Preparation and Characterization of 4-Azoniaheptatrienyl, 4-Azaheptatrienyl, Ruthenapyrrolinone, and Pyrrolinyl Complexes of Ruthenium

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The allenylidene complex [Ru(η^5-C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4 (**1**) adds the N−H bond of diallylamine to afford the *N*-allyl-4-azonia-1,3,6-heptatrienyl derivative [Ru(η^5-C_5H_5)-{C(CH=CPh_2)=N(CH_2CH=CH_2)$_2$}(CO)(P^iPr_3)]BF_4 (**2**). Treatment of **2** with sodium methoxide in tetrahydrofuran produces the deprotonation of the NCH_2 group of one of the allyl groups and the formation of a 1:1 mixture of the ruthenapyrrolinone complex (R_{Ru},R_C- S_{Ru},S_C)-Ru(η^5-C_5H_5)[=-C(CH=CPh_2)-=N(CH_2CH=CH_2)CH(CH=CH_2)C=O}(P^iPr_3) (**3**) and the pyrrolinyl compound (R_{Ru},S_C- S_{Ru},R_C)-Ru(η^5-C_5H_5){C=CHCPh_2CH(CH=CH_2)NCH_2CH=CH_2}(CO)(P^iPr_3) (**4**). Protonation of **4** with HBF_4·OEt_2 in diethyl ether initially leads to the heterocyclic derivative (R_{Ru},S_C- S_{Ru},R_C)-[Ru(η^5-C_5H_5){C=N(CH_2CH=CH_2)CH(CH=CH_2)-CPh_2CH_2}(CO)(P^iPr_3)]BF_4 (**5**), containing a C−N double bond. In dichloromethane, complex **5** is unstable and evolves into the *N*-allyl-4-azonia-1,3,5-heptatrienyl complex [Ru(η^5-C_5H_5)-{C(CH=CPh_2)=N(CH=$CHCH_3$)CH_2CH=CH_2}(CO)(P^iPr_3)]BF_4 (**6**). The process involves the opening of the five-membered heterocycle and a proton transfer from the −CH_2CN− group to the =CH_2 carbon atom of the vinyl substituent of the heterocycle. Complex **1** also reacts with allylamine. The reaction leads to the 4-azonia-1,3,6-heptatrienyl derivative [Ru(η^5-C_5H_5){C(CH=CPh_2)=NH(CH_2CH=CH_2)}(CO)(P^iPr_3)]BF_4 (**7**). In contrast to **2**, the deprotonation of **7** with sodium methoxide in tetrahydrofuran takes place at the nitrogen atom. In toluene at 70 °C, the resulting 4-aza-1,3,6-heptatrienyl complex Ru(η^5-C_5H_5){C(CH=CPh_2)=NCH_2CH=CH_2}(CO)(P^iPr_3) (**8**) isomerizes into the conjugated 4-aza-1,3,5-heptatrienyl derivative Ru(η^5-C_5H_5){C(CH=CPh_2)=NCH=$CHCH_3$}(CO)(P^iPr_3) (**9**), as a result of a 1,3-sigmatropic rearrangement in the allyl unit. Complexes **3**, **4**, **5**, and **9** have been characterized by X-ray diffraction analysis.

Introduction

The hydroamination of alkynes in the presence of transition metal complexes is an attractive route to prepare numerous classes of organonitrogen molecules.[1] Two basic approaches have been employed to effect aminations and involve either alkyne or amine activation routes. Alkyne activation is generally accomplished with late transition metals, which render π-alkyne intermediates. The coordination of the alkyne to the metallic center enhances its electrophilic character, making the alkyne susceptible to undergoing the direct nucleophilic addition of the amine.[2]

The evidence that vinylidene-metal intermediates are easily formed from terminal alkynes and transition metals, especially from ruthenium(II) complexes,[3] brings along an alternative alkyne activation route. The reactivity of the vinylidene-metal moiety is dominated by the electrophilicity and nucleophilicity of the C_α and C_β atoms, respectively.[4] As a result, one of the N−H bonds of primary amines adds across the highly polarized C_α−C_β double bond of the vinylidene to afford "aminocarbene derivatives".[5]

EHT-MO calculations on the allenylidene compounds L_nM=C=C=CR_2 indicate that the carbon atoms of the unsaturated chain are alternatively electron-poor and electron-rich, starting from the metal center.[6] Hence, electrophilic centers are located at the C_α and the C_γ atoms, while the C_β atom is a nucleophilic site. In

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(1) (a) Müler, T. E.; Beller, M. *Chem. Rev.* **1988**, *98*, 675. (b) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (c) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935.

(2) See for example: (a) Kadota, I.; Shibuya, A.; Lutete, L. M.; Yamamoto, Y. J. *Org. Chem.* **1999**, *64*, 4570. (b) Hartung, C. G.; Tillack, A.; Trauthwein, H.; Beller, M. *J. Org. Chem.* **2001**, *66*, 6339.

(3) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977.

(4) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(5) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (b) Bianchini, C.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1995**, *14*, 3152. (c) Bianchini, C.; Purches, G.; Zanobini, F.; Peruzzini, M. *Inorg. Chim. Acta* **1998**, *272*, 2261.

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agreement with this and with the behavior of vinylidene compounds, the addition of the N−H bond of primary and secondary amines to the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ and other electronically related rhenium and tungsten compounds has been observed.[7] The X-ray structure determination of the complex $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NEt_2\}(CO)(P^iPr_3)]BF_4$ and the analysis of the ellipticities of the $Ru-C_\alpha$ and $C_\alpha-N$ bonds of the model compound $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CH_2)=NH_2\}(CO)(PH_3)]^+$ suggest that the resulting complexes from the N−H addition are better described as azoniabutadienyl species, where the contribution of the aminocarbene resonance form is not relevant.[8]

In the presence of bases, there is a marked difference in behavior between the tertiary azoniabutadienyl complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NR_2\}(CO)(P^iPr_3)]BF_4$ and the secondary azoniabutadienyl compounds $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=N(R)H\}(CO)(P^iPr_3)]BF_4$. Treatment of $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NR_2\}(CO)(P^iPr_3)]BF_4$ with sodium methoxide produces the deprotonation of the $CH=CPh_2$ group of the unsaturated η^1-carbon donor ligand and the formation of the corresponding aminoallenyl derivatives $Ru(\eta^5\text{-}C_5H_5)\{C(NR_2)=C=CPh_2\}(CO)(P^iPr_3)$. Under the same conditions, the deprotonation of $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=N(R)H\}(CO)(P^iPr_3)]BF_4$ takes place at the nitrogen atom. Thus, the reactions of the latter with sodium methoxide lead to the azabutadienyl derivatives $Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NR\}(CO)(P^iPr_3)$.[8]

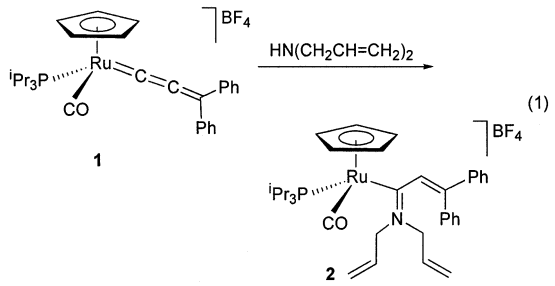
In reactions with secondary and primary amines containing a second nucleophilic atom, the allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ is active not only at the $C_\alpha-C_\beta$ double bond but also at the C_γ atom. The additions afford 1,2,3-diheterocyclization products. The stability of the formed cycles depends on the nature of the amine. The reactions with pyrazoles lead to pyrazolo[1,2-*a*] pyrazolyl complexes, which yield functionalized alkynyl derivatives by treatment with sodium methoxide.[9] However, the reactions with 2-aminopyridine and thioisonicotinamide give rise to polyheterocycles, which are stable in basic medium, as a consequence of the presence of a NH bond in one of the heterocycles. The NH bond can be deprotonated, preventing in this way the ring opening.[10]

N-Heterocycles are also generated by deprotonation of azoniabutadienyl ligands when the initial amine contains a remote C−C triple bond. Thus, we have recently shown that the addition of primary and secondary propargylamines to the allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$, followed by the deprotonation of the resulting azoniabutadienyl derivatives, affords 2-azabicyclo[3.1.0]hexen-2-enyl, dihydropyridiniumyl, and dihydronaphthopyrrolyl complexes.[11] These heterocycles are the result of the addition of the nitrogen atom of the amines to the C_α atom of the allenylidene and one or two C−C couplings. The number of 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.

Allylamines contain a C−C double bond instead of a C−C triple bond, and the NCH_2 group is fairly acidic. In the search for new reactions and novel types of organometallic compounds, we have now studied the reactivity of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ toward diallylamine and allylamine. In this paper, we report the formation of 4-azonia-1,3,6-heptatrienyl derivatives which have one more potential site of deprotonation than the previously reported azoniabutadienyl derivatives. They allow the preparation of novel conjugated and nonconjugated 4-azaheptatrienyl, metallaheterocyclic, and heterocyclic compounds.

Results and Discussion

1. Diallylamine. Similarly to other secondary amines, the N−H bond of this amine 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 diallylamine to a dichloromethane solution of **1** leads to the tertiary *N*-allyl-4-azonia-1,3,6-heptatrienyl derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=N(CH_2CH=CH_2)_2\}(CO)(P^iPr_3)]BF_4$ (**2**), which was isolated as a yellow solid in 94% yield according to eq 1.



In agreement with the presence of C−N and C−C double bonds in **2**, its IR spectrum in Nujol shows bands at 1639 and 1598 cm^{-1}. The C−N double bond prevents the rotation of the $N(allyl)_2$ unit in solution at room temperature. Thus, in the ^1H NMR spectrum in chloroform-*d*, resonances corresponding to two inequivalent allyl groups are observed, at 5.81 and 5.70 (CH=), 5.60, 5.54, 5.28, and 5.10 (CH_2=), and 4.83 and 4.78 (CH_2) ppm. The resonance due to the CH= proton of the CH=CPh_2 unit appears at 6.73 ppm. The $^{13}C\{^1H\}$ NMR spectrum agrees well with the ^1H NMR spectrum; the allyl groups display six resonances at 128.7 and 128.6 (CH=), 123.3 and 123.1 (CH_2=), and 64.4 and 57.8 (CH_2) ppm. The C_α atom of the η^1-carbon donor ligand gives rise to a doublet at 244.9 ppm, with a C−P coupling constant of 9.4 Hz, while the resonances due to the CH=

(6) (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. (c) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A.; Schrickel, J. *Organometallics* **1996**, *15*, 3556. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (e) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585.

