Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ as Entry to Novel Unsaturated η^1-Carbon Ligands Containing Azetidine and Hexahydroquinoline Skeletons

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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 dicyclohexylcarbodiimide to give the iminiumazetidinylidenemethyl complex $[Ru(\eta^5\text{-}C_5H_5)\{CH{=}CCPh_2N(Cy){=}C{=}N{=}C(CH_2)_4CH_2\}(CO)(PPr^i_3)]BF_4$ (**2**), as a 4:1 mixture of isomers *Z* (**2a**) and *E* (**2b**). The structure of **2a** was determined by an X-ray investigation, revealing a Ru−C distance of 2.070(4) Å. Treatment of the isomeric mixture of **2** with sodium methoxide in tetrahydrofuran at room temperature affords the iminoazetidinylidenemethyl complex $Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2N(Cy)C{=}NC{=}CH(CH_2)_3CH_2\}(CO)(PPr^i_3)$ (**6**), which reacts with $HBF_4{\cdot}OEt_2$ to give $[Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2N(Cy)C{=}N(H)C{=}CH(CH_2)_3CH_2\}(CO)(PPr^i_3)]BF_4$ (**7**), as a result of the protonation of the exocyclic nitrogen atom of the unsaturated η^1-carbon ligand of **6**. In the solid state and in solution at low temperature, complex **7** is stable. However, in solution at room temperature, complex **7** evolves into $[Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2C(CH_2)_4CN(H){=}CNHCy\}(CO)(PPr^i_3)]BF_4$ (**8**), which reacts with sodium methoxide in tetrahydrofuran at room temperature to give the hexahydroquinolinylidenemethyl complex $Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2C(CH_2)_4CN{=}CNHCy\}(CO)(PPr^i_3)$ (**9**), as a result of the deprotonation of the endocyclic nitrogen atom of **8**. The structure of **9** was also determined by an X-ray investigation, revealing, in this case, a Ru−C distance of 2.113(4) Å. The formation of the azetidine and hexahydroquinoline skeletons of the ligands of these compounds is discussed.

Introduction

Azetidines are an interesting class of four-membered heterocyclic compounds that exhibit various biological activities such as antihypertensive, antiinflammatory, antiarrhythmic, antidepressant and monoamine oxidase inhibitory activities.[1]

The azetidine skeleton is difficult to synthesize due to its ring strain. At first glance, the most straightforward route to prepare this type of compound should be a polar [2+2] cycloaddition between an imine and an electron-rich alkene. However, this reaction has been restricted to a few exceptional cases.[2] Accordingly, several alternative methods have been used. Azetidines can be prepared via the direct alkylation of benzhydrylamine with 1-bromo-3-chloropropane and subsequent hydrogenolysis.[3] 2-Methyleneazetidines have been synthesized in high yield via closure of *N*-aryl *β*-chloro ketimines induced by potassium *tert*-butoxide.[4] Highly selective reductions of *β*-lactams, direct-tandem bis-*β*-lactams, and tandem bis-*β*-lactams to the corresponding azetidines and bisazetidines have been successfully performed by using diisobutylaluminum hydride, monochlorohydroalane, and dichloroalane.[5] Reactions of isocyanides with 1-phthalimidoaziridines have led to 1-phthalimidoazetidines by [1+3] cycloaddition to the azomethine ylides, which are in equilibrium with the aziridines.[6] A general route to prepare 2-substituted azetidines involves anodic acetoxylation of *N*-tosylazetidine followed by nucleophilic displacement of the acetate by nucleophiles such as trimethylsilylcyanide, allyltrim-

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ethylsilane, 2-methoxyfuran, and trimethylphosphite.[7] Azetidium salts can be formed by cyclization of 3-aminopropanol with trifluoromethanesulfonic anhydride.[8]

