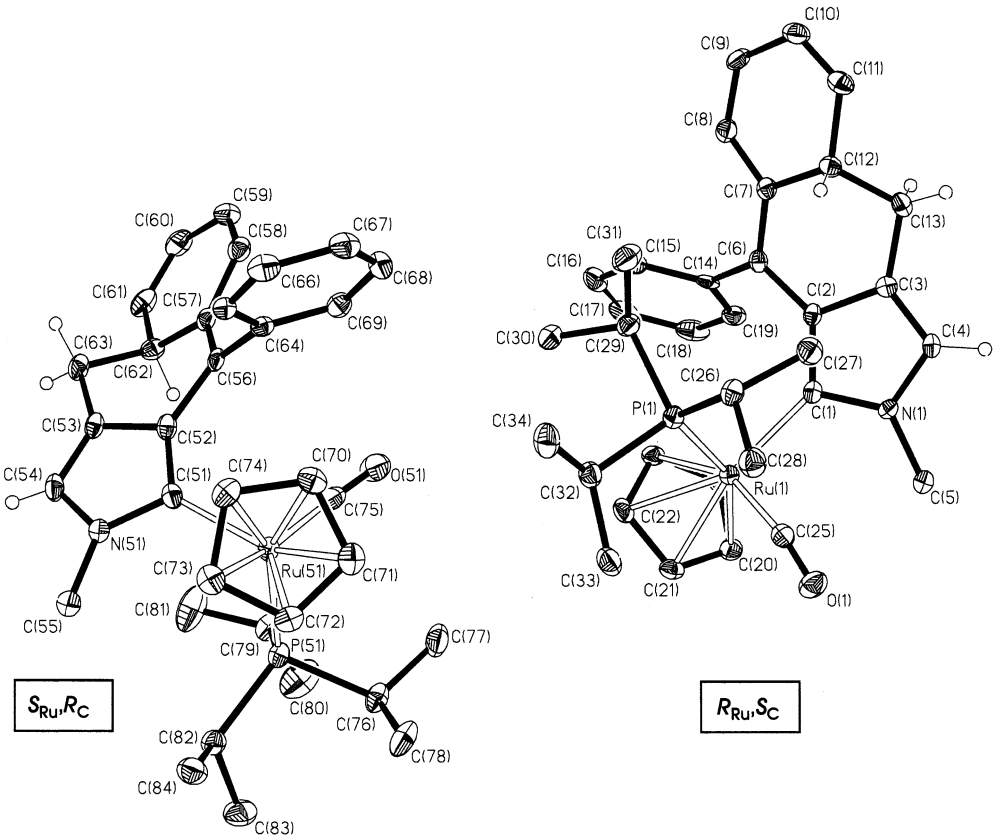


Figure 3. Molecular diagram of the two enantiomers in the asymmetric unit of the complex ($R_{Ru}S_C$,$S_{Ru}R_C$)-[Ru(η^5-C_5H_5)-{9-phenyl-3,3a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}(CO)(P^iPr_3)] (**7a**). Thermal ellipsoids are shown at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for ($R_{Ru}S_C$,$S_{Ru}R_C$)-Ru(η^5-C_5H_5){9-phenyl-4,4a-dihidronaphtho(2,3-*c*)-1-pyrrolyl}(CO)(P^iPr_3) (7a)

