1,2,3-Diheterocyclization Reactions on the Allenylidene Ligand of a Ruthenium Complex

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The allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**) reacts with pyrazole to afford $[Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(Ph)_2N(CH)_3N\}(CO)(PPr^i_3)]BF_4$ (**2**) as a result of the addition of pyrazole to the allenylidene of **1**. The structure of **2** was determined by an X-ray investigation, revealing a Ru−C(bicycle) distance of 2.073(4) Å. Treatment of **2** with sodium methoxide deprotonates the bicycle, which also undergoes an opening process to give the functionalized alkynyl derivative $Ru(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph)_2N(CH)_3N\}(CO)(PPr^i_3)$ (**3**). The reactions of **1** with 3,5-dimethylpyrazole and 3-methylpyrazole lead to $[Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(Ph)_2NC(R)CHC(CH_3)N\}(CO)(PPr^i_3)]BF_4$ (R = CH_3 (**8**), H (**9**)). In the presence of sodium methoxide, complex **9** affords $Ru(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph)_2N(CH)_2C(CH_3)N\}(CO)(PPr^i_3)$ (**10**). The allenylidene ligand of **1** also adds pyridine-2-thiol. In this case, the reaction product is $[Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(Ph)_2N(CH)_4CS\}(CO)(PPr^i_3)]BF_4$ (**11**), which yields the allenyl derivative $Ru(\eta^5\text{-}C_5H_5)\{C[SC(CH)_4N]{=}C{=}CPh_2\}(CO)(PPr^i_3)$ (**12**) by reaction with sodium methoxide.

Introduction

As a part of our study on the chemistry of the five-coordinate complex $RuHCl(CO)(PPr^i_3)_2$,[1] we have previously shown that this compound is a useful starting material for the preparation of new cyclopentadienylruthenium compounds, including the allenylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**).[2]

An analysis of the electronic structure of this complex[3] suggests that 60% of the LUMO is located on the allenylidene ligand, mainly on the C_α (23%) and C_γ (31%) carbon atoms, while 20% of the HOMO is located on the C_β atom of the same ligand. So, the C_α and C_γ atoms are electrophilic centers and C_β is nucleophilic.[4]

In agreement with this, complex **1** reacts with water, alcohols, thiols, and benzophenone imine to afford α,β-unsaturated-hydroxycarbene, -alkoxycarbene, -(alkylthio)carbene, and -2-azaallenyl compounds, which are a result of the addition of the H−X bond of the above-mentioned RXH molecules to the C_α−C_β double bond of the allenylidene of **1**. By deprotonation, the hydroxycarbene compound gives an acyl derivative and the alkoxycarbene, thioalkoxycarbene, and 2-azaallenyl complexes yield allenyl derivatives.[2]

The reactions of **1** with the RXH molecules require transition states which favor the transfer of the electrophilic hydrogen atom from the RXH substrates to the C_β atom of the allenylidene, by means of an X- - -C_α interaction. Thus, RH molecules such as phenylacetylene and methane, which do not contain an X nucleophilic leading heteroatom, do not react with **1**. The products resulting from the formal addition of the H−C(sp) bond of phenylacetylene and a H−C(sp^3) bond of methane to the C_α−C_β and C_β−C_γ double bonds of the allenylidene of **1**, $[Ru(\eta^5\text{-}C_5H_5)\{C(C{\equiv}CPh)CH{=}CPh_2\}(CO)(PPr^i_3)]^+$ and $[Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(Ph)_2CH_3\}(CO)(PPr^i_3)]^+$, respectively, are obtained by a general synthetic strategy, which is in agreement with the electronic character of the carbon atoms of the allenylidene, and involves the initial nucleophilic attack of a carbanion at the C_α or C_γ atoms of the allenylidene ligand and the subsequent protonation of the resulting allenyl or alkynyl derivatives.[4]

Because the allenylidene of **1** has two electrophilic and one nucleophilic centers, we asked ourselves whether the reactions of this compound with molecules containing two nucleophilic heteroatoms and an electrophilic hydrogen atom could give rise to 1,2,3-diheterocyclizations. Although the reactivity of transition-metal allenylidene compounds is presently attracting considerable

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(3) (a) EHT-MO calculations on the allenylidene complexes $Mn(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(CO)_2$ and $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)(PPh_3)_2]^+$ have been also carried out, see refs 3b and 3c, respectively. (b) Berke, H.; Huttner, G.; von Seyerl, J. *Z. Naturforsch.* **1981**, *36b*, 1277. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.
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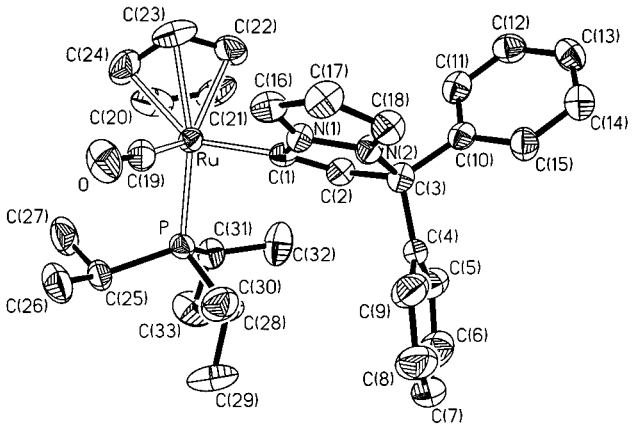
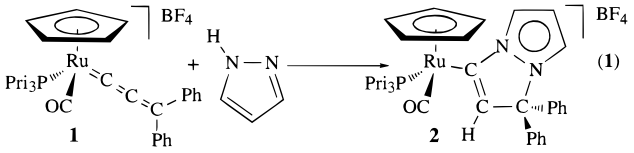


Figure 1. Molecular diagram for complex [Ru(η^5-C_5H_5)-{C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (**2**). Thermal ellipsoids are shown at 50% probability.

interest,[5] related reactions have not been previously carried out. In this paper we report the answer to this question.