(7) (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (c) Mantovani, N.; Marvelli, L.; Rossi, R.; Bertolasi, V.; Bianchini, C.; de los Ríos, I.; Peruzzini, M. *Organometallics* **2002**, *21*, 2382.

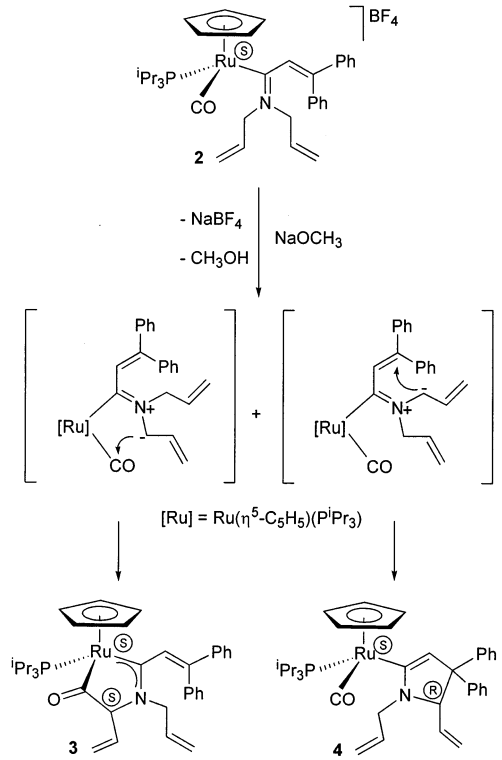
(8) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

(9) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate; E. *Organometallics* **1998**, *17*, 3567.

(10) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 4327.

(11) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, 22,162.

Scheme 1



CPh_2 unit are observed at 137.9 (CH) and 141.3 (CPh_2) ppm, as singlets. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 63.1 ppm.

The above-mentioned spectroscopic data agree well with those reported for related tertiary ruthenium-azoniabutadienyl complexes.[8,11] However, in the presence of bases, there are marked differences in behavior between the known compounds of this type and **2**. In contrast to the general trend, the deprotonation of **2** does not occur at the $CH{=}CPh_2$ group but at one of the NCH_2-carbon atoms. Although the allyl units are inequivalent, the deprotonation of both moieties is equally favored. As a result, the treatment at room temperature of **2** with sodium methoxide in tetrahydrofuran affords a 1:1 isomeric mixture of the ruthenapyrrolinone complex (R_{Ru},R_C- S_{Ru},S_C)-Ru(η^5-C_5H_5)[=C(CH=CPh_2)=N($CH_2CH{=}CH_2$)CH($CH{=}CH_2$)C=O](P^iPr_3) (**3**) and the pyrrolinyl compound (R_{Ru},S_C- S_{Ru},R_C)-Ru(η^5-C_5H_5)-{C=$CHCPh_2CH(CH{=}CH_2)NCH_2CH{=}CH_2$}(CO)-($P^iPr_3$) (**4**).

The formation of **3** involves the deprotonation of the allyl group disposed *trans* to the $CH{=}CPh_2$ unit, followed by the intramolecular attack of the deprotonated NCH-carbon atom to the carbonyl ligand. Complex **4** is the result of the deprotonation of the allyl group *trans* disposed to the metallic center and the subsequent intramolecular nucleophilic attack of the deprotonated NCH-carbon atom to the CPh_2-carbon atom of the $CH{=}CPh_2$ moiety (Scheme 1).[12] Both the formation of **3** and the formation of **4** can be rationalized as dipolar 1,5-electrocyclizations.[13] This type of reactions has no precedents in transition metal-allenylidene chemistry.

(12) Only the enantiomers of **3** and **4** resulting from the S_{Ru} enantiomer of **2** are shown.

The chemical behavior of the allenylidene ligand of **1** is much more versatile than the chemical behavior of the vast majority of the allenylidene ligands of the iron triad complexes.[14] This fact has been ascribed to the π-acidic nature of the carbonyl group, which enhances the reactivity associated with the allenylidene spine. The preparation of the ruthenapyrrolinone complex **3** proves that the carbonyl ligand of **1** not only plays an indirect role in the reactivity of the allenylidene group but also can be determinant to the formation of novel organometallic compounds, playing a direct role.

The high degree of stereocontrol in the formation of both **3** and **4** should be pointed out. As a result of the prochirality of the NCH_2 carbon atoms, two pairs of enantiomers of each isomer could be formed during the reaction. However, according to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the crude reaction, only one pair of **3** and one pair of **4** are obtained. This suggests that the configuration of the ruthenium atom of **1**, and therefore of **2**, determines the configuration of the asymmetric NCH− carbon atom of the heterocycles of **3** and **4**.

The pair of the ruthenapyrrolinone complex **3** was separated from the crude reaction by extraction in pentane. The treatment of the isomeric mixture of **3** and **4** with this solvent affords an orange solution and a yellow solid. The cooling of the solution at −20 °C gives rise to pure orange crystals of the pair of **3**, while the crystallization in toluene−pentane of the yellow solid yields pure yellow crystals of the pair of **4**. The X-ray diffraction analysis of the crystals indicates that **3** is the racemic mixture R_{Ru},R_C−S_{Ru},S_C; while **4** is the racemic mixture S_{Ru},R_C−R_{Ru},S_C.

Figure 1 shows a view of the molecular geometry of the enantiomer R_{Ru},R_C of **3**. 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 and the C_α atoms of the five-membered ring are close to 93°, while the C(1)−Ru−C(22) angle is 79.9(3)°. The ruthenapyrrolinone skeleton is almost planar. The deviations from the best plane are 0.054(3)° (Ru), −0.058(3)° (C(1)), 0.026(4)° (N), 0.033(4)° (C(16)), and −0.055(4)° (C(22)).

The Ru−C(1) distance (1.884(6) Å) is similar to the related bond lengths in the α, β-unsaturated carbene compound [RuCl(CHCH=CPh_2)(CO)(P^iPr_3)$_2$]BF_4 (1.874(3) Å),[15] the alkoxycarbene complex [Ru(κ^3N-HBpz$_3$)-{C(OCH_3)$CH_2CO_2CH_3$}(dippe)]BPh_4 (1.86(2) Å),[16] and the cyclopentadienylcarbene complexes [Ru(η^5-C_5H_5)-{C(OCH_3)CH_2CH_3}(PPh_3)$_2$]PF_6 (1.956(6) Å)[17] and [Ru-(η^5-C_5H_5){C(OCH_3)CH_2Ph}(CHIRAPHOS)]PF_6 (1.93(2)

(13) (a) Bird, C. W.; Cheesman, G. W. H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, Part 3, p 105. (b) Esteban, S.; Cornego, P.; Barthelemy, C. *Química Orgánica Heterocíclica*; Universidad de Educación a Distancia: Madrid, 1992; p 191.

(14) (a) Esteruelas, M. A.; López, A. M. In *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001; Chapter 7, pp 189−284. (b) Baya, M.; Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E.; Rodríguez, J. R. *Organometallics* **2002**, *21*, 1841.

(15) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeir, B. *Organometallics* **1994**, *13*, 4258.

(16) Jiménez-Tenorio, M. A.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1997**, *16*, 5528.

(17) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Enantiomer R_{Ru},R_C $Ru(\eta^5\text{-}C_5H_5)[{=}C(CH{=}CPh_2){=}N(CH_2CH{=}CH_2)CH(CH{=}CH_2)C{=}O\}(P^iPr_3)$ (3)

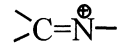
Ru−P	2.306(2)	N−C(16)	1.472(9)
Ru−C(1)	1.884(6)	N−C(19)	1.451(8)
Ru−C(22)	1.984(7)	C(1)−C(2)	1.473(9)
Ru−C(32)	2.310(8)	C(2)−C(3)	1.336(9)
Ru−C(33)	2.301(7)	C(16)−C(17)	1.506(10)
Ru−C(34)	2.274(6)	C(16)−C(22)	1.530(10)
Ru−C(35)	2.224(7	C(17)−C(18)	1.278(11)
Ru−C(36)	2.252(7)	C(19)−C(20)	1.477(11)
O−C(22)	1.219(7)	C(20)−C(21)	1.297(12)
N−C(1)	1.367(8)		
P−Ru−C(1)	92.96(18)	N−C(1)−C(2)	113.9(6)
P−Ru−C(22)	93.8(2)	N−C(16)−C(17)	110.2(6)
P−Ru−M[a]	125.6	N−C(16)−C(22)	108.0(6)
C(1)−Ru−C(22)	79.9(3)	N−C(19)−C(20)	112.4(6)
C(1)−Ru−M	129.1	C(1)−N−C(16)	113.0(6)
C(22)−Ru−M	122.7	C(1)−N−C(19)	129.5(6)
Ru−C(1)−N	122.9(5)	C(1)−C(2)−C(3)	131.6(7)
Ru−C(1)−C(2)	122.9(5)	C(16)−N−C(19)	117.6(6)
Ru−C(22)−O	128.2(5)	C(16)−C(17)−C(18)	125.4(8)
Ru−C(22)−C(16)	115.4(5)	C(17)−C(16)−C(22)	113.4(6)
O−C(22)−C(16)	116.1(6)	C(19)−C(20)−C(21)	126.2(8)

[a] M is the midpoint of the C(32)−C(36) Cp ligand.