	asymmetric unit			asymmetric unit	
	$R_{Ru}S_C$	$S_{Ru}R_C$		$R_{Ru}S_C$	$S_{Ru}R_C$
Ru(1)−P(1)	2.3211(7)	2.3568(7)	C(2)−C(3)	1.434(3)	1.434(3)
Ru(1)−C(1)	2.133(2)	2.107(3)	C(2)−C(6)	1.468(3)	1.469(3)
Ru(1)−C(20)	2.248(3)	2.237(2)	C(3)−C(4)	1.344(3)	1.339(4)
Ru(1)−C(21)	2.237(2)	2.277(3)	C(3)−C(13)	1.494(3)	1.491(4)
Ru(1)−C(22)	2.247(2)	2.275(3)	C(6)−C(7)	1.370(3)	1.370(3)
Ru(1)−C(23)	2.271(2)	2.264(3)	C(7)−C(8)	1.435(3)	1.436(3)
Ru(1)−C(24)	2.264(3)	2.223(3)	C(7)−C(12)	1.527(3)	1.525(3)
Ru(1)−C(25)	1.822(3)	1.820(3)	C(8)−C(9)	1.338(3)	1.333(3)
N(1)−C(1)	1.398(3)	1.394(3)	C(9)−C(10)	1.446(3)	1.444(4)
N(1)−C(4)	1.375(3)	1.372(3)	C(10)−C(11)	1.325(3)	1.326(4)
N(1)−C(5)	1.444(3)	1.435(3)	C(11)−C(12)	1.492(3)	1.493(4)
C(1)−C(2)	1.412(3)	1.409(3)	C(12)−C(13)	1.536(4)	1.528(4)
M(1)[a]−Ru(1)−P(1)	126.46(8)	128.85(8)	C(2)−C(3)−C(4)	107.3(2)	107.2(2)
M(1)−Ru(1)−C(1)	122.64(10)	119.96(10)	C(2)−C(3)−C(13)	121.2(2)	120.6(2)
M(1)−Ru(1)−C(25)	121.63(11)	124.89(12)	C(2)−C(6)−C(7)	118.5(2)	117.9(2)
P(1)−Ru(1)−C(1)	93.17(7)	96.94(7)	C(3)−C(13)−C(12)	107.0(2)	106.7(2)
P(1)−Ru(1)−C(25)	88.01(8)	86.46(8)	C(4)−N(1)−C(5)	120.0(2)	120.4(2)
C(1)−Ru(1)−C(25)	95.84(10)	89.05(11)	C(6)−C(7)−C(8)	124.7(2)	125.1(2)
Ru(1)−C(1)−N(1)	120.22(17)	124.43(18)	C(6)−C(7)−C(12)	117.8(2)	117.9(2)
Ru(1)−C(1)−C(2)	135.27(18)	131.58(19)	C(7)−C(8)−C(9)	122.9(3)	123.7(3)
N(1)−C(1)−C(2)	103.6(2)	103.8(2)	C(7)−C(12)−C(11)	114.9(2)	114.9(2)
N(1)−C(4)−C(3)	108.5(2)	108.7(2)	C(7)−C(12)−C(13)	108.1(2)	108.0(2)
C(1)−N(1)−C(4)	111.5(2)	111.4(2)	C(8)−C(9)−C(10)	121.4(3)	120.8(3)
C(1)−N(1)−C(5)	128.5(2)	128.2(2)	C(9)−C(10)−C(11)	120.3(3)	120.7(3)
C(1)−C(2)−C(3)	108.8(2)	108.7(2)	C(10)−C(11)−C(12)	123.1(2)	123.0(3)
C(1)−C(2)−C(6)	134.9(2)	134.1(2)	C(11)−C(12)−C(13)	112.7(2)	113.2(2)

[a] M(1) represents the midpoint of the C(20)−C(24) Cp ligand. The related atoms of the two independent molecules are numbered by *n* (R_{Ru},S_C) and *n* + 50 (S_{Ru},R_C).

Å).[15] The N(1)−C(4) (1.375(3) Å) and N(51)−C(54) (1.372(3) Å) distances are about 0.02 Å shorter than the N(1)−C(1) (1.398(3) Å) and N(51)−C(51) (1.394(3) Å) bond lengths, and all four lie between those found for the C−N double bonds in **3**, **5**, Schiff bases, hydrazones, and related compounds (about 1.29 Å) and those ex-

pected for a C−N single bond such as N(1)−C(5) (1.444(3) Å) or N(51)−C(55) (1.435(3) Å). The C(1)−C(2) (1.412(3) Å) and C(2)−C(3) (1.434(3) Å) distances, and C(51)−C(52) (1.409(3) Å) and C(52)−C(53) (1.434(3) Å) distances, are significantly shorter (between 0.03 and 0.06 Å) than the length of a $C(sp^2)-C(sp^2)$ single bond (about 1.47 Å). In addition, it should be noted that these structural parameters show a decrease of bond order, within the five-membered rings, in the sequences C(3)−C(4)−N(1)−C(1)−C(2)−C(3) and C(53)−C(54)−N(51)−C(51)−C(52)−C(53).