A few examples of azetidinylidene transition-metal complexes have been also reported. In 1974 E. O. Fischer observed that $(CO)_5Cr{=}C(OH)Me$ reacted with dicyclohexylcarbodiimide in dichloromethane solution to produce the iminoazetidinylidene complex $(CO)_5Cr\{{=}CN(Cy)C(=NCy)CH_2\}$.[9] The alkoxycarbene $(CO)_5WC(OEt)Ph$ reacts with alkenyl isocyanides to give 3-aza-1,2,4-pentatriene complexes, which add a second molecule of isocyanide to afford 1-azafulvene and azetidin-2-ylidene derivatives by competitive [4+1] and [3+1] cycloadditions, respectively. Azetidinylidene complexes of tungsten and chromium have been also prepared by addition of imines to carbene or allenylidene compounds.[10] Iron alkoxycarbene complexes undergo formal [1+1+2] cycloaddition reactions with isocyanides to afford iminoazetidinylidene compounds.[11] Similarly, formal [2+2] cycloaddition of iron−,[12] rhenium−, and manganese−vinylidene[13] complexes with imines yield azetidinylidene derivatives. Azatitanacyclobutane complexes have been prepared by [2+2] cycloaddition of Ti=C and N=C units.[14]

We have previously shown that the solvato complex $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PPr^i_3)]BF_4$ reacts with 1,1-diphenyl-2-propyn-1-ol to afford the allenylidene compound $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**). The diphenylallenylidene ligand of **1** has been found to be the master key for the development of extensive organometallic chemistry, including α,β-unsaturated-hydroxycarbene, -alkoxycarbene, -(alkylthio)carbene, and -2-azaallenyl, functionalized allenyl, acyl,[15] (acetylide)carbene, cyclic carbene, vinylidene, alkynyl,[16] tetrahydronaphthofuranyl,[18] pyrazolopyrazolyl,[17] ortho ester alkenyl, lactonyl,[19] and allenylphosphine[20] derivatives.

The exceptional chemical properties of the allenylidene fragment of **1** prompted us to ask ourselves whether this fragment should also be capable of generating the azetidine skeleton by a [2+2] cycloaddition with dicyclohexylcarbodiimide.

Although the reactivity of transition metal allenylidene compounds is presently attracting considerable interest,[21] up to now, [2+2] cycloaddition-type reaction of allenylidene ligands has been observed only three times. In 1996, H. Fischer and co-workers showed that alkynyl complexes $L_nMC{\equiv}CR$ (M = Fe, Ni) undergo a regioselective [2+2] cycloaddition to the $C_\alpha{=}C_\beta$ bond of diarylallenylidene complexes $(CO)_5MC{=}C{=}C(C_6H_4R\text{-}p)_2$ (M = Cr, W) providing 1,3-dimetalated cyclobutenylidene derivatives in high yield.[22] The same group has recently reported that the reactions of the above-mentioned allenylidene complexes with ynamines afford two products, alkenylallenylidene and cyclobutenylidene compounds. The first one is formed via cycloaddition of the C≡C bond of the ynamine to the $C_\beta{-}C_\gamma$ bond of the allenylidene ligand and subsequent cycloreversion, while the second one is the result of the cycloaddition of the ynamines to the $C_\alpha{-}C_\beta$ double bond of the allenylidene.[23] We have observed that the allenylidene ligand of $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CPh_2)(PPr^i_3)$ reacts with dimethyl acetylenedicarboxylate to give $Os(\eta^5\text{-}C_5H_5)Cl\{C{=}C(CO_2CH_3)C(CO_2CH_3){=}C{=}CPh_2\}(PPr^i_3)$, via a stepwise cycloaddition to the $C_\alpha{-}C_\beta$ double bond of the allenylidene to form a η^1-cyclobutenyl intermediate, which rapidly ring-opens to afford the allenylvinylidene product.[24]

In this paper, we report a new [2+2] cycloaddition reaction on an allenylidene fragment which allows the formation of the azetidine skeleton and is the entry to novel organometallic compounds containing new unsaturated η^1-carbon ligands with four- and six-membered heterocycles.

Results and Discussion

1. Synthesis of Azetidinylidenemethyl Complexes. Treatment of red dichloromethane solutions of **1** with 1 equiv of dicyclohexylcarbodiimide at room temperature affords orange solutions, from which the iminiumazetidinylidenemethyl complex $[Ru(\eta^5\text{-}C_5H_5)\{CH{=}CCPh_2N(Cy){=}C{=}N{=}C(CH_2)_4CH_2\}(CO)(PPr^i_3)]BF_4$ (**2**) was isolated as a yellow solid in 88% yield. The solid is a 4:1 mixture of the isomers *Z* and *E* shown in eq 1.