Å).[18] However, it is about 0.1 Å shorter than the Ru−C distances found in the compounds *fac*,*cis*-[(PNP)$RuCl_2$-{C[NH{(*S*)-(−)-CH(Me)(1-naphthyl)}]CH_2Ph}] (1.99(2) Å)[19] and Ru(η^5-C_5H_5)I(CO){C(NHMe)Ph} (2.009(6) Å),[20] which have been described as aminocarbene derivatives, and about 0.14 Å shorter than the Ru−C bond length reported for the azoniabutadienyl species [Ru(η^5-C_5H_5)-{C(CH=CPh_2)=NEt_2}(CO)(P^iPr_3)]BF_4 (2.063(6) Å).[8]

The N−C(1) distance (1.367(8) Å) is about 0.1 Å shorter than the N−C(19) and N−C(16) single-bond lengths (1.451(8) and 1.472(9) Å, respectively), while it is about 0.04 Å longer than the C−N distances found in the "aminocarbene complexes" *fac*,*cis*-[(PNP)$RuCl_2$-{C[NH{(*S*)-(−)-CH(Me)(1-naphthyl)}]CH_2Ph}] (1.32(2) Å)[19] and Ru(η^5-C_5H_5)I(CO){C(NHMe)Ph} (1.301(7) Å)[20] and the azoniabutadienyl derivative [Ru(η^5-C_5H_5)-{C(CH=CPh_2)=NEt_2}(CO)(P^iPr_3)]BF_4 (1.306(7) Å).[8] The angles around the nitrogen atom are between 113.0(6)° and 129.5(6)°, whereas the angles around C(1) are between 113.9(6)° and 122.9(5)°.

According to the previously mentioned structural parameters, the bonding situation in the sequence Ru−C(1)−N can be described as aminocarbene, with a significant contribution of the resonance form B (Scheme 2). The contribution of the latter to the structure of **3** is much smaller than the contribution of the related form



to the structures of *fac*,*cis*-[(PNP)$RuCl_2${C[NH{(*S*)-(−)-CH(Me)(1-naphthyl)}]CH_2Ph}] and Ru(η^5-C_5H_5)I(CO)-{C(NHMe)Ph}.

The C(16)−C(22) (1.530(10) Å), Ru−C(22) (1.984(7) Å), and O−C(22) (1.219 (7) Å) distances compare well with

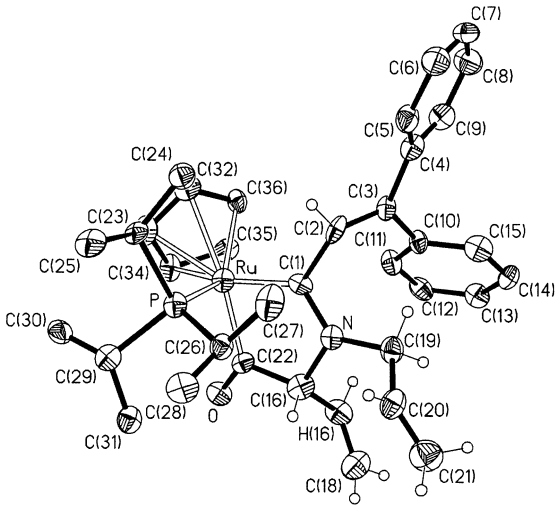
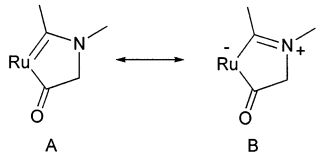


Figure 1. Molecular diagram of the enantiomer R_{Ru},R_C $Ru(\eta^5\text{-}C_5H_5)[{=}C(CH{=}CPh_2){=}N(CH_2CH{=}CH_2)CH(CH{=}CH_2)C{=}O\}(P^iPr_3)$ (**3**). Thermal ellipsoids are shown at 50% probability.

Scheme 2



the related bond lengths in the acyl derivative [Ru(η^5-C_5H_5){C(O)CH=CPh_2}(CO)(P^iPr_3)]BF_4 (1.502(3), 2.060-(2), and 1.212(3) Å, respectively).[21] In agreement with the sp^2-hybridization at C(22), the angles around this atom are between 115.4(5)° and 128.2(5)°.

The IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **3** are consistent with the structure shown in Figure 1. In the IR spectrum in Nujol, the most noticeable absorption is that corresponding to the ν(C=O) vibration, which appears at 1581 cm^{-1}. The ^{1}H NMR spectrum in benzene-d_6 shows the resonance corresponding to the C(16)-H proton of the ruthenapyrrolinone skeleton at 4.02 ppm, as a doublet with a H−H coupling constant of 8.7 Hz. In the ^{13}C{^{1}H} NMR spectrum, the C(1) and C(22) carbon atoms display doublets at 262.2 and 259.8 ppm, with C−P coupling constants of 11.5 and 14.3 Hz, respectively, while the C(16) carbon atom gives rise to a singlet at 91.9 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 67.9 ppm.

Figure 2 shows a view of the molecular geometry of the enantiomer S_{Ru},R_C of the pyrrolinyl complex **4**. 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 a face. The P−Ru−C(36) and P−Ru−C(1) angles are 87.84(12)° and 89.83(10)°, respectively. These values agree well with the ideal value of 90°. However the C(1)−Ru−C(36) angle (99.65(15)°) strongly deviates from 90°, suggesting that the heterocycle and the carbonyl ligands experience a large steric hindrance.

(18) Consiglio, G.; Morandini, F.; Ciani, G. F.; Sirani, A. *Organometallics* **1986**, *5*, 1976.

(19) Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Organometallics* **1999**, *18*, 2376.

(20) Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349.

(21) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

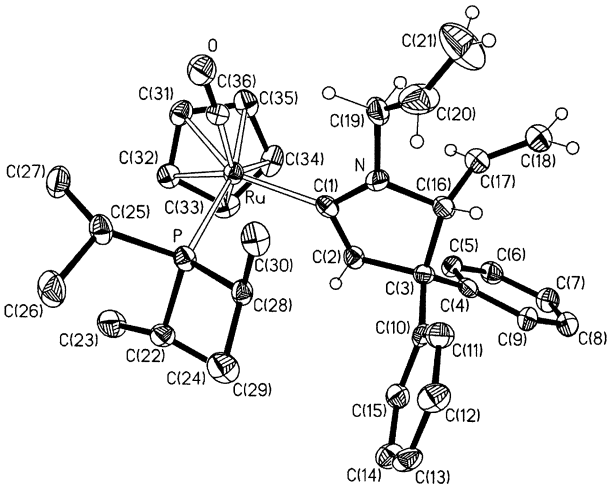


Figure 2. Molecular diagram of the enantiomer S_{Ru},R_C $Ru(\eta^5\text{-}C_5H_5)\{C{=}CHCPh_2CH(CH{=}CH_2)NCH_2CH{=}CH_2\}(CO)(P^iPr_3)$ (**4**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Enantiomer S_{Ru},R_C $Ru(\eta^5\text{-}C_5H_5)\{C{=}CHCPh_2CH(CH{=}CH_2)NCH_2CH{=}CH_2\}(CO)(P^iPr_3)$ (4)

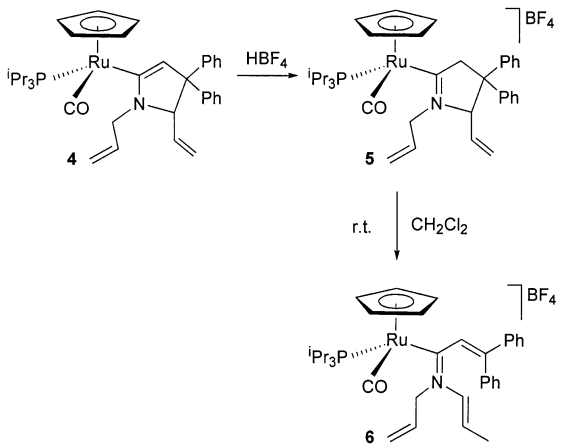
Ru−P	2.3274(11)	N−C(16)	1.482(4)
Ru−C(1)	2.077(4)	N−C(19)	1.429(4)
Ru−C(31)	2.266(3)	C(1)−C(2)	1.346(4)
Ru−C(32)	2.272(3)	C(2)−C(3)	1.522(5)
Ru−C(33)	2.258(4)	C(3)−C(16)	1.555(5)
Ru−C(34)	2.246(4)	C(16)−C(17)	1.496(5)
Ru−C(35)	2.261(4)	C(17)−C(18)	1.312(5)
Ru−C(36)	1.796(4)	C(19)−C(20)	1.446(6)
O−C(36)	1.180(4)	C(20)−C(21)	1.271(6)
N−C(1)	1.430(4)		
P−Ru−C(1)	89.83(10)	N−C(16)−C(3)	103.0(3)
P−Ru−C(36)	87.84(12)	N−C(16)−C(17)	111.7(3)
P−Ru−M[a]	129.9	C(1)−N−C(16)	109.1(3)
C(1)−Ru−C(36)	99.65(15)	C(1)−N−C(19)	124.9(3)
C(1)−Ru−M	118.1	C(1)−C(2)−C(3)	113.6(3)
C(36)−Ru−M	122.9	C(2)−C(3)−C(16)	99.2(3)
Ru−C(1)−N	130.1(2)	C(3)−C(16)−C(17)	113.6(3)
Ru−C(1)−C(2)	122.7(3)	C(16)−N−C(19)	116.2(3)
N−C(1)−C(2)	107.1(3)		

[a] M is the midpoint of the C(31)−C(35) Cp ligand.

This appears to be a consequence of the presence of an allyl substituent at the nitrogen atom.

The heterocycle contains a double bond between the C(1) and C(2) atoms (1.346(4) Å). The Ru−C(1) distance (2.077(4) Å), which is about 0.2 Å longer than the Ru−C(1) bond length in **3**, compares well with those found in the alkenyl complexes $[Ru\{(E)\text{-}CH{=}CHCMe_3\}Cl(CO)(Me_2Hpz)(PPh_3)_2]$ (2.063(7) Å)[22a] and $[Ru\{(E)\text{-}CH{=}CHCMe_3\}(CO)\{NH{=}C(Me)(Me_2Hpz)\}(PPh_3)_2]PF_6$ (2.067(8) Å).[22b] This 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)[6d] and $[Ru(\eta^5\text{-}C_5H_5)\{C(PHPh_2){=}C{=}CPh_2\}(CO)(P^iPr_3)]BF_4$ (2.139(5) Å),[22c] where a Ru−C(sp^2) single bond is proposed to exist. The N−C(1) (1.430(4) Å) and N−C(19) (1.429(4) Å) distances are statistically identical. They are about 0.07 Å longer than the N−C(1) distance in **3** and support the existence of N−C single bonds between the nitrogen and the C(1) and C(19) atoms. The N−C(16) bond length (1.482(4) Å) agrees well with a N−C(sp^3) single bond.