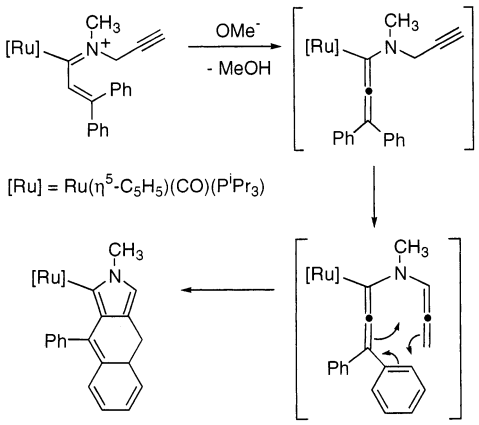
The central six-membered ring of both enantiomers significantly deviates from planarity, showing a boat conformation with the $C(sp^3)$ atom C(13) (R_{Ru},S_C) or C(63) (S_{Ru},R_C) away from the bulky triisopropylphosphine ligand. The ring contains a C−C double bond, between the carbon atoms C(6)−C(7) (1.370(3) Å, R_{Ru},S_C) or C(56)−C(57) (1.370(3) Å, S_{Ru},R_C).

In contrast to the central six-membered ring, the outer six-membered ring is almost planar. The bond lengths in the sequences C(7)−C(8)−C(9)−C(10)−C(11) (1.435(3), 1.338(3), 1.446(3), 1.325(3) Å) and C(57)−C(58)−C(59)−C(60)−C(61) (1.436(3), 1.333(3), 1.444(4), 1.326(4) Å) clearly indicate delocalized bonding between these atoms with the double-bond character mainly centered on C(8)−C(9) and C(10)−C(11) (R_{Ru},S_C) and C(58)−C(59) and C(60)−C(61) (S_{Ru},R_C). The angles between the planar rings are 30.75(11)°for the R_{Ru},S_C enantiomer and 29.70(12)° for the S_{Ru},R_C enantiomer.

The positions of the C−C double bonds within the polycyclic ligands of both diastereomers are also supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of the isomeric mixture in benzene-d_6 at room temperature. The ^1H NMR spectrum shows the resonances corresponding to the triisopropylphosphine and the cyclopentadienyl ligands along with 18 signals, which according to a $^1H-^1H$ COSY NMR spectrum were assigned as indicated (δ):[16] 6.93, 6.66 (H_8); 6.71, 6.78 (H_3); 6.07, 6.02 (H_6); 5.97, 5.75 (H_5); 5.60, 5.50 (H_7); 4.01, 3.97 (H_{4a}); 3.17, 3.78 (CH_3); 2.95, 2.90 (H_4); 2.69, 2.60 ($H_{4'}$). In the $^{13}C\{^1H\}$ NMR spectrum the most noticeable resonances are 2 doublets at 135.8 (J_{C-P} = 10.6 Hz) and 134.9 ppm (J_{C-P} = 13.8 Hz), assigned to C_1, and 14 singlets assigned according to the $^1H-^{13}C$ HETCOR NMR spectrum as indicated (δ): 131.1, 130.9 (C_5); 127.5, 127.9 (C_8); 123.8, 124.2 (C_6); 121.1, 118.1 (C_3); 119.8, 119.2 (C_7); 43.1, 41.9 (C_{4a}); 30.6, 31.1 (C_4). The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 63.8 and 63.1 ppm.

The formation of **7a** and **7b** (**7**) can be rationalized according to Scheme 4. Since the formation of **7** involves the deprotonation of **6** (the isomeric mixture of **6a** and **6b**) and it is well-known that the deprotonation of

Scheme 4



tertiary azoniabutadienyl complexes proceeds by extraction of the proton of the $CH{=}CPh_2$ group,[10] it is reasonable to assume that one of the key steps of the process is the formation of an aminoallenyl intermediate. It is also well-known that bases can catalyze the isomerization of propargylic into allenic moieties;[17] therefore, another key step of the process should be the isomerization of the aminopropargyl group into aminoallenyl. In this context, it should be noted that, under the conditions of the reaction shown in eq 5, complex **4** is stable. This suggests that the aminopropargyl units have a higher tendency toward isomerization than the iminopropargyl units.

The new polycyclic ligand is the result of two carbon−carbon couplings in **6**, the C_β atom of the original C_3 chain with the central carbon atom of the propargyl unit and, at the same time, an ortho carbon atom of one of the two phenyl groups with the terminal (C(sp)) atom. These couplings can be rationalized as an intramolecular Diels−Alder reaction in an allenylamino−diphenylallenyl intermediate, where the $C_\beta-C_\gamma$ double bond and one of the two phenyl groups of the diphenylallenyl fragment act as an inner−outer ring diene and the $C{=}CH_2$ double bond of the another allenyl fragment acts as a dienophile. The formation of two diastereomers in the reaction is the consequence of the chirality of the ruthenium and the two possible approaches of the dienophile to the diene.