Results and Discussion

1. Reaction of [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ with Pyrazole. Treatment of red dichloromethane solutions of **1** with 2 equiv of pyrazole at room temperature leads, after 5 min, to colorless solutions from which the complex [Ru(η^5-C_5H_5){C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (**2**) is isolated as a result of the addition of pyrazole to the allenylidene ligand of **1** (eq 1).



Complex **2** was obtained as a white solid in 86% yield and characterized by elemental analysis, IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopies, and X-ray diffraction. A view of the molecular geometry is shown in Figure 1. 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, and the angles formed by the triisopropylphosphine, the carbonyl group and the unsaturated η^1-carbon ligand are close to 90°.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Ru(η^5-C_5H_5)-{C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (2)

Ru−P	2.350(1)	N(1)−C(16)	1.354(6)
Ru−C(1)	2.073(4)	N(1)−N(2)	1.357(4)
Ru−C(19)	1.843(3)	N(2)−C(3)	1.479(5)
C(1)−C(2)	1.323(5)	N(2)−C(18)	1.341(5)
C(2)−C(3)	1.522(5)	C(16)−C(17)	1.395(7)
C(3)−C(4)	1.531(5)	C(17)−C(18)	1.382(6)
C(3)−C(10)	1.518(6)	O−C(19)	1.158(4)
N(1)−C(1)	1.461(5)		
P−Ru−G(1)[a]	127.1(2)	N(1)−C(1)−C(2)	103.3(3)
P−Ru−C(1)	92.4(1)	N(1)−N(2)−C(3)	110.8(3)
P−Ru−C(19)	90.9(2)	N(2)−N(1)−C(1)	111.5(3)
G(1)-Ru−C(1)[a]	118.8(2)	N(2)−C(3)−C(2)	97.9(3)
G(1)-Ru−C(19)[a]	124.1(2)	N(2)−C(3)−C(4)	111.2(3)
C(1)−Ru−C(19)	94.9(2)	N(2)−C(3)−C(10)	108.4(3)
Ru−C(19)−O	174.6(3)	C(2)−C(3)−C(4)	106.8(3)
Ru−C(1)−C(2)	135.2(3)	C(2)−C(3)−C(10)	117.4(3)
C(1)−C(2)−C(3)	116.1(3)	C(4)−C(3)−C(10)	114.1(3)
Ru−C(1)−N(1)	121.3(2)		

[a] G(1) is the midpoint of the C(20)−C(24) Cp ligand.

The unsaturated η^1-carbon ligand can be described as a cationic 1,1-diphenylpyrazolo[1,2-a]pyrazol-3-yl group.[6] The Ru−C(1) distance (2.073(4) Å) is slightly longer than those found in the alkenyl complexes Ru(η^5-C_5H_5){C(=CHCO$_2$CH$_3$)OC(O)CH$_3$}(PPh$_3$) (2.002(2) Å),[7] Ru{C[=C(CO$_2$CH$_3$)CH=CHC(CH$_3$)$_3$]C(O)OCH$_3$}Cl(CO)(PPh$_3$)$_2$ (2.03(1) Å),[8] Ru{(*E*)-CH=CHC$_3$H$_7$}Cl(CO)(Me$_2$Hpz)(PPh$_3$)$_2$ (2.05(1) Å),[9] Ru{(*E*)-CH=CHCMe$_3$}Cl(CO)(Me$_2$Hpz)(PPh$_3$)$_2$ (2.063(7) Å),[10] and [Ru{(*E*)-CH=CHCMe$_3$}(CO){NH=C(Me)(Me$_2$pz)}(PPh$_3$)$_2$]PF$_6$ (2.067(8) Å)[11] and slightly shorter than the Ru−C bond lengths in the complexes Ru(η^5-C_5H_5){C(=CHPh)OPr^i}(CO)(PPh$_3$) (2.103(6) Å),[12] [Ru{C(=CHCO$_2$CH$_3$)CO$_2$CH$_3$}(CO)(NCCH$_3$)$_2$(PPh$_3$)$_2$]ClO$_4$ (2.12(5) Å),[13] and Ru(CH$_3$){(*E*)-CH=CHPh}(CO)$_2$(PPr$^i_3$)$_2$ (2.141(3) Å),[14] where a Ru−C(sp^2) single bond has been also proposed. The C(1)−C(2) distance of 1.323(5) Å is in agreement with the sample mean of carbon−carbon bond lengths for double bonds (1.32(1) Å).[15] In accordance with the sp^2 hybridization for C(1), the angles Ru−C(1)−N(1) and Ru−C(1)−C(2) are 121.3(2)° and 135.2(3)°, respectively.

The C(1)−N(1) (1.461(5) Å) and C(3)−N(2) (1.479(5) Å) distances are statistically identical and similar to the N−C single-bond distances found in Schiff bases (about 1.47 Å) and amides (between 1.46 and 1.48 Å). How-

(5) For some recent examples, see: (a) Touchard, D.; Pirio N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (b) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495. (c) Braun, T.; Meuer, P.; Werner, H. *Organometallics* **1996**, *15*, 4075. (d) Werner, H. *J. Chem. Soc., Chem. Commun.* **1997**, 903. (e) Werner, H.; Lass, R. W.; Gevert, V.; Wolf, J. *Organometallics* **1997**, *16*, 4077. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (g) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406. (h) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (i) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373.

(6) Transition-metal compounds containing ligands of this type have not been previously reported.

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(13) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P. *J. Organomet. Chem.* **1989**, *373*, 249.

(14) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685.