Scheme 3



The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **4** in benzene-d_6 are consistent with the structure shown in Figure 2. In the ^1H NMR spectrum the most noticeable resonance is a singlet at 4.50 ppm, corresponding to the C(2)-H proton. In the $^{13}C\{^1H\}$ NMR spectrum the C(1) atom displays a doublet at 156.5 ppm, with a C−P coupling constant of 12.7 Hz, while the C(2), C(16), and C(3) atoms give rise to singlets at 115.4, 73.2, and 64.1 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 68.6 ppm.

Complex **4** reacts with tetrafluoroboric acid. The addition of 1.0 equiv of this acid to a diethyl ether solution of **4** gives the cationic derivative $(R_{Ru},S_C\text{-}S_{Ru},R_C)\text{-}[Ru(\eta^5\text{-}C_5H_5)\{C{=}N(CH_2CH{=}CH_2)CH(CH{=}CH_2)\text{-}CPh_2CH_2\}(CO)(P^iPr_3)BF_4$ (**5**), which was isolated as a yellow solid in 85% yield. Complex **5**, which is an isomer of **2**, is the result of the addition of the proton of the acid to the C(2) atom of **4** (Scheme 3).

The crystallization of the yellow solid in methanol−toluene affords crystals suitable for an X-ray diffraction study. Figure 3 shows a view of the structure of the cation of the enantiomer R_{Ru},S_c of **5**. Selected bond distances and angles are collected in Table 3. The geometry around the ruthenium atom is like that of **4**, i.e., close to octahedral with the cyclopentadienyl ligand occupying one face. In this case, the heterocycle experiences steric hindrance with both the carbonyl and the phosphine ligands. This is revealed by the angles C(1)−Ru−C(27) (94.19(18)°) and P−Ru−C(1) (96.25(12)°), which are greater than the ideal value of 90°. As a consequence of the opening of these angles, the P−Ru−C(27) angle is reduced to 86.00(16)°.

The Ru−C(1) distance (2.010(4) Å) is about 0.12 Å longer than the Ru−C(1) bond length in **3** and only 0.06 Å shorter than the Ru−C(1) distance in **4**. The Ru−C(1) distance in **5** compares well with the Ru−C distance in the azoniabutadienyl derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NEt_2\}(CO)(P^iPr_3)]BF_4$ (2.063(6) Å), where the contribution of the α,β-unsaturated aminocarbene resonance form to the structure of the complex is not relevant.[8] The N−C(1) distance (1.317(4) Å) is statiscally

(22) (a) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988. (b) López, J.; Santos, A.; Romero, A.; Echavarren, A. M. *J. Organomet. Chem.* **1993**, *443*, 221. (c) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1998**, *17*, 5434.

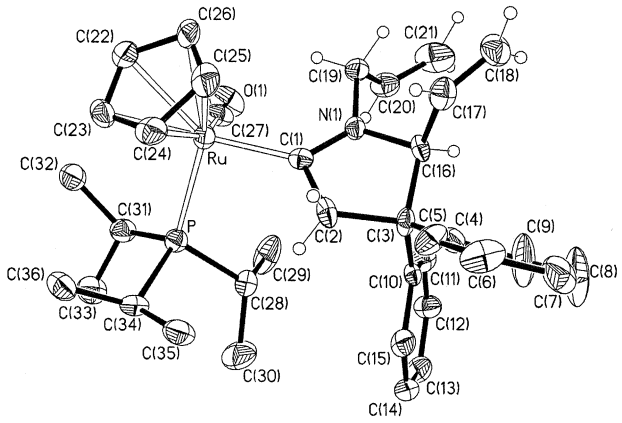


Figure 3. Molecular diagram of the cation of the enantiomer R_{Ru},S_C [Ru(η^5-C_5H_5){C(=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)CPh$_2$CH$_2$}(CO)(P^{i}Pr$_3$)]BF$_4$ (**5**). Thermal ellipsoids are shown at 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Enantiomer R_{Ru},S_C [Ru(η^5-C_5H_5){C(=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)CPh$_2$CH$_2$}(CO)(P^{i}Pr$_3$)]BF$_4$ (5)

Ru−P	2.3434(13)	N(1)−C(16)	1.492(5)
Ru−C(1)	2.010(4)	N(1)−C(19)	1.468(5)
Ru−C(22)	2.257(4)	C(1)−C(2)	1.525(6)
Ru−C(23)	2.245(4)	C(2)−C(3)	1.557(6)
Ru−C(24)	2.246(4)	C(3)−C(16)	1.547(6)
Ru−C(25)	2.247(5)	C(16)−C(17)	1.488(6)
Ru−C(26)	2.231(4)	C(17)−C(18)	1.305(6)
Ru−C(27)	1.837(4)	C(19)−C(20)	1.476(6)
N(1)−C(1)	1.317(4)	C(20)−C(21)	1.313(6)
P−Ru−C(1)	96.25(12)	N(1)−C(1)−C(2)	104.3(4)
P−Ru−C(27)	86.00(16)	N(1)−C(16)−C(17)	108.5(4)
P−Ru−M[a]	127.5	C(1)−N(1)−C(16)	116.0(4)
C(1)−Ru−C(27)	94.19(18)	C(1)−N(1)−C(19)	126.7(4)
C(1)−Ru−M	117.3	C(1)−C(2)−C(3)	108.0(4)
C(27)−Ru−M	126.7	C(2)−C(3)−C(16)	98.7(4)
Ru−C(1)−N	131.1(3)	C(3)−C(16)−C(17)	116.4(4)
Ru−C(1)−C(2)	123.6(3)	C(16)−N(1)−C(19)	116.0(3)

[a] M is the midpoint of the C(22)−C(26) Cp ligand.

identical with the length of the C−N double bond in the above-mentioned azoniabutadienyl derivative (1.306(7) Å) and about 0.17 Å shorter than the N−C(19) (1.468(5) Å) and N−C(16) (1.492(5) Å) distances, which are statistically identical and agree well with C(sp^3)−N single bonds. The angles around the N atom are between 116.0(4)° and 126.7(4)°. The C(1)−C(2) (1.525(6) Å), C(2)−C(3) (1.557(6) Å), and C(3)−C(16) (1.547(6) Å) distances are consistent with C(1)−C(2), C(2)−C(3), and C(3)−C(16) single bonds.[23]

In the solid state, complex **5** is stable at room temperature. However in dichloromethane as solvent, it evolves to afford a new isomer (vide infra). As a consequence, the ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{1}H NMR spectra of **5** were recorded at −80 °C. At this temperature, the ^{31}P{^{1}H} NMR spectrum contains a singlet at 61.3 ppm. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonances are those corresponding to the carbon atoms of the five-membered skeleton of the heterocycle. The C(1) atom gives rise to a doublet at 243.5 ppm, with a C−P coupling constant of 9.6 Hz, while the C(16), C(2), and C(3) atoms display singlets at 75.5, 56.1, and 55.1 ppm, respectively. The ^{1}H NMR spectrum is complex and uninformative; according to the ^{1}H−^{13}C HETCOR NMR spectrum, the resonances corresponding to the CH$_2$ protons of the five membered hetero-ring are observed at 5.17 and 4.20 ppm.

The isomerization of **5** affords the *N*-allyl-4-azonia-1,3,5-heptatrienyl derivative [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH=CHCH$_3$)CH$_2$CH=CH$_2$}(CO)(P^{i}Pr$_3$)]BF$_4$ (**6** in Scheme 3). The process involves the opening of the five-membered hetero-ring, formally as a consequence of the split of the C(3)−C(16) bond, along with a proton transfer from C(2) to C(18). In dichloromethane at room temperature, the transformation of **5** into **6** is quantitative after 2 h.

During the isomerization of **5** into **6**, the formation of spectroscopically detectable concentrations of **2** was not observed, suggesting that **6** is more stable than **2** from a thermodynamic point of view. In accordance with this, in dichloromethane at room temperature, the transformation of **6** into **2** does not occur, even after a week. However, the isomerization of **2** into **6** is also not observed. In agreement with the kinetic inertia of **2**, several studies have indicated that the isomerization of *N*,*N*-allylamines into the corresponding enamines usually requires the presence of t-BuOK, LDA, or KH as catalysts.[24] Such a 1,3 sigmatropic rearrangement has been also observed in a byproduct during the ring-closing metathesis of *N*,*N*-diallyltosylamide catalyzed by the complex [*p*-(cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)]-BF$_4$.[25]

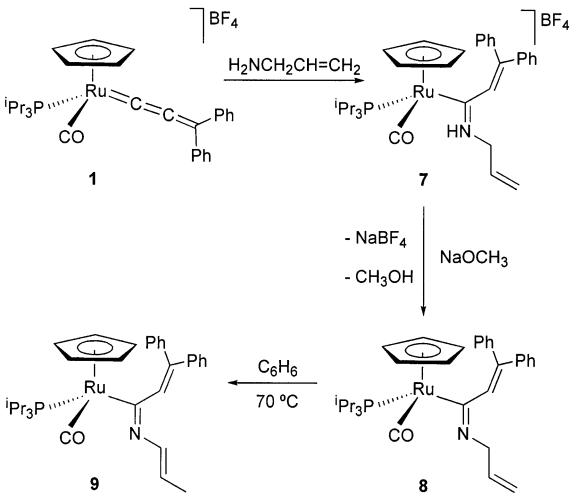
Complex **6** was isolated as a yellow solid. The presence of the *N*-allyl-4-azonia-1,1-diphenyl-1,3,5-heptatrien-3-yl ligand is strongly supported by the IR and the ^{1}H and ^{13}C{^{1}H} NMR spectra. The IR spectrum in Nujol shows bands at 1640 and 1599 cm^{-1}, corresponding to the C−N and C−C double bonds. In the ^{1}H NMR spectrum in dichloromethane-d_2, the resonance due to the protons of the methyl group appears at 1.92 ppm, as a double doublet with H−H coupling constants of 6.9 and 1.5 Hz, whereas the resonance corresponding to the olefinic =CHCH$_3$ proton is observed at 6.08 ppm, as a doublet quartet, by spin coupling with the methyl protons and the NCH= proton. The value of the coupling constant corresponding to the latter (13.8 Hz) is consistent with a *trans* disposition of the methyl group and nitrogen atom at the carbon−carbon double bond. According to the ^{1}H−^{1}H COSY and ^{1}H−^{13}C HETCOR spectra, the resonance corresponding to the NCH= proton lies at 7.06 ppm, masked between the phenyl resonances. The allyl substituent displays resonances at 5.65 (CH=), 5.26 and 4.72 (CH$_2$), and 5.23−5.14 (=CH$_2$) ppm. The resonance due to the CH= proton of the CH=CPh$_2$ unit appears at 6.79 ppm, as a singlet. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the propenyl group of the azoniaheptatrienyl skeleton are observed at 137.1 (NCH=), 120.9 (=

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

(24) (a) Sauer, J.; Prahl, H. *Tetrahedron Lett.* **1966**, 2863. (b) Riviere, M.; Lattes, A. *Bull. Soc. Chim. Fr.* **1968**, 4430. (c) Sauer, J.; Prahl, H. *Chem. Ber.* **1969**, *102*, 1917. (d) Beeken, P.; Fowler, F. W. *J. Org. Chem.* **1980**, *45*, 1336. (e) Eish, J. J.; Shah, J. H. *J. Org. Chem.* **1991**, *56*, 2955.