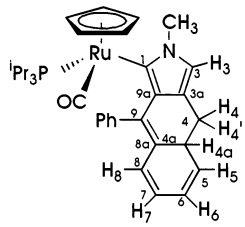
Concluding Remarks

This paper gives new evidence of the high potential of the chemistry of the allenylidene complexes. The behavior of the allenylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(=C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ toward three different propargylamines has been studied, and three novel types of cycloaddition reactions have been discovered, which have given rise to three novel types of organometallic compounds.

The new heterocyclic ligands are the result of the addition of the nitrogen atom of the amine to the C_α atom of the allenylidene and one or two C−C couplings. The number of new C−C bonds formed depends on both the nature of the amine (primary or secondary) and the substituents at the C_α atom of the propargyl unit.

(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. J. *Chem. Soc., Dalton Trans.* **1989**, S1.

(16)



(17) Huntsman, W. D. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1980; Chapter 15.

Experimental Section

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting material [Ru(η^5-C_5H_5){C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (**1**) was prepared as described in ref 8a. In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NHCH$_2$C≡CH}(CO)(P^{i}Pr$_3$)]BF$_4$ (2). A deep red solution of [Ru(η^5-C_5H_5)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (**1**; 150 mg, 0.24 mmol) in 6 mL of dichloromethane was treated with propargylamine (18 μL, 0.26 mmol). The mixture was stirred at room temperature for 5 min, and the solution became orange. The solvent was removed in vacuo, and the residue was treated with 10 mL of diethyl ether to afford a yellow suspension. The solution was decanted, and the solid was washed twice with diethyl ether and dried in vacuo. Yield: 155 mg (94%). Anal. Calcd for $C_{33}H_{41}BF_4NOPRu$: C, 57.73; H, 6.02; N, 2.04. Found: C, 57.89; H, 5.90, N, 2.13. IR (Nujol, cm^{-1}): ν(NH) 3361 (m), ν(≡CH) 3256 (m), ν(C≡C) 2120 (w), ν(CO) 1955 (vs), ν(C=N) and ν(C=C) 1598 (m) and 1568 (w), ν(BF$_4$) 1030 (br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.83 (br, 1H, NH), 7.45−7.02 (m, 10H, Ph), 6.67 (s, 1H, =CH), 4.89 (s, 5H, Cp), 4.55 (ddd, $^2J_{H-H}$ = 16.8, $^3J_{H-H}$ = 4.8, $^4J_{H-H}$ = 2.1, 1H, CH$_2$), 4.42 (ddd, $^2J_{H-H}$ = 16.8, $^3J_{H-H}$ = 6.9, $^4J_{H-H}$ = 2.1, 1H, CH$_2$), 2.37 (dd, $^4J_{H-H}$ = $^4J'_{H-H}$ = 2.1, 1H, ≡CH), 2.23 (m, 3H, PC*H*CH$_3$), 1.28 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 13.5, PCHC*H*$_3$), 1.27 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 14.7, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$): δ 247.9 (d, J_{P-C} = 10.5, Ru−C), 204.1 (d, J_{P-C} = 16.6, CO), 142.5 (s, =CPh$_2$), 141.0, 138.6 (both s, C$_{ipso}$ Ph), 133.3 (s, =CH), 130.5, 129.1, 128.6, 128.5, 128.3 (all s, Ph), 86.9 (s, Cp), 75.8 (s, *C*≡CH), 74.0 (s, C≡*C*H), 40.1 (s, NHCH$_2$), 28.7 (d, J_{P-C} = 23.8, P*C*HCH$_3$), 20.1, 19.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 62.4 (s).