The formation of **2a** and **2b** (Scheme 1) can be rationalized as a [2+2] cycloaddition of one of the two carbon−nitrogen double bonds of the dicyclohexylcarbodiimide to the $C_\beta{-}C_\gamma$ double bond of the allenylidene of **1**, to give the intermediate **4**, which rapidly evolves into **5**, by an Alder-ene reaction, where the $C_\alpha{-}C_\beta$

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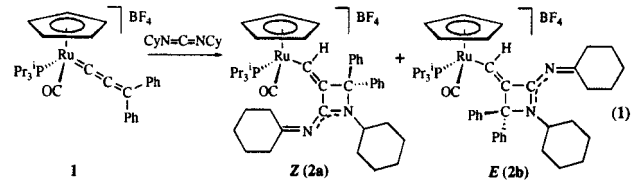
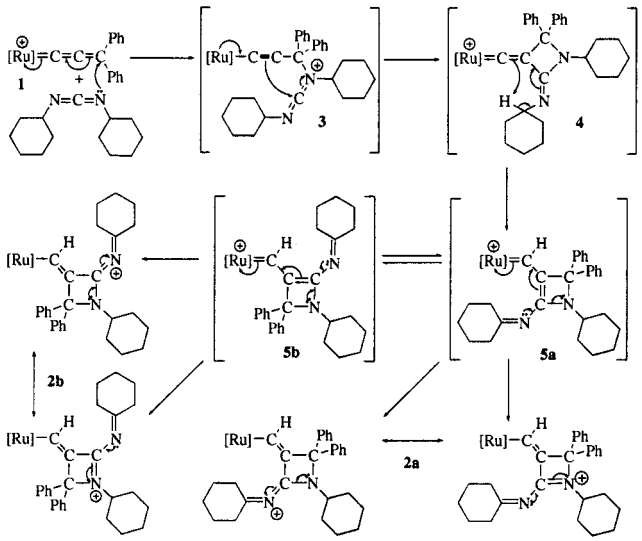


double bond of **4** acts as an enophile. The formation of the isomers *Z* (**2a**) and *E* (**2b**) of **2** suggests that the intermediate **5** exists as a mixture in equilibrium of the isomers **5a** and **5b**.

Scheme 1



[Ru] = Ru(η^5-C_5H_5)(CO)(PPr^i_3)

The [2+2] cycloaddition possibly occurs via a polar mechanism by attack of one of the N atoms of the carbodiimide on the C_γ atom of the allenylidene, to give **3**. In this context, it should be noted that EHT-MO calculations on the model compound [Ru(η^5-C_5H_5)(C=C=CH_2)(CO)(PH_3)]$^+$ indicate that 31% of the LUMO of the complex is located on the C_γ atom of the allenylidene ligand.[16] A similar mechanism has been proposed for the cycloaddition of aromatic imines to the C_γ−C_δ double bond of the butatrienylidene ligand of the cation [Ru(η^5-C_5H_5)(C=C=C=CH_2)(PPh_3)$_2$]$^+$.[25]

Isomer *Z* (**2a**) was obtained as a pure crystalline solid by crystallization in dichloromethane−diethyl ether and characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation **2a** 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 one face of the octahedron, and the angles formed by the triisopropylphosphine, the carbonyl group, and the unsaturated η^1-carbon ligand are close to 90°.

The atoms C(16), C(17), C(18), N(1), C(37), and N(2) of the unsaturated η^1-carbon ligand, which form a 2-iminium-3-methyleneazetidine skeleton, are almost planar. The deviations from the plane are −0.049(4) [C(16)], 0.026(4) [C(17)], 0.054(4) [C(18)], -0.055(3) [N(1)], 0.027(4) [C(37)], and 0.013 (3) [N(2)] Å.