(25) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847.

Scheme 4



*C*HCH$_3$), and 15.5 (CH$_3$) ppm, as singlets, whereas those corresponding to the allyl substituent appear at 128.5 (CH═), 121.8 (═CH$_2$), and 57.7 (NCH$_2$) ppm also as singlets. The Ru−C carbon atom gives rise to a doublet at 247.8 ppm, with a C−P coupling constant of 9.4 Hz, while the resonances due to CH and CPh$_2$ carbon atoms of the CH═CPh$_2$ unit are observed at 138.2 and 138.9 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 63.1 ppm.

2. Allylamine. Similarly to diallylamine, one of the N−H bonds of allylamine is added to the C$_\alpha$−C$_\beta$ double bond of the allenylidene ligand of **1** to afford the secondary 4-azonia-1,3,6-heptatrienyl derivative [Ru(η^5-C$_5$H$_5$){C(CH═CPh$_2$)═NH(CH$_2$CH═CH$_2$)}(CO)(P^{i}Pr$_3$)]BF$_4$ (**7** in Scheme 4), which was isolated as a yellow solid in 86% yield.

The IR spectrum of **7** in Nujol shows a ν(NH) band at 3316 cm^{-1}, along with ν(C═N) and ν(C═C) bands at 1613 and 1545 cm^{-1}. In the ^{1}H NMR spectrum in chloroform-*d*, the most noticeable resonances are those due to the ═NH proton and the ═CH hydrogen atom of the CH═CPh$_2$ unit, which are observed as singlets at 9.92 and 6.55 ppm, respectively. The resonances corresponding to the allyl group appear at 5.91 (CH═), 5.28 and 5.27 (═CH$_2$), and 4.37 (CH$_2$). In the ^{13}C{^{1}H} NMR spectrum the C$_\alpha$ atom displays a doublet at 243.3 ppm, with a C−P coupling constant of 10.6 Hz, while the olefinic carbon atoms of the unit CH═CPh$_2$ give rise to singlets at 141.3 (═CPh$_2$) and 133.8 (═CH) ppm. The allyl resonances are observed at 129.0 (CH═), 121.3 (═CH$_2$), and 55.1 (NCH$_2$) ppm, also as singlets. The ^{31}P-{^{1}H} NMR spectrum shows a singlet at 63.1 ppm.

According to the behavior observed for **2** and those previously reported for the azoniabutadienyl ligands stabilized by the [Ru(η^5-C$_5$H$_5$)(CO)(P^{i}Pr$_3$)]$^+$ metallic fragment,[8] at first glance, the 4-azonia-1,3,5-heptatrienyl ligand of **7** could have three Brönsted acidic centers: the NH group, the ═CH− of the CH═CPh$_2$ moiety, and the CH$_2$− unit of the allyl group. However, the addition of 2.0 equiv of sodium methoxide to a tetrahydrofuran solution of **7** selectively deprotonates the nitrogen atom. The reaction affords the neutral 4-aza-1,3,6-heptatrienyl complex Ru(η^5-C$_5$H$_5$){C(CH═CPh$_2$)═NCH$_2$CH═CH$_2$}(CO)(P^{i}Pr$_3$) (**8** in Scheme 4), which was isolated as a yellow solid in 70% yield. The formation of metallaheterocyclic or heterocyclic compounds related to **3** and **4** was not observed.

The behavior of **7** is the same as that previously reported for secondary azoniabutadienyl derivatives, where the deprotonation at the nitrogen atom is favored with regard to the deprotonation at the CH═CPh$_2$ unit. The comparison of the behavior of **7** with that of **2** indicates that in secondary 4-azonia-1,3,6-heptatrien-3-yl derivatives the deprotonation at the nitrogen atom is more favored than the deprotonation at the NCH$_2$− carbon atom of the allyl group. So, since the comparison of the behavior of **2** with that of the previously reported tertiary azoniabutadienyl compounds shows that the deprotonation at the NCH$_2$− carbon atom is more favored than the deprotonation at the CH═CPh$_2$ unit, the results here reported reveal that in 4-azonia-1,3,6-heptatrien-3-yl ligands the Brönsted acidity decreases in the sequence NH > NCH$_2$ > CH═CPh$_2$.

The most noticeable feature in the IR spectrum of **8** in Nujol is the absence of any ν(NH) band. The ν(C═N) and ν(C═C) vibrations are observed at 1599 and 1541 cm^{-1}. The ^{1}H NMR spectrum in benzene-d_6 shows the CH═ resonance of the CH═CPh$_2$ unit at 6.85 ppm, as a singlet, whereas the resonances corresponding to the allyl unit are observed at 6.25 (CH═), 5.31 and 5.12 (═CH$_2$), and 4.47 and 4.25 (CH$_2$) ppm. The ^{13}C{^{1}H} NMR spectrum shows a doublet at 195.4 with a C−P coupling constant of 11.5 Hz, corresponding to the C$_\alpha$ atom. The resonances due to the CH═ and ═CPh$_2$ carbon atoms of the CH═CPh$_2$ unit are observed as singlets at 141.2 and 141.6 ppm, respectively. The allyl carbon atoms also display singlets at 139.0 (CH═), 113.8 (═CH$_2$), and 60.9 (NCH$_2$) ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 68.9 ppm.

In solution complex **8** is unstable and isomerizes into the conjugated 4-aza-1,3,5-heptatrienyl derivative Ru(η^5-C$_5$H$_5$){C(CH═CPh$_2$)═NCH═CHCH$_3$}(CO)(P^{i}Pr$_3$) (**9** in Scheme 4). In benzene-d_6 at 70 °C, the transformation is almost quantitative after 24 h. The formation of **9** involves a 1,3-hydrogen shift within the allyl unit of **8**. In this context, we note that the treatment of secondary allylamines with sodium-alkyl reagents promotes the deprotonation of the nitrogen atom, to afford sodium amides where the allyl group has undergone a 1,3-sigmatropic rearrangement.[26] In contrast the treatment of secondary allylamines with lithium-alkyl reagents promotes a double deprotonation, which takes place at both the nitrogen atom and the ═CH$_2$ carbon atom of the allyl group. In this case, the deprotonation is not accompanied by the isomerization of the allyl chain.[27]

Complex **9** was isolated at −78 °C from a saturated pentane solution, as yellow microcrystals. In the absence of the solvent, the crystals are unstable and evolve into a yellow oil. Crystals containing two benzene-d_6 molecules and suitable for an X-ray diffraction study were obtained in a NMR tube, from a benzene-d_6 solution. Figure 4 shows a view of the structure of this compound, and selected bond distances and angles are collected in Table 4.

(26) Andrews, P. C.; Calleja, S. M.; Maguire, M.; Nichols, P. J. *Eur. J. Inorg. Chem.* **2002**, 1583.

(27) (a) Yus, M.; Foubelo, F.; Falvello, L. R. *Tetrahedron: Asymmetry* **1995**, *6*, 2081. (b) Andrews, P. C.; Calleja, S. M.; Maguire, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3640.

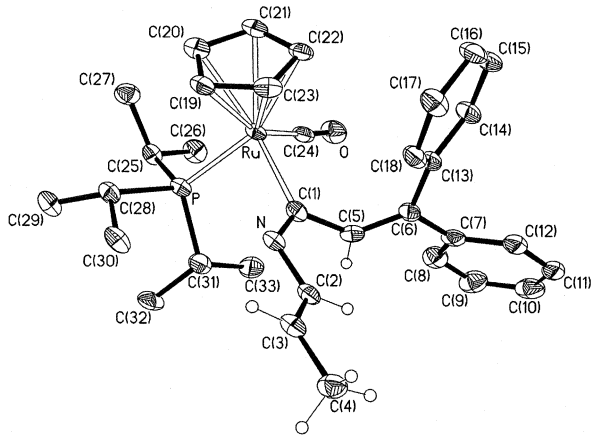


Figure 4. Molecular diagram of the complex Ru(η^5-C_5H_5)-{C(CH=CPh$_2$)=NCH=CHCH$_3$}(CO)(P^{i}Pr$_3$) (**9**). Thermal ellipsoids are shown at 50% probability.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Complex Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NCH=CHCH$_3$}(CO)(P^{i}Pr$_3$) (9)

Ru−P	2.3245(11)	Ru−C(24)	1.831(4)
Ru−C(1)	2.071(4)	N−C(1)	1.303(4)
Ru−C(19)	2.276(4)	N−C(2)	1.404(5)
Ru−C(20)	2.274(4)	C(1)−C(5)	1.491(5)
Ru−C(21)	2.261(4)	C(2)−C(3)	1.331(5)
Ru−C(22)	2.251(4)	C(5)−C(6)	1.343(5)
Ru−C(23)	2.265(4)		
P−Ru−C(1)	92.02(10)	Ru−C(1)−C(5)	118.6(3)
P−Ru−C(24)	94.47(12)	N−C(1)−C(5)	121.2(3)
P−Ru−M[a]	126.0	N−C(2)−C(3)	122.2(4)
C(1)−Ru−C(24)	91.79(15)	C(1)−N−C(2)	118.9(3)
C(1)−Ru−M	118.1	C(1)−C(5)−C(6)	129.8(4)
C(24)−Ru−M	125.3	C(2)−C(3)−C(4)	124.1(4)
Ru−C(1)−N	120.1(3)		

[a] M is the midpoint of the C(22)−C(26) Cp ligand.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying a face. The angles formed by the triisopropylphosphine, the carbonyl, and the azaheptatrienyl ligands are between 91.79(15)° (C(1)−Ru−C(24)) and 94.47(12)° (P−Ru−C(24)), indicating that, in this case, the ligands do not experience a significant steric hindrance.