Preparation of Ru(η^5-C_5H_5){4-methylidene-6,6-diphenyl-2-azabicyclo[3.1.0]hex-2-en-1-yl}(CO)(P^{i}Pr$_3$) (3). A yellow suspension of **2** (500 mg, 0.73 mmol) in 10 mL of methanol was treated with an excess of KOH (100 mg, 1.78 mmol) and stirred at room temperature for 4 h. The mixture became green, and the solvent was removed in vacuo. Dichloromethane was added, and the suspension was filtered to remove potassium tetrafluoroborate. Solvent was evaporated, and the residue was washed three times with methanol to afford a yellow solid, which was dried in vacuo. Yield: 223 mg (51%). Anal. Calcd for $C_{33}H_{40}NOPRu$: C, 66.20; H, 6.73; N, 2.34. Found: C, 65.90; H, 6.26, N, 2.21. IR (Nujol, cm^{-1}): ν(CO) 1913 (vs), ν(C=N) and ν(C=C) 1624 (w) and 1595 (m). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.51−6.94 (m, 10H, Ph), 6.80 (s, 1H, N=CH), 5.20 (s, 1H, =CH$_2$), 4.98 (s, 5H, Cp), 4.91 (s, 1H, =CH$_2$), 3.14 (s, 1H, CH), 1.96 (m, 3H, PC*H*CH$_3$), 1.04 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 14.1, PCHC*H*$_3$), 0.91 (dd, 9H, J_{H-H} = 7.1, J_{P-H} = 12.1, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus APT, plus HETCOR): δ 208.7 (d, J_{P-C} = 20.2, CO), 157.8 (s, N=CH), 156.5 (s, *C*=CH$_2$), 147.4, 143.1 (both s, C$_{ipso}$ Ph), 134.3, 130.3, 127.6, 125.3, 125.2 (all s, Ph), 108.5 (s, =*C*H$_2$), 86.8 (s, Cp), 62.8 (d, J_{P-C} = 10.1, Ru−C), 57.8 (s, CPh$_2$), 42.7 (s, CH), 26.8 (d, J_{P-C} = 20.7, P*C*HCH$_3$), 20.6, 19.3 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 64.5 (s).

Preparation of Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NCH$_2$C≡CH}(CO)(P^{i}Pr$_3$) (4). A brown solution of **2** (150 mg, 0.22 mmol) in 10 mL of THF was treated with sodium methoxide (28.9 mg, 0.54 mmol) and stirred at room temperature for 5 h. The solvent was removed in vacuo. Toluene was added, and the suspension was filtered to remove sodium tetrafluoroborate. Solvent was evaporated, and the residue was washed with pentane to afford a white solid, which was dried in vacuo. Yield: 91 mg (70%). Anal. Calcd for $C_{33}H_{40}NOPRu$: C, 66.20; H, 6.73; N, 2.34. Found: C, 66.54; H, 6.54, N, 2.21. IR (Nujol, cm^{-1}): ν(C≡C) 2022 (w), ν(CO) 1910 (vs), ν(C=N) and ν(C=C) 1594 (w) and 1530 (m). ^{1}H NMR (300 MHz, 223 K, CD_2Cl_2): δ 7.34−7.10 (m, 10H, Ph), 6.63 (s, 1H, =CH), (s, 5H, Cp), 4.26 (AB system, 2H, $\Delta\nu$ = 33.2 Hz, J_{H-H} = 16.5, CH$_2$), 2.35 (m, 3H, PC*H*CH$_3$), 2.26 (s, 1H, ≡CH), 1.26 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 13.8, PCHC*H*$_3$), 1.20 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 13.2, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, 223 K, CD_2Cl_2): δ 208.2 (d, J_{P-C} = 18.1, CO), 204.2 (d, J_{P-C} = 12.1, Ru−C), 143.8, 141.0 (both s, C$_{ipso}$ Ph), 140.3 (s, =CH), 133.1 (s, =CPh$_2$), 130.6, 128.6, 128.5, 128.3, 128.0, 127.2 (all s, Ph), 87.3 (s, Cp), 83.0 (s, *C*≡CH), 70.6 (s, C≡*C*H), 45.8 (s, NCH$_2$), 28.0 (d, J_{P-C} = 23.0, P*C*HCH$_3$), 20.8, 19.7 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 223 K, CD_2Cl_2): δ 66.0 (s).

Preparation of the Isomeric Mixture of 3a-*d* and 3b-*d*. A white suspension of Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NCH$_2$C≡CH}(CO)(P^{i}Pr$_3$) (**4**; 100 mg, 0.17 mmol) in methanol-d_4 was stirred for 4 h, and the suspension became yellow. The solvent was removed in vacuo to afford a yellow residue.

The ^{1}H NMR spectrum of the residue shows a 95% yield of the monodeuterated compound in the =CH$_2$ positions with a 0.5:0.5 intensity ratio.

^{2}H NMR (C_6H_6): δ 5.22 (br, =C*D*H), 4.98 (br, =CH*D*).