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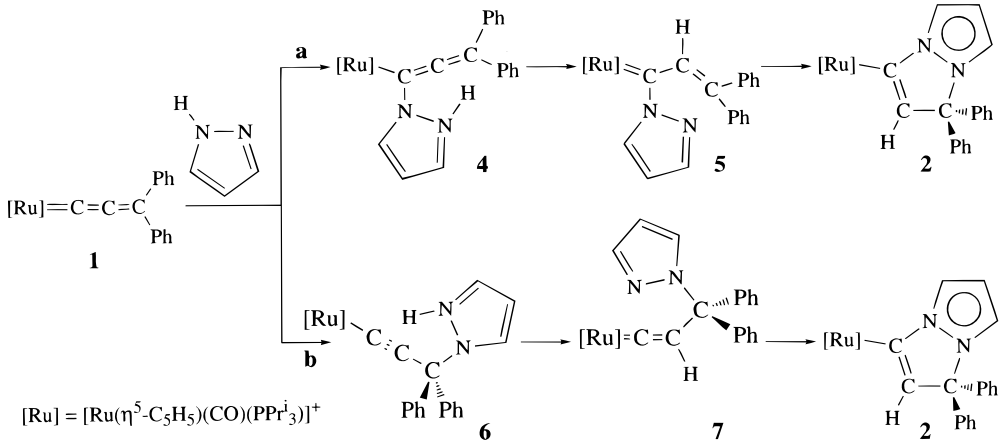
Scheme 1

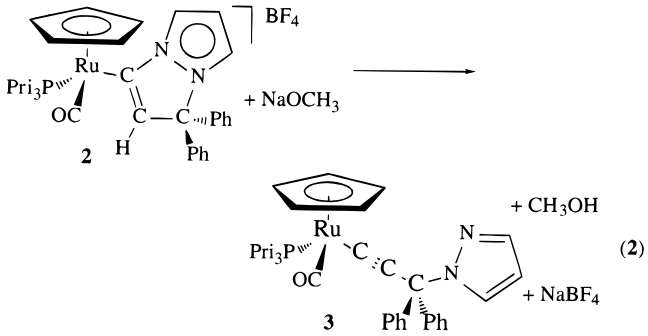


ever, they are about 0.1 Å longer than the N(1)−C(16) (1.354(6) Å) and N(2)−C(18) (1.341(5) Å) bond lengths, which, between them, are also statistically identical and similar to those found in bridge pyrazolato ligands of binuclear transition-metal compounds (about 1.34 Å).[15] The C(16)−C(17) (1.395(7) Å), C(17)−C(18) (1.382(6) Å), and N(1)−N(2) (1.357(4) Å) distances also agree well with those found in the later type of compounds.

Both five-membered rings of the bicycle are almost planar. For the N(1)−N(2)−C(3)−C(2)−C(1) ring, the deviations from the best plane are 0.003(3) [N(1)], −0.021(3) [N(2)], 0.043(4) [C(3)], −0.039(4) [C(2)], and 0.028(4) [C(1)] Å and the related parameters for the N(1)−N(2)−C(18)−C(17)−C(16) ring are 0.002(3) [N(1)], −0.002(3) [N(2)], 0.000(4) [C(18)], 0.002(4) [C(17)], and −0.005(5) [C(16)] Å. The dihedral angle formed by the least-squares planes through the atoms of both cycles is 5.0(1)°. Similar values for the dihedral angle have been found in related organic bicycles.[16]

In agreement with the salt character of **2**, its IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1053 cm^{-1}. In the ^1H NMR spectrum in chloroform-*d*, the most noticeable resonance is a singlet at 6.12 ppm corresponding to the RuC═CH proton. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the Ru−C═ carbon atom appears at 144.7 ppm as a doublet with a C−P coupling constant of 13.6 Hz whereas the resonance corresponding to the ═CH− carbon atom is observed at 137.2 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 66.6 ppm.

Treatment of **2** with sodium methoxide in tetrahydrofuran at room temperature deprotonates the bicycle, which also undergoes an opening process to give the functionalized alkynyl derivative Ru(η^5-C_5H_5){C≡CC-$(Ph)_2$N(CH)$_3$N}(CO)(PPr$^i_3$) (**3**, eq 2). Ruthenium and rhodium compounds containing functionalized alkynyl ligands of the type M−C≡C−C(OR)R′$_2$ have been recently prepared by nucleophilic addition at the C_γ atom of allenylidene ligands.[17]



(2)

Complex **3** was isolated as a white solid in 74% yield. The presence of an alkynyl group in this complex is mainly supported by its IR and $^{13}C\{^1H\}$ NMR spectra. In the IR spectrum in Nujol, the ν(C≡C) band is observed at 2098 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the C_α atom of the alkynyl ligand appears at 100.2 ppm as a doublet with a C−P coupling constant of 21.3 Hz and that due to the C_β atom is observed at 107.1 ppm, also as a doublet but with a C−P coupling constant of 0.9 Hz.

Because both the C_α and C_γ atoms of the allenylidene unit of **1** are electrophilic centers, the formation of **2** could occur by the reaction pathways shown in Scheme 1. According to pathway **a**, the first step of the reaction shown in eq 1 should be the attack of pyrazole to the C_α atom of the allenylidene to give an allenyl intermediate, which could evolve to a functionalized α,*β*-unsaturated carbene derivative by hydrogen transfer from the other nitrogen atom of the pyrazole group to the central carbon atom of the allenyl unit. Finally, the attack of the free nitrogen atom of the pyrazole group at the C_γ atom of the carbene should afford the bicyclic ligand. According to pathway **b**, the reaction shown in eq 1, should proceed by the initial addition of pyrazole at the C_γ atom of allenylidene ligand of **1**. The alkynyl intermediate formed could afford a functionalized vinylidene species as a result of the intramolecular attack of the acidic hydrogen atom of the pyrazole to the C_β atom of the alkynyl unit. Finally, the nucleophilic attack of the free nitrogen atom of the pyrazole to the C_α atom of the vinylidene should give the bicyclic group.

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The addition of electrophiles to the electron-rich C_β atom of metal alkynyl complexes has been described on many occasions and is the best known entry into the synthesis of vinylidene derivatives.[18] So, if the reaction shown in eq 1 proceeds via the pathway **b** of Scheme 1, the protonation of the alkynyl complex **3** should afford a functionalized vinylidene intermediate **7**, which subsequently should evolve into **2**.