The azaheptatrienyl ligand coordinates to the ruthenium center by the C(1) atom, which is disposed in α position with regard to the nitrogen. The Ru−C(1) distance (2.071(4) Å) is statiscally identical with the Ru−C(1) bond length in **4** and consistent with a Ru−C(sp^2) single bond. The bond lengths in the sequence C(3)−C(2)−N−C(1)−C(5)−C(6)(1.331(5), 1.404(5), 1.303(4), 1.491(5), and 1.343(5) Å) support the 4-aza-1,3,5-heptatrienyl formulation. Both C(2)−C(3) and N−C(1) double bonds show an *E* configuration.

The ^{1}H NMR spectrum of **9** in chloroform-*d* agrees well with the structure shown in Figure 4. The methyl group of the azaheptatrienyl skeleton displays a doublet at 1.70 ppm, with a H−H coupling constant of 6.9 Hz, whereas the C(3)H=C(2)H unit gives rise to a doublet at 7.38 (C(2)H) ppm and a double quartet at 5.89 (C(3)H) ppm, with a *trans* H−H coupling constant of 13.2 Hz. The resonance corresponding to the C(5)H proton appears at 7.03 ppm, as a singlet. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonances are a doublet (J(C−P) = 12.9 Hz) at 206.1 ppm and five singlets at 144.4, 142.3, 140.6, 118.5, and 15.3 ppm, corresponding to the C(1), C(6), C(2), C(5), C(3), and C(4) carbon atoms, respectively, of the azaheptatrienyl skeleton. The ^{31}P-{^{1}H} NMR spectrum contains a singlet at 69.2 ppm.

Concluding Remarks

We have recently reported that, from the organometallic and organic synthesis point of view, the potentiality of the transition metal allenylidene compounds can become greater than that of the carbene complexes of type L$_n$M=CR$_2$.[11] This paper gives new evidence pointing in this direction. The hydroamination of the allenylidene ligand of [Ru(η^5-C_5H_5)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ with allylamines increases the number of reactive centers of the starting complex, including the carbonyl group, and generates 4-azonia-1,3,6-heptatrienyl species with three alternative Brönsted acidic points. As a consequence of the versatile chemistry of this new type of species, the novel metallaheterocycle Ru(η^5-C_5H_5)[=C(CH=CPh$_2$)=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)C=O}(P^{i}Pr$_3$), the heterocycles Ru(η^5-C_5H_5){C=CHCPh$_2$CH(CH=CH$_2$)NCH$_2$CH=CH$_2$}(CO)(P^{i}Pr$_3$) and [Ru(η^5-C_5H_5){C=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)-CPh$_2$CH$_2$}(CO)(P^{i}Pr$_3$)BF$_4$, and the conjugated azaheptatrienyl derivative Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NCH=CHCH$_3$}(CO)(P^{i}Pr$_3$) have been discovered and fully characterized, including X-ray diffraction analysis.

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.[21] In the NMR spectra, chemical shifts are expressed in ppm downfield from Me$_4$Si (^{1}H and ^{13}C) and 85% H$_3$PO$_4$ (^{31}P). Coupling constants, *J*, are given in hertz. The atom labels for complexes **3**, **4**, **5**, and **9** are the same as those in Figures 1−4, respectively.

Preparation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH$_2$CH=CH$_2$)$_2$}(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**) (200 mg, 0.32 mmol) in 6 mL of dichloromethane was treated with diallylamine (43.5 μL, 0.352 mmol). The mixture was stirred for 15 min at room temperature, and the solution became yellow. The solvent was removed in vacuo, and the residue was treated with 6 mL of diethyl ether at −70 °C to afford a pale yellow suspension. The solution was decanted, and the solid was washed twice with diethyl ether and dried in vacuo. Yield: 220 mg (94%). Anal. Calcd for $C_{36}H_{44}BF_4NOPRu$: C, 59.34; H, 6.50; N, 1.92. Found: C, 59.10; H, 6.65; N, 1.97. IR (Nujol, cm^{-1}): ν(CO) 1936(vs), ν(C=N) and ν(C=C) 1639(m) and 1598(w), ν-(BF$_4$) 1105(br). ^{1}H NMR (300 MHz, 293 K, CDCl$_3$): δ 7.51−7.05 (m, 10H, Ph), 6.73 (s, 1H, =CH), 5.81 (m, 1H, C*H*=CH$_2$), 5.70 (m, 1H, C*H*=CH$_2$), 5.60 (d, $^3J_{H-H}$ = 17.1, 1H, =CH$_2$, H *cis* to NCH$_2$), 5.54 (d, $^3J_{H-H}$ = 10.5, 1H, =CH$_2$, H *trans* to NCH$_2$), 5.28 (d, $^3J_{H-H}$ = 10.2, 1H, =CH$_2$, H *trans* to NCH$_2$), 5.10 (d, $^3J_{H-H}$ = 16.5, 1H, =CH$_2$, H *cis* to NCH$_2$), 4.83 (m, 1H, NCH$_2$), 4.78 (m, 1H, NCH$_2$), 4.70 (s, 5H, Cp), 4.64 (m, 1H, NCH$_2$), 4.36 (m, 1H, NCH$_2$), 2.31 (m, 3H, PC*H*CH$_3$), 1.21 (dd, 18H, 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 244.9 (d, J_{P-C} = 9.4, Ru-C$_\alpha$), 204.3 (d, J_{P-C} = 18.2, CO), 141.3 (s, =CPh$_2$), 138.7 and 138.2 (both s, C$_{ipso}$ Ph), 137.9 (s, =CH), 130.2, 129.3, 128.4, 128.3 (all s, Ph), 128.7 and 128.6 (both s, CH=), 123.3 and 123.1 (both s, =

CH_2), 86.4 (s, Cp), 64.4 and 57.8 (both s, NCH_2), 28.6 (d, J_{P-C} = 23.2, P*C*HCH$_3$), 20.1 and 19.9 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 63.1 (s).

Deprotonation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N-(CH$_2$CH=CH$_2$)$_2$}(CO)(P^{i}Pr$_3$)]BF$_4$ (2) with Sodium Methoxide. Formation of the Isomeric Mixture (R_{Ru},R_C-S_{Ru},S_C)-Ru(η^5-C_5H_5)[=C(CH=CPh$_2$)=N(CH$_2$CH=CH$_2$)CH-(CH=CH$_2$)C=O}(P^{i}Pr$_3$) (3) and (R_{Ru},S_C- S_{Ru},R_C)-Ru(η^5-C_5H_5){C=CHCPh$_2$CH(CH=CH$_2$)NCH$_2$CH=CH$_2$}(CO)-(P^{i}Pr$_3$) (4). A pale yellow solution of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH$_2$CH=CH$_2$)$_2$}(CO)(P^{i}Pr$_3$)] (**2**) (400 mg, 0.55 mmol) in 6 mL of tetrahydrofuran was treated with sodium methoxide (59.8 mg, 1.09 mmol). The mixture was stirred for 15 min at room temperature, and the color changed to deep red. The solvent was removed in vacuo. Dichloromethane was added, and the suspension was filtered to eliminate sodium tetrafluoroborate. The solvent was removed in vacuo, and the residue was treated with 6 mL of pentane to afford an orange suspension. The solution was decanted, and the solid was washed twice with pentane and dried in vacuo. The solid obtained was a mixture of two isomers, Ru(η^5-C_5H_5)[=C(CH=CPh$_2$)=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)C=O}(P^{i}Pr$_3$) (**3**) and Ru-(η^5-C_5H_5){C=CHCPh$_2$CH(CH=CH$_2$)NCH$_2$CH=CH$_2$}(CO)(P^i-Pr$_3$) (**4**) in a 1:1 molar ratio. Yield: 282 mg (80%). Washing the mixture several times with pentane leads to the separation of the two isomers. Complex **4** was obtained as a yellow solid and complex **3** was obtained as pure orange crystals from a saturated solution of the mixture in pentane at −20 °C.

Spectroscopic data for 3:[28] IR (Nujol, cm^{-1}): ν(C=C) 1635, ν(CO) 1581 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.41−7.02 (m, 10H, Ph), 5.73 (ddd, 1H, $J_{H^{16}-H^{17}}$ = 8.7, $J_{H^{17}-H^{18A}}$ = 10.2, $J_{H^{17}-H^{18B}}$ = 17.1, CH^{17}=), 5.52 (dddd, 1H, $J_{HH^{20}-H^{19A}}$ = 5.7, $J_{H^{20}-H^{19B}}$ = 8.7, $J_{H^{20}-H^{21A}}$ = 11.1, $J_{H^{20}-H^{21B}}$ = 17.7, C*H*^{20}=CH$_2$), 5.30 (dd, 1H, $J_{H^{21A}-H^{20}}$ = 11.1, $J_{H^{21A}-H^{21B}}$ = 1.8, CH=C*H*^{21A}, H trans to NCH$_2$), 5.24 (dd, 1H, $J_{H^{21B}-H^{20}}$ = 17.7, $J_{H^{21A}-H^{21B}}$ = 1.8, CH=C*H*^{21B}, H cis to NCH$_2$), 4.87 (s, 5H, Cp), 4.84 (d, 1H, $J_{H^{18A}-H^{17}}$ = 10.2, CH=C*H*^{18A} H *cis* to H^{17}), 4.82 (d, 1H, $J_{H^{18B}-H^{17}}$ = 17.1, CH=C*H*^{18B} H *trans* to H^{17}), 4.64 (dd, 1H, $J_{H^{19A}-H^{19B}}$ = 14.2, $J_{H^{19A}-H^{20}}$ = 5.7, NCHC*H*^{19A}), 4.02 (d, $J_{H^{16}-H^{17}}$ = 8.7, OCCH^{16}), 3.43 (dd, $J_{H^{19A}-H^{19B}}$ = 14.2, $J_{H^{19B}-H^{20}}$ = 8.7, NCHC*H*^{19B}), 1.87 (m, 3H, PC*H*CH$_3$), 1.07 (dd, 9H, J_{H-H} = 7.8, J_{H-P} = 12.9, PCHC*H*$_3$), 1.03 (dd, 9H, J_{H-H} = 7.5, J_{H-P} = 13.2, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K plus APT plus HETCOR): δ 262.2 (d, J_{P-C} = 11.5, Ru−C^1), 259.8 (d, J_{P-C} = 14.3, CO), 144.8, 140.5 (both s, C_{ipso}), 137.6 (s, *C*^{2}H=CPh$_2$), 133.4 (s, *C*^{20}H=CH$_2$), 132.8 (s, *C*^{18}H=CH$_2$), 130.7, 129.3, 129.4, 128.8, 128.3, 128.0 (all s, CPh), 129.4 (s, =*C*^{3}Ph$_2$), 119.8 (s, CH=*C*^{21}H$_2$), 119.1 (s, CH=*C*^{17}H$_2$), 91.9 (s, C^{16}H), 85.9 (s, Cp), 53.1 (s, NC^{19}H$_2$), 28.4 (d, J_{P-C} = 20.3, P*C*HCH$_3$), 20.5 and 20.4 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 67.9 (s). MS (FAB$^+$): *m*/*z* 643 (M$^+$ + 2H).