Preparation of [Ru(η^5-C_5H_5)(2,2-diethyl-5-diphenylidene-2,5-dihydropyridinium-6-yl)(CO)(P^{i}Pr$_3$)]BF$_4$ (5). A deep red solution of [Ru(η^5-C_5H_5)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]-BF$_4$ (**1**; 350 mg, 0.56 mmol) in 6 mL of dichloromethane was treated with 1,1-diethylpropargylamine (83 μL, 0.62 mmol). The mixture was stirred for 30 min, and the solution became dark yellow. The solvent was removed in vacuo, and the residue was treated with 6 mL of diethyl ether to afford a yellow suspension. The solution was decanted, and the solid was washed twice with diethyl ether, dried in vacuo, and recrystallized from a dichloromethane−diethyl ether mixture. Yield: 270 mg (65%). Anal. Calcd for $C_{37}H_{49}BF_4NOPRu$: C, 59.84; H, 6.65; N, 1.88. Found: C, 59.60; H, 6.43; N, 1.80. IR (Nujol, cm^{-1}): ν(NH) 3323 (m), ν(CO) 1945 (vs), ν(C=N) and ν(C=C) 1609 (m) and 1530 (w), ν(BF$_4$) 1100 (br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.61 (br, 1H, NH), 7.40−7.02 (m, 10H, Ph), 6.30 (d, J_{H-H} = 9.6, CH=), 5.75 (d, J_{H-H} = 9.6, CH=), 4.90 (s, 5H, Cp), 2.25 (m, 2H, CH$_2$), 2.13 (m, 3H, PC*H*CH$_3$), 1.72−1.54 (m, 2H, CH$_2$), 1.19 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 13.8, PCHC*H*$_3$), 1.14 (dd, 9H, J_{H-H} = 7.5, J_{P-H} = 15.0, PCHC*H*$_3$), 0.97 (t, 3H, J_{H-H} = 7.5, CH$_3$), 0.91 (t, J_{H-H} = 7.2, CH$_3$). ^{13}C NMR (75.4 MHz, 293 K, $CDCl_3$): δ 237.4 (d, J_{C-P} = 9.8, Ru−C$_\alpha$), 205.7 (d, J_{C-P} = 18.5, CO), 147.7 (s, *C*=CPh$_2$), 142.8 (s, =CPh$_2$), 141.3, 141.2 (both s, C$_{ipso}$), 136.4 (s, CH=), 131.5 (s, CH=), 130.6, 129.0, 128.9, 128.6, 128.3, 127.8, 126.7 (all s, Ph), 86.8 (s, Cp), 69.6 (s, C(Et)$_2$), 29.1 (s, CH$_2$), 27.9 (d, (d, J_{C-P} = 23.1, P*C*HCH$_3$), 26.8 (s, CH$_2$), 20.1, 19.0 (both s, PCH*C*H$_3$), 8.7, 8.2 (both s, CH$_3$).

Preparation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH$_3$)-CH$_2$C≡CH}(CO)(P^{i}Pr$_3$)]BF$_4$ (6). A deep red solution of [Ru-(η^5-C_5H_5)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (**1**; 150 mg, 0.24 mmol) in 6 mL of dichloromethane was treated with *N*-methylpropargylamine (22 μL, 0.26 mmol). The mixture was stirred for 15 min, and the solution became dark orange. The solvent was removed in vacuo, and the residue was treated with 6 mL of diethyl ether to afford a pale yellow suspension. The solution was decanted, and the solid was washed twice with diethyl ether and dried in vacuo. The solid obtained was a mixture of two isomers, **6a** and **6b**, in a 7:3 molar ratio. Yield: 156 mg (93%). Anal. Calcd for $C_{34}H_{43}BF_4NOPRu$: C, 58.30; H, 6.19; N, 2.0. Found: C, 57.92; H, 6.08; N, 2.18. IR (Nujol, cm^{-1}): ν(≡CH) 3524 (m), ν(C≡C) 2123 (w), ν(CO) 1964 (vs), ν(C=N) and ν(C=C) 1599 (m) and 1550 (w), ν(BF$_4$) 1064 (br).

Table 4. Crystal Data and Data Collection and Refinement Details for 3, 5, and 7a

	3	5	7a
Crystal Data			
formula	$C_{33}H_{40}NOPRu$	$C_{37}H_{49}BF_4NOPRu$	$C_{34}H_{42}NOPRu$
mol wt	598.70	742.62	612.73
symmetry, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	11.2753(5)	14.9386(12)	12.6201(7)
b, Å	13.6961(6)	11.9727(10)	14.6901(8)
c, Å	17.9585(7)	20.7213(16)	16.5516(9)
α, deg			70.624(1)
β, deg	94.062(1)	106.129(2)	82.439(1)
γ, deg			81.567(1)
V, Å^3	2766.3(2)	3560.2(5)	2852.1(3)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.438	1.385	1.427
Data Collection and Refinement Details			
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.710 73	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	0.652	0.536	0.634
2θ range, deg	3, 56	3, 56	3, 56
temp, K	100	100	100
no. of data collected	33 352	24 356	35 094
no. of unique data	6699 (R_{int} = 0.0629)	8310 (R_{int} = 0.0670)	13 312 (R_{int} = 0.0386)
no. of params/restraints	356/0	435/0	723/0
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0321	0.0433	0.0341
wR2[b] (all data)	0.0656	0.0605	0.0618
S[c] (all data)	0.961	0.727	0.824