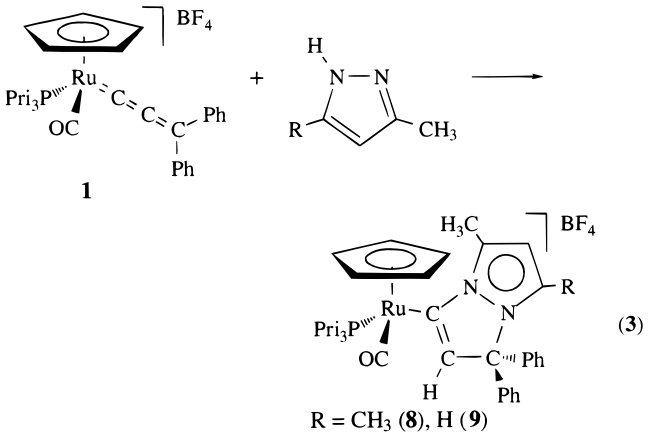
The addition at room temperature of 1 equiv of $HBF_4 \cdot OEt_2$ to **3** using dichloromethane as the solvent initially gives rise to a change of color in the solution, from colorless to the characteristic red of the allenylidene, to finally afford a new colorless solution from which the bicyclic complex **2** was isolated. The presence of the red color during the transformation suggests that the formation of **2** by protonation of **3** in dichloromethane involves the initial release of pyrazole and its subsequent condensation with the allenylidene of **1**. In agreement with this, the ^1H NMR spectrum of the reaction mixture in dichloromethane-d_2 shows resonances of **1**, **2**, and **3**. Furthermore, we have also observed that the addition of 1 equiv of $HBF_4 \cdot OEt_2$ to diethyl ether solutions of **3** produces the precipitation of **1** and the formation of a diethyl ether solution of pyrazole.

These observations suggest (i) the most nucleophilic center of **3** is the free nitrogen atom of the pyrazole group and (ii) the splitting of the N−C bond of **6** is faster than the hydrogen transfer from the N−H nitrogen atom to the C_β atom of the alkynyl unit. So, it appears to be reasonable to reject pathway **b**.

At first glance, one could also think that the formation of **2**, according to eq 1, takes place by initial electrophilic attack of the N−H pyrazole proton at the C_β atom of the allenylidene to give a dicationic α,β-unsaturated carbyne intermediate and subsequent nucleophilic addition of the two nitrogen atoms of the pyrazolato anion at the C_α and C_γ atoms of the carbyne. This, which is in agreement with the placement of 20% of the HOMO of **1** in C_β, must be also rejected because complex **1** does not show any nucleophilic character. In fact, the treatment of dichloromethane solutions of **1** with 1 equiv of $HBF_4 \cdot OEt_2$ does not produce any change in **1**.

Complex **1** also reacts with substituted pyrazoles. The reactions of **1** with 3,5-dimethylpyrazole and 3-methylpyrazole in dichloromethane lead to the bicyclic complexes $[Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(Ph)_2NC(R)CHC(CH_3)N\}(CO)(PPr^i_3)]BF_4$ (R = CH_3 (**8**), H (**9**)). Complex **8** was isolated as a colorless oil in 85% yield, while complex **9** was obtained as a white solid in 83% yield (eq 3).

The ^1H NMR spectrum of **8** in chloroform-*d* shows singlets at 2.92 and 1.93 ppm corresponding to the methyl groups of the bicyclic ligand. Irradiation of the resonance at 2.92 ppm gives an increase in the resonance of the cyclopentadienyl protons (3.16%), whereas the resonances of the phenyl groups are not affected. However, irradiation of the resonance at 1.93 ppm gives increases in the *ortho*-phenyl resonances at 6.95 (2.89%) and 7.10 ppm (2.44%), whereas the resonance of the cyclopentadienyl protons is not affected. According to these NOE experiments, we assign the resonance at 2.92 ppm to the methyl group situated at the side of the metallic fragment and the resonance at 1.93 ppm to the methyl group located at the side of the phenyl groups. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the Ru−C= and =C−H carbon atoms appear at 140.0 and 139.3 ppm as doublets with C−P coupling constants of 12.9 and 4.6 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 64.0 ppm.



In the ^1H NMR spectrum of **9** in chloroform-*d*, the most noticeable resonances are those due to the protons RuC=CH, C_5H_5, and CH_3 of the bicyclic ligand, which appear as singlets at 6.05, 4.34, and 2.97 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the Ru−C= and =CH− carbon atoms appear at 142.3 and 138.6 ppm as doublets with C−P coupling constants of 12.9 and 4.1 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 64.2 ppm.

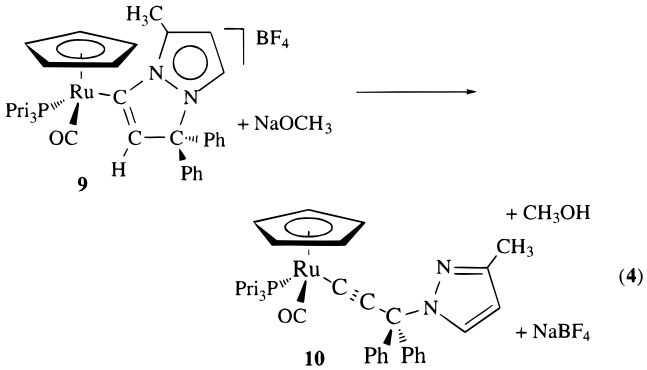
The position of the methyl group in this bicycle was determined by means of a NOE experiment. Irradiation of the methyl resonance (δ 2.97) gave an increase in the resonance of the cyclopentadienyl protons (3.2%), whereas the resonances of the phenyl groups were not affected.