Spectroscopic data for 4:[28] IR (Nujol, cm^{-1}): ν(CO) 1910 (s), ν(C=C) 1639, 1592, and 1505. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.44−7.04 (m, 10H, Ph), 6.24 (dddd, 1H, $J_{H^{20}-H^{21A}}$ = 16.7, $J_{H^{20}-H^{21B}}$ = 9.7, $J_{H^{20}-H^{19B}}$ = 6.7, $J_{H^{20}-H^{19A}}$ = 3.9, C*H*^{20}=CH$_2$), 5.55 (ddd, 1H, $J_{H^{17}-H^{18A}}$ = 17.3, $J_{H^{17}-H^{18B}}$ = $J_{H^{17}-H^{16}}$ = 9.9, CH^{17}=), 5.35 (dd, 1H, $J_{H^{21A}-H^{20}}$ = 16.7, $J_{H^{21A}-H^{21B}}$ = 1.8, =CH^{21A}, H *cis* to NCH$_2$), 5.22 (dd, 1H, $J_{H^{21B}-H^{20}}$ = 9.7, $J_{H^{21A}-H^{21B}}$ = 1.8, =CH^{21B}, H *trans* to NCH$_2$), 4.94 (dd, 1H, $J_{H^{18A}-H^{17}}$ = 17.3, $J_{H^{18A}-H^{18B}}$ = 2.2, =CH^{18A}, H *trans* to H^{17}), 4.90 (s, 5H, Cp), 4.85 (dd, 1H, $J_{H^{18B}-H^{17}}$ = 9.9, $J_{H^{18A}-H^{18B}}$ = 2.2, =CH^{18B}, H *cis* to H^{17}), 4.75 (dd, 1H, $J_{H^{19A}-H^{19B}}$ = 15.2, $J_{H^{19A}-H^{20}}$ = 3.9, NCH*H*^{19A}), 4.69 (d, 1H, $J_{H^{16}-H^{17}}$ = 9.9, CH^{16}), 4.50 (s, 1H, =CH^2), 3.78 (dd, $J_{H^{19A}-H^{19B}}$ = 15.2, $J_{H^{19B}-H^{20}}$ = 6.7, NCH*H*^{19B}). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, plus APT, plus HETCOR, C_6D_6): δ 209.7 (d, J_{P-C} = 21.7, CO), 156.5 (d, J_{P-C} = 12.7, Ru-C^1), 150 and 148.9 (both s, C_{ipso}), 139.2 (s, C^{20}H=), 138.1 (s, C^{17}H=), 130.5, 128.3, 127.4, 127.1, 126.4, 126.0, 125.2 (all s, C_{Ph}), 116.8 (s, =C^{18}H$_2$), 115.7 (s, =C^{21}H$_2$), 115.4 (s, C^{2}H=), 86.4 (s, Cp), 73.2 (s, NC^{16}H), 64.1 (s, C^{3}Ph$_2$), 53.7 (s, NC^{19}H$_2$), 26.6 (d, J_{P-C} = 22.6, P*C*HCH$_3$), 20.9 and 19.8 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 68.6 (s). MS (FAB$^+$): *m*/*z* 642 (M$^+$ + H).

Preparation of (R_{Ru},S_C- S_{Ru},R_C)-[Ru(η^5-C_5H_5){C=N-(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)CPh$_2$CH$_2$}(CO)(P^{i}Pr$_3$)BF$_4$ (5). An orange suspension of Ru(η^5-C_5H_5){C=CHCPh$_2$CH(CH=CH$_2$)NCH$_2$CH=CH$_2$}(CO)(P^{i}Pr$_3$) (**4**) (110 mg, 017 mmol) in 6 mL of diethyl ether was treated with tetrafluoroboric acid (23.5 μL, 017 mmol). After 5 min at room temperature a yellow solid was formed. The mixture was stirred for 15 min. The solution was decanted, and the solid was washed twice with diethyl ether and dried in vacuo. Yield: 106 mg (85%). Anal. Calcd for $C_{36}H_{47}NOPRuBF_4$: C, 59.34; H, 6.50; N, 1.92. Found: C, 58.86; H, 6.08, N, 2.10. IR (Nujol, cm^{-1}): ν(CO) 1947 (s), ν-(C=C) and ν(C=N) 1642 and 1593. ^1H NMR (300 MHz, CD_2Cl_2, 193 K): δ 7.37−7.05 (m, 10H, Ph), 5.94 (m, 1H, CH^{20}=), 5.73 (br, 1H, =CH^{17}), 5.71 (br, 1H, =CH$_2^{21}$ or =CH$_2^{18}$), 5.47 (br, 1H, NCH^{16}), 5.46 (br, 1H, =CH$_2^{21}$ or =CH$_2^{18}$), 5.34 (s, 5H, Cp), 5.17 (br, 1H, CH*H*^{2A}), 4.20 (m, 1H, CH*H*^{2B}), 3.92 (m, 1H, NC^{19}H$_2$), 3.81 (m, 1H, NC^{19}H$_2$), 2.16 (br, 3H, PC*H*CH$_3$), 1.10 (br, 18H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 193 K plus APT plus HETCOR): δ 243.5 (d, J_{P-C} = 9.6, Ru-C^1), 204.8 (d, J_{P-C} = 17.9, Ru-CO), 143.9 and 141.1 (both s, C_{ipso}), 129.7 and 129.1 (both s, C^{20}H= and C^{17}H=), 128.4, 128.2, 128.0, 127.3, 126.8, and 126.4 (all s, C_{Ph}), 124.6 and 124.3 (both s, =C^{18}H$_2$ and =C^{21}H$_2$), 75.5 (s, NC^{16}H), 65.6 (s, NC^{19}H$_2$), 56.1 (s, C^{2}H$_2$), 55.1 (s, C^{3}Ph$_2$), 18.8 (br, P*C*HCH$_3$), 14.8 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 193 K): δ 61.3 (s).

Preparation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=N(CH=CHCH$_3$)CH$_2$CH=CH$_2$}(CO)(P^{i}Pr$_3$)]BF$_4$ (6). A yellow solution of [Ru(η^5-C_5H_5){C=N(CH$_2$CH=CH$_2$)CH(CH=CH$_2$)-CPh$_2$CH$_2$}(CO)(P^{i}Pr$_3$)BF$_4$ (**5**) (150 mg, 121 mmol) in 5 mL of dichloromethane was stirred for 2 h at room temperature. The solvent was removed in vacuo, and the residue was treated with 5 mL of diethyl ether to afford a yellow suspension. The solution was decanted, and the solid was dried in vacuo. The solid was crystallized at room temperature from dichloromethane−diethyl ether to give amber crystals. Yield: 120 mg (80%). Anal. Calcd for $C_{36}H_{47}NOPRuBF_4$: C, 59.34; H, 6.50; N, 1.92. Found: C, 58.98; H, 6.11, N, 2.09. IR (Nujol, cm^{-1}): ν(CO) 1951 (vs), ν(C=N) and ν(C=C) 1640 (m) and 1599 (w), ν(BF$_4$) 1053 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293 K plus COSY): δ 7.46−6.96 (m, 11H, Ph + NCH=), 6.79 (s, 1H, C*H*=CPh$_2$), 6.08 (dq, 1H, J_{H-H} = 13.8, J_{H-H} = 6.9, =C*H*CH$_3$), 5.65 (m, 1H, C*H*=CH$_2$), 5.26 (m, 4H, NCH$_2$), 5.23−5.14 (m, 2H, =CH$_2$), 4.72 (m, 1H, NCH$_2$), 2.30 (m, 3H, PC*H*CH$_3$), 1.92 (dd, 3H, J_{H-H} = 6.9, J_{H-H} = 1.5, CH$_3$), 1.28 (dd, 9H, J_{H-H} = 7.1, J_{P-H} = 14.6, PCHC*H*$_3$), 1.26 (dd, 9H, J_{H-H} = 7.1, J_{P-H} = 14.1, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K plus APT plus HETCOR): δ 247.8 (d, J_{C-P} = 9.4, Ru-C$_\alpha$), 204.1 (d, J_{C-P} = 18.2, CO), 141.4 and 140.3 (both s, C_{ipso}), 138.9 (s, CPh$_2$), 138.2 (s, *C*H=CPh$_2$), 137.1 (NCH=), 130.6, 129.6, 128.9, 128.6, 128.2 (all s, CPh), 128.5 (s, *C*H=CH$_2$), 121.8 (s, =CH$_2$), 120.9 (s, =*C*HCH$_3$), 87.4 (s, Cp), 57.7 (s, NCH$_2$), 28.9 (d, J_{C-P} = 23.3, P*C*HCH$_3$), 20.1 and 19.9 (both s, PCH*C*H$_3$), 15.5 (s, CH$_3$). $^{31}P-\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 193 K): δ 63.1 (s).