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF $= S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

NMR data for isomer **6a**: ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.49−7.01 (m, 10H, Ph), 6.60 (s, 1H, =CH), 5.01 (d, 2H, $^4J_{H-H}$ = 2.1, CH_2), 4.78 (s, 5H, Cp), 3.72 (s, 3H, CH_3), 2.64 (d, 1H, $^4J_{H-H}$ = 2.1, ≡CH), 2.40 (m, 3H, PC*H*CH_3), 1.29−1.20 (m, 18H, PCHC*H*$_3$); ^{13}C NMR (75.4 MHz, 293 K, $CDCl_3$) δ 244.0 (d, J_{C-P} = 9.8, Ru−C$_\alpha$), 204.0 (d, J_{C-P} = 17.4, CO), 141.4 (s, =C*P*h$_2$), 139.1, 138.6 (both s, C$_{ipso}$), 138.3 (s, =CH), 130.4, 129.1, 128.8, 128.5, 128.4 (all s, Ph), 86.3 (s, Cp), 77.1 (s, C≡*C*H), 75.7 (s, *C*≡CH), 53.8 (s, NCH_2), 43.6 (NCH_3), 28.4 (d, J_{C-P} = 23.3, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 63.1 (s).

NMR data for isomer **6b**: ^{1}H NMR (300 MHz, 293 K, $CDCl_3$) δ 7.49−7.01 (m, 10H, Ph), 6.70 (s, 1H, =CH), 5.01 (d, 2H, $^4J_{H-H}$ = 2.1, CH_2), 4.72 (s, 5H, Cp), 3.80 (s, 3H, CH_3), 2.64 (d, 1H, $^4J_{H-H}$ = 2.1, ≡CH), 2.31 (m, 3H, PC*H*CH_3), 1.29−1.20 (m, 18H, PCHC*H*$_3$); ^{13}C NMR (75.4 MHz, 293 K, $CDCl_3$) δ 243.6 (d, J_{C-P} = 9.1, Ru−C$_\alpha$), 204.2 (d, J_{C-P} = 18.1, CO), 141.5 (s, =C*P*h$_2$), 140.6, 138.5 (both s, C$_{ipso}$), 137.1 (s, =CH), 130.6, 129.1, 128.9, 128.4, (all s, Ph), 86.7 (s, Cp), 76.1 (s, C≡*C*H), 74.8 (s, *C*≡CH), 49.5 (s, NCH_3), 43.6 (NCH_2), 28.5 (d, J_{C-P} = 23.1, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$); ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$) δ 62.6 (s).

Preparation of [Ru(η^5-C_5H_5){9-phenyl-4,4a-dihydronaphtho[2,3-*c*]-1-pyrrolyl}(CO)(P^{i}Pr$_3$)]BF$_4$ (7). A pale yellow solution of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH_3)CH_2C≡CH}(CO)(P^{i}Pr$_3$)]BF_4 (**6**; 250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at −78 °C was treated with sodium methoxide (39 mg, 0.71 mmol). The mixture was stirred for 40 min, and the color changed to bright yellow. Solvent was evaporated to dryness. Pentane was added, the suspension was filtered to eliminate sodium tetrafluoroborate, and the solution was recovered at −78 °C. Solvent was evaporated in vacuo to afford a bright yellow solid. The solid obtained was a mixture of two diastereomers in a 1:1 molar ratio. Yield: 188 mg (85%). Anal. Calcd for $C_{34}H_{42}NOPRu$: C, 66.50; H, 7.06; N, 2.28. Found: C, 66.45; H, 7.04; N, 2.03. IR (Nujol, cm^{-1}): ν(CO) 1925, 1898 (vs), ν-(Ph, C=C), 1590, 1534 (both w).