The selective formation of **9** with the methyl group at the side of the metallic fragment merits some further comment. The pyrazoles exist in solution as mixtures of annular tautomers in different proportions, depending upon the nature of the substituents. In the majority of cases, the difference of free energy between both tautomers is low enough for the chemical reactivity to be unrelated to the equilibrium constant. In all the known 3(5)-substituted pyrazoles, the 3-substituted tautomer predominates with the possible exception of 3(5)-methylpyrazole in which the 5-methyl tautomer slightly predominates.[19] So, if the reactions shown in eqs 1 and 3 proceed via pathway **a** of Scheme 1, only the 3-methylpyrazole tautomer, the minor one in the tautomeric equilibrium, is active.

Similarly to **2**, complex **9** reacts with sodium methoxide in tetrahydrofuran at room temperature to afford the functionalized alkynyl derivative $Ru(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph)_2N(CH)_2C(CH_3)N\}(CO)(PPr^i_3)$ (**10**), which was isolated as a pale yellow solid in 79% (eq 4).

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

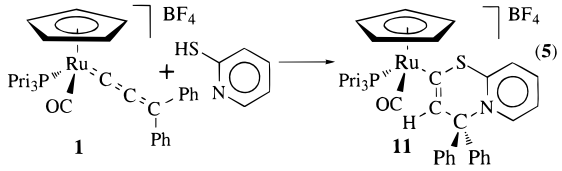
(19) Elguero, J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Potts, K. T., Eds.; Pergamon Press: Oxford, 1984; Vol. 5, Chapter 4.04.



(4)

The most characteristic spectroscopic features of **10** are the C≡C stretching frequency in the IR spectrum in Nujol, which is observed at 2105 cm^{-1}, and two doublets with C−P coupling constants of 0.9 and 21.6 Hz in the $^{13}C\{^1H\}$ NMR spectrum at 107.1 and 99.7 ppm, for the C_β and C_α alkynyl carbon atoms, respectively.

2. Reaction of [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ with Pyridine-2-thiol. Treatment of dichloromethane solutions of **1** with 1 equiv of pyridine-2-thiol leads, after 5 min, to the complex [Ru(η^5-C_5H_5)-{C=CHC(Ph)$_2$N(CH)$_4$CS}(CO)(PPr$^i_3$)]BF$_4$ (**11**), which is formed as a result of the addition of pyridine-2-thiol to the allenylidene ligand of **1** (eq 5).

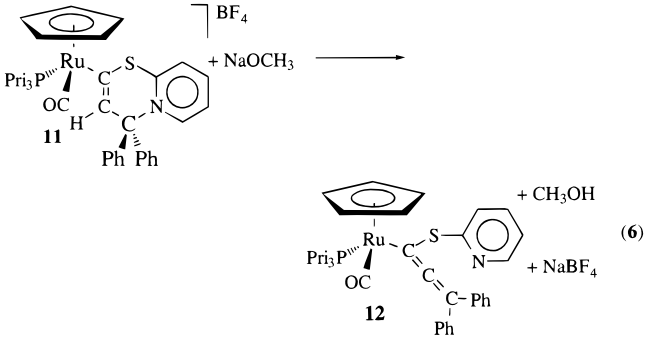


(5)

Complex **11** was isolated as a yellow solid in 92% yield. The saline character of the compound is supported by the IR spectrum in Nujol, which contains the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1051 cm^{-1}. In the ^1H NMR spectrum, the most noticeable resonance is that corresponding to the RuC=CH proton, which appears at 6.38 ppm as a singlet. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the RuC= carbon atom appears at 142.1 ppm as a doublet with a C−P coupling constant of 12.8 ppm while that corresponding to the RuC=*C*H carbon is observed at 132.1 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 66.3 ppm.

Similarly to **2** and **9**, complex **11** undergoes deprotonation in the presence of sodium methoxide. However, in contrast to **2** and **9**, the reaction product is not an alkynyl derivative but the allenyl complex Ru(η^5-C_5H_5)-{C[SC(CH)$_4$N]=C=CPh$_2$}(CO)(PPr$^i_3$) (**12**), which was isolated as a yellow solid in 62% yield (eq 6).

The IR spectrum of **12** in Nujol shows the characteristic C=C=C stretching frequency at 1869 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum contains the resonances due to the carbon atoms of the allenyl unit at 198.3 (C_β), 103.9 (C_γ), and 88.6 (C_α) ppm. The first and second resonances appear as singlets, while the third one is observed as a doublet with a C−P coupling constant of 12.1 Hz.



(6)

The protonation of **12** with $HBF_4 \cdot OEt_2$ in dichloromethane and diethyl ether as solvents regenerates **11**. This suggests that the formation of **11** according to eq 5 proceeds by the reaction pathway shown in Scheme 2. In this context, it should be mentioned that we have previously proved that the addition of thiols to the allenylidene ligand of **1** and the protonation of (alkylthio)allenyl complexes leads to α,*β*-unsaturated (alkylthio)carbene derivatives.[2]

Concluding Remarks

This study has shown that, in fact, the allenylidene ligand of the complex [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ (**1**) undergoes 1,2,3-diheterocyclization reactions with organic molecules containing two nucleophilic heteroatoms and one electrophilic hydrogen atom. The reaction products contain bicyclic ligands formed by five- and six-membered rings, depending upon the nature of the organic substrate. One of the rings of the bicycle can be opened by deprotonation with sodium methoxide to give selectively functionalized alkynyl and allenyl derivatives.

In conclusion, we report the discovery of a new reaction which affords the preparation of a new type of organometallic compounds containing η^1-carbon diheterobicyclic ligands.