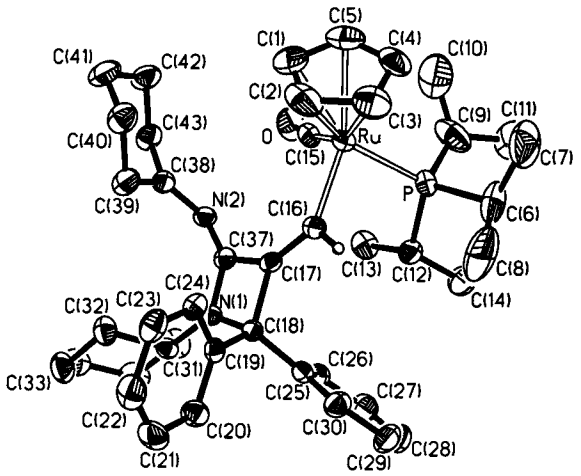


Figure 1. Molecular diagram of the complex [Ru(η^5-C_5H_5)-{(*Z*)-CH=CCPh_2N(Cy)=C=N=C$(CH_2)_4CH_2$}(CO)(PPr^i_3)]-BF_4 (**2a**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of the Complex [Ru(η^5-C_5H_5){(*Z*)-CH=CCPh_2N(Cy)=C=N=C$(CH_2)_4CH_2$}-(CO)(PPr^i_3)]BF_4 (2a)

Ru−P	2.3571(11)	C(18)−N(1)	1.545(5)
Ru−C(15)	1.875(5)	N(1)−C(31)	1.482(5)
Ru−C(16)	2.070(4)	N(1)−C(37)	1.340(5)
C(16)−C(17)	1.346(5)	C(37)−C(17)	1.470(5)
C(17)−C(18)	1.580(5)	C(37)−N(2)	1.369(5)
C(18)−C(19)	1.534(5)	N(2)−C(38)	1.297(5)
C(18)−C(25)	1.530(5)		
P−Ru−C(15)	89.73(14)	C(17)−C(18)−C(25)	113.0(3)
P−Ru−C(16)	88.15(11)	C(17)−C(18)−N(1)	84.0(2)
P−Ru−G(1)[a]	128.0(2)	C(18)−N(1)−C(31)	132.3(3)
C(15)−Ru−C(16)	97.5(2)	C(18)−N(1)−C(37)	92.9(3)
C(15)−Ru−G(1)[a]	121.5(2)	N(1)−C(37)−N(2)	128.1(4)
C(16)−Ru−G(1)[a]	122.6(2)	N(1)−C(37)−C(17)	96.1(3)
Ru−C(16)−C(17)	135.3(3)	C(37)−N(2)−C(38)	123.9(3)
C(16)−C(17)−C(18)	133.8(3)	C(37)−C(17)−C(16)	139.3(4)
C(17)−C(37)−N(2)	135.7(4)	C(37)−C(17)−C(18)	86.7(3)
C(17)−C(18)−C(19)	116.6(3)	C(37)−N(1)−C(31)	134.0(3)

[a] G(1) is the midpoint of the C(1)−C(5) Cp ligand.

The Ru−C(16) distance [2.070(4) Å] lies within the range 2.03(1)[26]−2.141(3)[27] Å, where a Ru−C(sp^2) single bond has been proposed to exist. The C(16)−C(17) distance of 1.346(5) Å, which is about 0.02 Å longer than the carbon−carbon double bond length found in 4-benzylidene-1-*tert*-butyl-2-(*tert*-butylimino)-3-phenylazetidine [1.327(2) Å],[28] is in agreement with the sample mean of carbon−carbon bond lengths for double bonds [1.32(1) Å].[29] The angle Ru−C(16)−C(17) is 135.3(3)°.

The endocyclic N(1)−C(37) [1.340(5) Å] and exocyclic C(37)−N(2) [1.369(5) Å] bond lengths indicate electron delocalization over these three atomic centers, while the C(17)−C(18) [1.580(5) Å] and C(18)−N(1) [1.545(5) Å] distances reveal the tension within the four-membered heterocycle. The C(17)−C(18) bond length is about 0.1 Å longer than the sample mean of the C(sp^2)−C(sp^3)

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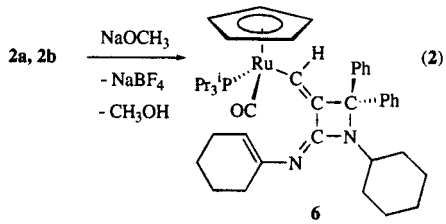
single-bond distance [1.48(3) Å][29] and the C(18)−N(1) bond length is about 0.06 Å longer than the single bond N(1)−C(31) distance [1.482(5) Å]. The angles within the heterocycle are between 84.0(2)° and 96.1(3)°. A similar situation has been observed in the organic salts 1-benzhydrylazetidindimethyliminium chloride[30] and *trans*-2-dimethylamino-3-*p*-nitrophenyl-1,4-diphenyl-3,4-dihydro-1-azetium perchlorate.[31]