^{1}H and ^{13}C{^{1}H} NMR data for one diastereoisomer: ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ 7.16−6.98 (m, 5H, Ph), 6.93 (d, 1H, $J_{H_7-H_8}$ = 9.9, H$_8$), 6.71 (s, 1H, H$_3$), 6.07 (m, 1H, H$_6$), 5.97 (dd, 1H, $J_{H_5-H_6}$ = 9.9 Hz, $J_{H_{4a}-H_5}$ = 4.8 Hz, H$_5$), 5.60 (m, 1H, H$_7$), 4.47 (s, 5H, Cp), 4.01 (m, 1H, H$_{4a}$), 3.17 (s, 3H, CH_3), 2.95 (dd, 1H, $J_{H_{4'}-H_4}$ = $J_{H_4-H_{4a}}$ = 14.4, H$_4$), 2.69 (dd, 1H, $J_{H_{4e}-H_4}$ = 14.4, $J_{H_{4'}-H_{4a}}$ = 4.5, H$_{4'}$), 1.85 (m, 3H, PC*H*CH_3), 0.76 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 12.9, PCHC*H*$_3$), 0.75 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 14.1, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus HETCOR) δ 211.1 (d, J_{P-C} = 24.4, CO), 134.9 (d, J_{P-C} = 13.8, C$_1$), 143.7, 139.4, 137.6, 129.4, 121.1 (all s, C$_{ipso-Ph}$, C$_{3a}$, C$_{8a}$, C$_9$, C$_{9a}$), 132.7, 127.1, 126.5 (all s, Ph), 131.1 (s, C$_5$), 127.5 (s, C$_8$), 123.8 (s, C$_6$), 121.1 (s, C$_3$), 119.8 (s, C$_7$), 85.8 (s, Cp), 43.1 (s, C$_{4a}$), 41.4 (s, C$_3$), 30.6 (s, C$_4$), 28.5 (d, J_{P-C} = 21.6, P*C*HCH$_3$), 21.1 and 20.4 (both s, PCH*C*H$_3$).

^{1}H and ^{13}C{^{1}H} NMR data for the other diastereoisomer: ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ 7.16−6.98 (m, 5H, Ph), 6.66 (d, 1H, $J_{H_7-H_8}$ = 9.9, H$_8$), 6.78 (s, 1H, H$_3$), 6.02 (m, 1H, H$_6$), 5.75 (dd, 1H, J(H$_5$−H$_6$) = 9.3 Hz, $J_{H_{4a}-H_5}$ = 4.5 Hz, H$_5$), 5.50 (m, 1H, H$_7$), 4.27 (s, 5H, Cp), 3.97 (m, 1H, H$_{4a}$), 3.78 (s, 3H, CH_3), 2.90 (dd, 1H, $J_{H_{4'}-H_4}$ = $J_{H_4-H_{4a}}$ = 14.7, H$_4$), 2.60 (dd, 1H, $J_{H_{4'}-H_4}$ = 14.1, $J_{H_{4'}-H_{4a}}$ = 4.2, H$_{4'}$), 2.12 (m, 3H, PC*H*CH_3), 0.91 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 14.1, PCHC*H*$_3$), 0.85 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 13.8, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus HETCOR) δ 208.9 (d, J_{P-C} = 22.6, CO), 135.8 (d, J_{P-C} = 10.6, C$_1$), 143.7, 140.4, 138.3, 128.9, 119.8 (all s, C$_{ipso-Ph}$, C$_{3a}$, C$_{8a}$, C$_9$, C$_{9a}$), 132.7, 127.1, 125.7 (all s, Ph), 130.9 (s, C$_5$), 127.9 (s, C$_8$), 124.2 (s, C$_6$), 119.2 (s, C$_3$), 118.1 (s, C$_7$), 85.4 (s, Cp), 41.9 (s, C$_{4a}$), 40.5 (s, C$_3$), 31.1 (s, C$_4$), 28.4 (d, J_{P-C} = 21.6, P*C*HCH$_3$), 19.7 and 19.4 (both s, PCH*C*H$_3$).

^{31}P{^{1}H} NMR (121.4 MHz, 293K, C_6D_6): δ 63.8 and 63.1-(both s).

Structural Analysis of Complexes 3, 5, and 7a. X-ray data were collected for all complexes at low temperature on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal-focus, 2.4 kW sealed-tube source (molybdenum radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the Sadabs[18] program. The structures for all three compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[19] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-

hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. All the highest electronic residuals were observed in the close proximity of the Ru centers and make no chemical sense.

Crystal and data collection and refinement details are given in Table 4.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **3**, **5**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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