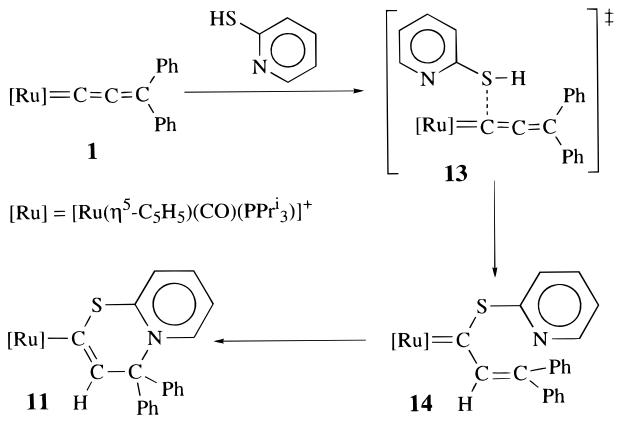
Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ (**1**) was prepared by the published method.[2]

NMR spectra were recorded on either a Varian UNITY 300, a Varian GEMINI 2000, 300 MHz, or a Bruker 300 ARX spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz. IR spectra were run on a Nicolet 550 spectrophotometer (Nujol mulls on polyethylene sheets or KBr pellets). Elemental analyses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of [Ru(η^5-C_5H_5){C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (2). A dark red solution of **1** (140 mg, 0.22 mmol) in 5 mL of dichloromethane was treated with pyrazole (31 mg, 0.44 mmol), and the mixture was stirred for 5 min. The solution became colorless, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a white solid. Yield: 134 mg (86%). Anal. Calcd for $C_{33}H_{40}BF_4N_2OPRu$: C, 56.67; H, 5.76; N, 4.00. Found: C, 56.69; H, 5.90; N, 4.00. IR (Nujol, cm^{-1}): ν(CO) 1929 (vs), ν(C=C) 1541 (m), ν(BF_4) 1053 (vs, br). ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 8.39 (d, 1H, *J*(HH) = 2.7, pz), 8.02 (d, 1H, *J*(HH) = 2.7, pz),

Scheme 2



7.37 (m, 6H, Ph), 7.08 (vt, 1H, *J*(HH) = 2.7, pz), 7.04 (m, 2H, Ph), 6.97 (m, 2H, Ph), 6.12 (s, 1H, Ru−C═CH), 5.32 (s, 5H, Cp), 2.09 (m, 3H, PC*H*CH$_3$), 1.00 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.5, PCHC*H*$_3$), 0.97 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.7, PCHC*H*$_3$).^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): *δ* 66.6 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$): *δ* 206.4 (d, *J*(PC) = 18.1, CO), 144.7 (d, *J*(PC) = 13.6, Ru−C═), 138.9, 137.7 (both s, C$_{ipsoPh}$), 137.2 (s, Ru−C═*C*H), 130.8, 128.6, 112.5 (all s, pz), 129.4, 129.3, 129.1, 126.8, 125.9 (all s, Ph), 85.6 (s, Cp), 80.8 (s, CPh_2), 26.5 (d, *J*(PC) = 26.5, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$), 19.0 (d, *J*(PC) = 1.3, PCH*C*H$_3$).

Preparation of Ru(*η*^{5}-C$_5$H$_5$){C≡CC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$) (3). A suspension of **2** (381 mg, 0.57 mmol) in 15 mL of tetrahydrofuran was treated with sodium methoxide (62 mg, 1.14 mmol) and stirred for 48 h. The mixture became orange, and the solvent was removed in vacuo. Toluene (15 mL) was added, and the suspension was filtered to eliminate sodium tetrafluoroborate. Solvent was evaporated, and the residue was washed with methanol to afford a white solid. Yield: 257 mg (74%). Anal. Calcd for $C_{33}H_{39}ON_2PRu$: C, 64.79; H, 6.43; N, 4.58. Found: C, 64.60; H, 5.94; N, 4.65. IR (Nujol, cm^{-1}): *ν*(C≡C) 2098 (m), *ν*(CO) 1928 (vs). ^{1}H NMR (300 MHz, 293 K, C_6D_6): *δ* 8.80 (d, 1H, *J*(HH) = 2.3, pz), 7.81 (m, 4H, Ph), 7.19 (m, 7H, Ph + pz), 6.27 (vt, 1H, *J*(HH) = 2.3, pz), 4.83 (s, 5H, Cp), 1.89 (m, 3H, PC*H*CH$_3$), 1.00 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.7, PCHC*H*$_3$), 0.79 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.2, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): *δ* 74.6 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus apt): *δ* 205.4 (d, *J*(PC) = 17.9, CO), 145.3, 145.1 (both s, C$_{ipsoPh}$), 139.5, 130.7 (both s, pz), 128.4, 128.1, 127.2, 127.1, 126.7, 126.6 (all s, Ph), 107.1 (d, *J*(PC) = 0.9, Ru−C≡*C*), 103.5 (s, pz), 100.2 (d, *J*(PC) = 21.3, Ru−*C*≡C), 85.3 (d, *J*(PC) = 0.9, Cp), 71.1 (s, CPh_2), 29.8 (d, *J*(PC) = 23.9, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), 19.2 (d, *J*(PC) = 1.8, PCH*C*H$_3$).

Preparation of [Ru(*η*^{5}-C$_5$H$_5$){C═CHC(Ph)$_2$NC(CH$_3$)-CHC(CH$_3$)N}(CO)(PPr$^i_3$)]BF$_4$ (8). A dark red solution of **1** (110 mg, 0.17 mmol) in 5 mL of dichloromethane was treated with 3,5-dimethylpyrazole (33 mg, 0.35 mmol), and the mixture was stirred for 30 min. The solution became colorless, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a colorless oil. Yield: 107 mg (85%). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): *δ* 7.37 (m, 6H, Ph), 7.10 (m, 2H, Ph), 6.95 (m, 2H, Ph), 6.51 (s, 1H, pz), 5.79 (s, 1H, Ru−C═CH), 5.25 (s, 5H, Cp), 2.92 (s, 3H, CH_3), 2.07 (m, 3H, PC*H*CH$_3$), 1.93 (s, 3H, CH_3), 0.94 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCHC*H*$_3$), 0.91 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.1, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): *δ* 64.0 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$): *δ* 207.5 (d, *J*(PC) = 21.2, CO), 142.5, 141.6 (both s, C$_{ipsoPh}$), 140.0 (d, *J*(PC) = 12.9, Ru−C═), 139.3 (d, *J*(PC) = 4.6, Ru−C═*C*H), 136.3, 134.4 (both s, C$_{ipso,pz}$), 129.5, 129.2, 129.0, 128.4, 128.1, 125.8 (all s, Ph), 113.9 (all s, pz), 85.8 (s, Cp), 78.9 (s, CPh_2), 25.3 (d, *J*(PC) = 23.0, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 18.8 (d, *J*(PC) = 1.4, PCH*C*H$_3$), 14.3, 11.5 (both s, pz-*C*H$_3$).