Preparation of [Ru(η^5-C_5H_5){C(CH=CPh$_2$)=NH(CH$_2$-CH=CH$_2$)}(CO)(P^{i}Pr$_3$)]BF$_4$ (7). A deep red solution of [Ru-(η^5-C_5H_5)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (**1**) (200 mg, 0.32 mmol) in 6 mL of dichloromethane was treated with allylamine (26

(28) All our attempts to achieve a valid elemental analysis determination for complexes **3** and **4** were unsuccessful. Even when we tried with crystals of the same crop that was used for the X-ray diffraction study, we could not obtain a satisfactory value.

Table 5. Crystal Data and Data Collection and Refinement for 3, 4, 5, and 9

	3	4	5	9
		Crystal Data		
formula	$C_{36}H_{46}NOPRu$	$C_{36}H_{46}NOPRu$	$C_{36}H_{47}BF_4NOPRu$	$C_{33}H_{42}NOPRu\cdot1.5\ C_6H_6$
molecular wt	640.78	640.78	728.60	717.88
color and habit	orange, irregular block	yellow, plate	cololess, irregular block	colorless, irregular block
size, mm	0.12,0.04,0.02	0.14,0.14,0.03	0.18,0.06,0.04	0.20,0.08,0.04
symmetry, s group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $C2/c$	triclinic, $P\bar{1}$
a, Å	9.521(4)	9.6984(12)	28.434(3)	9.674(2)
b, Å	15.691(6)	11.3808(15)	14.2093(15)	12.170(3)
c, Å	20.348(8)	15.840(2)	20.023(2)	15.904(3)
α, deg		108.998(2)		76.879(3)
β, deg	91.315(7)	95.494(2)	122.801(2)	86.662(3)
γ, deg		106.465(2)		87.046(3)
V, Å^3	3039(2)	1550.9(3)	6800.1(12)	1819.0(7)
Z	4	2	8	2
D_{calc}, g cm^{-3}	1.401	1.372	1.423	1.311
		Data Collection and Refinement		
diffractometer		Bruker Smart APEX		
λ(Mo Kα), Å		0.71073		
monochromator		graphite oriented		
scan type		ω scans		
μ, mm^{-1}	0.598	0.586	0.560	0.508
2θ, range, deg	3, 50	3, 57	3, 57	3, 57
temp, K	100.0(2)	100.0(2)	100.0(2)	100.0(2)
no. of data collect	29 818	18 914	20 473	21 506
no. of unique data	5472 (R_{int} = 0.2034)	7194 (R_{int} = 0.0694)	7902 (R_{int} = 0.1042)	8342 (R_{int} = 0.0637)
no. params/restraints	397/6	397/0	445/0	435/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0585	0.0474	0.0464	0.0488
wR_2[b] [all data]	0.1185	0.0655	0.0559	0.0991
S[c] [all data]	0.780	0.759	0.620	0.828

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

μL, 0.35 mmol). The mixture was stirred at room temperature for 15 min, and the solution became orange. The solvent was removed in vacuo, and the residue was treated with 6 mL of diethyl ether at −78 °C to afford a pale yellow suspension. The solution was decanted, and the solid was washed twice with diethyl ether and dried in vacuo. Yield: 190 mg (86%). Anal. Calcd for $C_{33}H_{43}BF_4NOPRu$: C, 57.56; H, 6.29; N, 2.03. Found: C, 57.53; H, 6.46; N, 2.31. IR (Nujol, cm^{-1}): ν(NH) 3316 (m), ν(CO) 1936 (vs), ν(C═N) and ν(C═C) 1613 (m) and 1545 (w), $\nu(BF_4)$ 1100 (br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.92 (br, 1H, NH), 7.50−7.11 (m, 10H, Ph), 6.55 (s, 1H, CH═CPh_2), 5.91 (m, 1H, C*H*═CH_2), 5.28 (d, $^3J_{H-H}$ = 17.1, 1H, ═CH_2, H *cis* to NCH_2), 5.27 (d, $^3J_{H-H}$ = 10.2, 1H, H *trans* to NCH_2), 4.91 (s, 5H, Cp), 4.37 (m, 2H, NCH_2), 2.26 (m, 3H, PC*H*CH_3), 1.30 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 14.4, PCHC*H*$_3$), 1.29 (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, $CDCl_3$): δ 243.3 (d, J_{P-C} = 10.6, Ru-C$_\alpha$), 204.6 (d, J_{P-C} = 17.1, CO), 141.3 (s, ═CPh_2), 141.0 and 138.7 (both s, C$_{ipso}$ Ph), 133.8 (s, *C*H═CPh_2), 130.4, 130.1, 128.5, 128.4, 128.3 (all s, Ph), 129.0 (s, *C*H═CH_2), 121.3 (s, ═CH_2), 86.9 (s, Cp), 55.1 (s, NCH_2), 28.8 (d, J_{P-C} = 23.9, P*C*HCH$_3$), 19.9 and 19.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 63.1 (s).

Preparation of Ru(η^5-C_5H_5){C(CH═CPh_2)═NCH_2CH═CH_2}(CO)(P^iPr_3) (8). A pale yellow solution of [Ru(η^5-C_5H_5)-{C(CH═CPh_2)═$NH(CH_2CH$═CH_2)}(CO)(P^iPr_3)]BF_4 (**7**) (285 mg, 0.41 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (45 mg, 0.82 mmol). The mixture was stirred at room temperature for 40 min, and the color changed to dark yellow. The solvent was removed in vacuo. Dichloromethane was added, and the suspension was filtered to remove potassium tetrafluoroborate. Solvent was evaporated to dryness, and the residue was treated with 6 mL of pentane at −78 °C to afford a yellow suspension. The solution was decanted, and the solid was washed twice with cold pentane and dried in vacuo. Yield: 172 mg (70%). Anal. Calcd for $C_{33}H_{42}NOPRu$: C, 65.98; H, 7.05; N, 2.33. Found: C, 65.80; H, 7.29, N, 2.14. IR (Nujol, cm^{-1}): ν(CO) 1919 (vs), ν(C═N) and ν(C═C) 1599 (w) and 1541 (m). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.63−7.04 (m, 10H, Ph), 6.85 (s, 1H, CH═CPh_2), 6.25 (m, 1H, C*H*═CH_2), 5.31 (dd, $^3J_{H-H}$ = 17.1, $^2J_{H-H}$ = 2.1, 1H, ═CH_2, H *cis* to NCH_2), 5.12 (dd, $^3J_{H-H}$ = 9.3, $^2J_{H-H}$ = 2.1, 1H, ═CH_2, H *trans* to NCH_2), 4.58 (s, 5H, Cp), 4.47 (br d, 1H, J_{H-H} = 15.6, NCH_2), 4.25 (br d, 1H, J_{H-H} = 15.6, NCH_2), 2.12 (m, 3H, PC*H*CH_3), 1.10 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 13.5, PCHC*H*$_3$), 0.96 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 12.6, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus APT): δ 208.5 (d, J_{P-C} = 16.1, CO), 195.4 (d, J_{P-C} = 11.5, Ru-C$_\alpha$), 144.7, (s, 2 C$_{ipso}$ Ph), 141.6 (s, ═CPh_2), 141.2 (s, *C*H═CPh_2), 139.0 (s, *C*H═CH_2), 130.7, 127.6, 128.7, 128.5, 128.1, 127.5, and 126.8 (all s, Ph), 113.8 (s, ═CH_2), 87.2 (s, Cp), 60.9 (s, NCH_2), 27.5 (d, J_{P-C} = 27.5, P*C*HCH$_3$), 19.9, 19.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 68.9 (s).

Preparation of Ru(η^5-C_5H_5){C(CH═CPh_2)═NCH═$CHCH_3$}(CO)(P^iPr_3) (9). A yellow solution of Ru(η^5-C_5H_5)-{C(CH═CPh_2)═NCH_2CH═CH_2}(CO)(P^iPr_3) (**8**) (125 mg, 0.21 mmol) in 5 mL of toluene was heated at 70 °C for 48 h. The solution was evaporated to dryness. The residue was treated with 3 mL of pentane and stored at −78 °C for 24 h to afford pale yellow microcrystals. The solution was decanted, and the crystals were washed twice with cold pentane and dried in vacuo to afford a yellow oil. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.66−7.05 (m, 10H, Ph), 7.38 (d, 1H, J_{H-H} = 13.2, NCH^2═), 7.03 (s, 1H, CH^5═CPh_2), 5.89 (dq, 1H, J_{H-H} = 13.2, J_{H-H} = 6.9, ═C*H*$^3CH_3$), 4.59 (s, 5H, Cp), 2.11 (m, 3H, PC*H*CH_3), 1.70 (d, 3H, J_{H-H} = 6.9, CH_3), 1.11 (dd, 9H, J_{H-H} = 7.2, J_{P-H} = 13.5, PCHCH_3), 0.97 (dd, 9H, J_{H-H} = 6.9, J_{P-H} = 12.9, PCHCH_3). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus APT): δ 208.1 (d, J_{P-C} = 19.8, CO), 206.1 (d, J_{P-C} = 12.9, Ru-C^1), 144.4 (s, ═C^6Ph_2), 142.3 (s, NC^2H═), 141.5 (s, C$_{ipso}$), 140.6 (s, C^5H═CPh_2), 137.4 (s, C$_{ipso}$), 130.8, 128.8, 128.5, 128.1, 126.9 (all s, Ph), 118.5 (s, ═*C*$^3HCH_3$), 87.3 (s, Cp), 27.9 (d, J_{P-C} = 22.1, P*C*HCH$_3$), 20.2 and 19.7 (both s, PCH*C*H$_3$), 15.5 (s, CH_3). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 69.2 (s). MS (FAB$^+$): m/z 602 (M^+ + H).

Structural Analysis of Complexes 3, 4, 5, and 9. 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, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets (**3**, **4**, and **9**) or over the hemisphere by a combination of three sets (**5**). Each frame exposure time was 10 or 30 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[29] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[30] 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, respectively.

(29) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. *SADABS*, Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.
(30) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *SHELXS-86* and *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

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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**, **4**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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