Preparation of [Ru(*η*^{5}-C$_5$H$_5$){C═CHC(Ph)$_2$N(CH)$_2$C-(CH$_3$)N}(CO)(PPr$^i_3$)]BF$_4$ (9). A dark red solution of **1** (80 mg, 0.13 mmol) in 5 mL of dichloromethane was treated with 3-methylpyrazole (11 *μ*L, 0.14 mmol), and the mixture was stirred for 10 min. The solution became colorless, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a white solid. Yield: 75 mg (83%). Anal. Calcd for $C_{34}H_{42}BF_4N_2OPRu$: C, 57.23; H, 5.93; N, 3.93. Found: C, 56.90; H, 6.05; N, 3.84. IR (Nujol, cm^{-1}): *ν*(CO) 1927 (vs), *ν*(C═C) 1549 (m), *ν*(BF$_4$) 1049 (vs, br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): *δ* 7.84 (d, 1H, *J*(HH) = 3.0, pz), 7.34 (m, 6H, Ph), 7.12 (m, 2H, Ph), 6.90 (m, 2H, Ph), 6.80 (d, 1H, *J*(HH) = 3.0, pz), 6.05 (s, 1H, Ru−C═CH), 4.34 (s, 5H, Cp), 2.97 (s, 3H, CH_3), 2.16 (m, 3H, PC*H*CH$_3$), 0.99 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.3, PCHC*H*$_3$), 0.98 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.7, PCHC*H*$_3$).^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): *δ* 64.2 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus dept): *δ* 207.5 (d, *J*(PC) = 20.7, CO), 142.3 (d, *J*(PC) = 12.9, Ru−C═), 141.5, 140.0 (both s, C$_{ipsoPh}$), 138.6 (d, *J*(PC) = 4.1, Ru−C═*C*H), 137.5 (s, C$_{ipso,pz}$), 129.7, 129.6, 129.3, 127.4, 125.6 (all s, Ph), 128.4, 114.4 (both s, pz), 85.9 (s, Cp), 80.8 (s, CPh_2), 25.5 (d, *J*(PC) = 23.4, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), 18.9 (d, *J*(PC) = 1.4, PCH*C*H$_3$), 14.4 (s, pz-*C*H$_3$).

Preparation of Ru(*η*^{5}-C$_5$H$_5$){C≡CC(Ph)$_2$N(CH)$_2$C-(CH$_3$)N}(CO)(PPr$^i_3$) (10). A suspension of **9** (308 mg, 0.45 mmol) in 12 mL of tetrahydrofuran was treated with sodium methoxide (49 mg, 0.90 mmol) and stirred for 2 h. The solution became orange, and the solvent was removed in vacuo. Toluene (15 mL) was added, and the mixture was filtered to eliminate sodium tetrafluoroborate. Solvent was evaporated, and the residue was washed with pentane to afford a pale yellow solid. Yield: 222 mg (79%). Anal. Calcd for $C_{34}H_{41}ON_2PRu$: C, 65.26; H, 6.60; N, 4.47. Found: C, 64.93; H, 6.17; N, 4.52. IR (Nujol, cm^{-1}): *ν*(C≡C) 2105 (m), *ν*(CO) 1931 (vs).^{1}H NMR (300 MHz, 293 K, C_6D_6): *δ* 8.22 (d, 1H, *J*(HH) = 2.2, pz), 7.36 (m, 2H, Ph), 7.25−7.11 (m, 8H, Ph), 5.92 (d, 1H, *J*(HH) = 2.2, pz), 5.12 (d, 5H, *J*(PH) = 0.9, Cp), 2.17 (s, 3H, pz-CH_3), 2.03 (m, 3H, PC*H*CH$_3$), 0.99 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.7, PCHC*H*$_3$), 0.94 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.2, PCHC*H*$_3$).^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): *δ* 75.2 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus dept): *δ* 205.8 (d, *J*(PC) = 18.4, CO), 148.8 (s, C$_{ipso,pz}$), 145.5, 145.4 (both s, C$_{ipsoPh}$), 131.5 (pz), 128.6, 128.3, 127.4, 127.3, 126.7, 126.6 (all s, Ph), 107.1 (d, *J*(PC) = 0.9, Ru−C≡*C*), 103.2 (pz), 99.7 (d, *J*(PC) = 21.6, Ru−*C*≡C), 85.4 (s, Cp), 70.7 (s, CPh_2), 26.8 (d, *J*(PC) = 24.4, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 19.2 (d, *J*(PC) = 1.8, PCH*C*H$_3$), 14.1 (s, pz-*C*H$_3$).

Preparation of [Ru(*η*^{5}-C$_5$H$_5$){C═CHC(Ph)$_2$N(CH)$_4$CS}-(CO)(PPr$^i_3$)]BF$_4$ (11). A solution of **1** (150 mg, 0.24 mmol) in 5 mL of dichloromethane was treated with pyridine-2-thiol (27 mg, 0.24 mmol), and the mixture was stirred for 5 min. The color turned from dark red to orange, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a yellow solid. Yield: 162 mg (92%). Anal. Calcd for $C_{35}H_{41}BF_4NOPRuS$: C, 56.61; H, 5.56; N, 1.89; S, 4.32. Found: C, 56.62; H, 5.90; N, 1.84; S, 4.76. IR (Nujol, cm^{-1}): *ν*(CO) 1939 (vs), *ν*(C═C) 1561 (m), *ν*(BF$_4$) 1051 (vs, br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): *δ* 8.38 (m, 1H, py), 7.81 (m, 1H, py), 7.71 (m, 2H, py), 7.39 (m, 6H, Ph), 6.85 (m, 4H, Ph), 6.38 (s, 1H, Ru−C═CH), 5.14 (s, 5H, Cp), 2.27 (m, 3H, PC*H*CH$_3$), 1.14 (dd, 9H, *J*(HH) = 6.5, *J*(PH) = 13.6, PCHC*H*$_3$), 1.12 (dd, 9H, *J*(HH) = 5.9, *J*(PH) = 12.7, PCHC*H*$_3$).^{31}P{^{1}H}

Table 2. Crystal Data and Data Collection and Refinement for the Complex [Ru(η^5-C_5H_5)-{C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (2)

Crystal Data	
formula	$C_{33}H_{40}BF_4N_2OPRu$
mol wt	699.54
color and habit	yellow, prismatic block
symmetry	orthorombic
space group	*Aba*2
a, Å	19.150(3)
b, Å	17.293(3)
c, Å	19.642(3)
V, Å^3; *Z*	6505(2); 8
D_{calc}, g cm^{-3}	1.429
Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED-2
λ(MoKα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	0.58
scan type	$\omega/2\theta$
2θ range, deg	$3° \le 2\theta \le 50°$
temp, K	223.0(2)
no. of data collect	6504
no. of unique data	5297(R_{int} = 0.0164)
no. of obsd data	4530 ($F_o \ge 4.0\ \sigma(F_o)$)
no. of params refined	389
R^a, R_w ^{b} (obsd data)	0.030, 0.027
R, w*R* (all data)	0.0391, 0.0301
goodness of fit^c	1.233

^{a} $R = \sum||[F_o - F_c)]|/\sum F_o$. ^{b} $R_w = \sum w^{1/2}|[F_o - F_c)]|/\sum w^{1/2}F_o$. ^{c} $S = \{\sum(w[F_o - F_c)])^2/(M - N)\}^{1/2}$, where *M* is the number of observed reflections and *N* is the number of parameters refined.

NMR (121.4 MHz, 293 K, $CDCl_3$): δ 66.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$): δ 205.9 (d, *J*(PC) = 18.1, CO), 154.9, 143.1 (both s, py), 142.1 (d, *J*(PC) = 12.8, Ru−C=), 140.2 (s, py), 139.6, 139.4 (both s, C_{ipsoPh}), 132.1 (s, Ru−C=*C*H), 129.5, 129.4, 128.8, 128.5, 125.4, 123.9 (all s, Ph), 129.1 (s, py), 85.9 (s, Cp), 78.8 (s, CPh_2), 27.6 (d, *J*(PC) = 23.3, P*C*HCH$_3$), 20.0, 19.6 (both s, PCH*C*H$_3$).

Preparation of Ru(η^5-C_5H_5){C[SC(CH)$_4$N]=C=CPh$_2$}(CO)(PPr$^i_3$) (12). A suspension of **11** (162 mg, 0.22 mmol) in 15 mL of tetrahydrofuran was treated with sodium methoxide (16 mg, 0.30 mmol) and stirred for 2 h. The color changed from orange to yellow, and the solvent was removed in vacuo. Toluene (15 mL) was added, and the mixture was filtered to eliminate sodium tetrafluoroborate. Solvent was evaporated, and the residue was washed with diethyl ether to afford a yellow solid. Yield: 89 mg (62%). Anal. Calcd for $C_{35}H_{40}NOPRuS$: C, 64.20; H, 6.16; N, 2.14; S, 4.90. Found: C, 64.12; H, 5.74; N 2.19; S, 5.19. IR (Nujol, cm^{-1}): ν(CO) 1913 (vs), ν(C=C=C) 1869 (m).^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 8.35 (m, 1H, py), 7.99−7.39 (m, 5H, Ph + py), 7.32−7.06 (m, 6H, Ph), 6.80 (m, 1H, py), 6.40 (m, 1H, py), 5.04 (s, 5H, Cp), 1.98 (m, 3H, PC*H*CH$_3$), 1.02 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.3, PCHC*H*$_3$), 0.80 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 13.0, PCHC*H*$_3$).$^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 50.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6, plus dept): δ 206.7 (d, *J*(PC) = 19.6, CO), 198.3 (s, =C=), 162.3 (s, $C_{ipso,py}$), 149.6 (s, py), 140.6, 140.5 (both s, C_{ipsoPh}), 135.3 (s, py), 128.8, 128.7, 128.3, 128.2, 125.9, 125.9 (all s, Ph), 127.3 (s, py), 120.5 (s, py), 103.9 (s, =CPh_2), 88.6 (d, *J*(PC) = 12.1, Ru−C=), 86.2 (s, Cp), 27.2 (d, *J*(PC) = 22.6, P*C*HCH$_3$), 20.3, 19.3 (both s, PCH*C*H$_3$).

X-ray Structure Analysis of Complex [Ru(η^5-C_5H_5)-{C=CHC(Ph)$_2$N(CH)$_3$N}(CO)(PPr$^i_3$)]BF$_4$ (2). Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated solution of **2** in dichlorometane. A summary of crystal data and refinement parameters is reported in Table 2. The yellow, prismatic crystal, of approximate dimensions 0.38 × 0.27 × 0.19 mm, was glued on a glass fiber and mounted on a Siemens-STOE AED-4 diffractometer. A group of 62 reflections in the range $20° \le 2\theta \le 40°$ was carefully centered at 223 K and used to obtain the unit cell dimensions by least-squares methods. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a numerical absorption correction.[20] The structure was solved by Patterson (Ru atom, SHELXTL-PLUS[20]) and conventional Fourier techniques and refined by full-matrix least-squares. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps or calculated in idealized positions and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ru and P, were taken from ref 21. The refinement converged to $R = 0.030$ and $R_w = 0.027$ [$F \ge 4\sigma(F)$], with weighting parameter $w^{-1} = \sigma^2F + 0.000152F^2$.

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Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, bond distances and angles and selected least-squares planes (17 pages). Ordering information is given on any current masthead page.

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