In the ^{1}H NMR spectrum of **2a**, the most noticeable resonance is a doublet [J(PH) = 5.9 Hz] at 9.71 ppm, corresponding to the RuCH= proton. In agreement with the structure shown in Figure 1, this resonance shows NOE effect (3%) with the resonance of the *ortho*-phenyl protons. In the ^{13}C{^{1}H} NMR spectrum, the resonance due to C(16) appears at 182.9 ppm as a doublet with a P−C coupling constant of 13.9 Hz, whereas the resonances corresponding to C(17), C(18), and C(37) appear at 142.4, 86.4, and 185.5 ppm, respectively, as singlets.

In the ^{1}H NMR spectrum of **2b**, the RuCH= resonance is observed at 10.27 ppm as a doublet with a P−H coupling constant of 6.2 Hz. In agreement with the *E*-stereochemistry around the RuCH=C double bond, in this case, a NOE effect between the RuCH resonance and that corresponding to the *ortho*-phenyl protons is not observed. In the ^{13}C{^{1}H} NMR spectrum, the RuCH= resonance appears at 180.4 ppm as a doublet with a P−C coupling constant of 12.7 Hz, and the resonances corresponding to =C, CPh_2, and N==C==N carbon atoms are observed at 144.1, 89.0, and 188.2 ppm, respectively, as singlets.

Treatment of the isomeric mixture of **2** with sodium methoxide in tetrahydrofuran at room temperature affords the iminoazetidinylidenemethyl complex Ru(η^5-C_5H_5){(*Z*)-CH=$\overline{CCPh_2N(Cy)C}$=$\overline{NC}$=$\overline{CH(CH_2)_3CH_2}$}(CO)($PPr^i_3$) (**6**) as a result of the deprotonation of a CH_2-C=N proton of the cyclohexylidene group of **2** (eq 2).



Complex **6** was obtained as a white solid in 74% yield and characterized by MS, elemental analysis, IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopies. In the ^{1}H NMR spectrum, in dichloromethane-d_2, the most noticeable resonances are a doublet [J(PH) = 3.3 Hz] at 7.02 ppm, a triplet [J(HH) = 3.7 Hz] at 4.89 ppm, and a triple triplet [J(HH) = 12.0 and 3.6 Hz] at 3.68 ppm, which, on the basis of a ^{1}H−^{1}H COSY spectrum, were assigned to the RuCH=, −CH=CN, and NCH− protons, respectively.

Although from the isomeric mixture of **2**, two stereochemistries at the carbon-carbon double bond of the unsaturated η^1-carbon ligand of **6** could be formed according to eq 2, *E* and *Z*, only one of them, *Z*, is obtained. This is supported by the fact that the irradiation of the RuCH= resonance produces a 3.45% NOE effect on the resonance of the *ortho*-phenyl protons. The selective formation of the *Z*-isomer of **6** appears to be related with the steric requirements of the triisopropylphosphine and azetidinylidenemethyl ligands, which are mutually *cis* disposed. Thus, as can be viewed in Figure 1, both phenyl groups of the unsaturated η^1-carbon ligand are away from the bulky phosphine ligand.

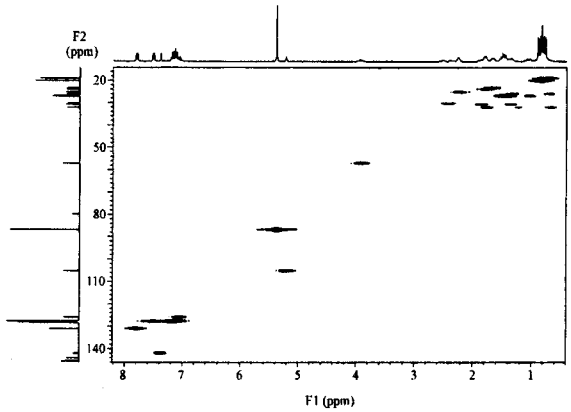


Figure 2. ^{1}H−^{13}C HETCOR NMR spectrum of the complex Ru(η^5-C_5H_5){(*Z*)-CH=$\overline{CCPh_2N(Cy)C}$=$\overline{NC}$=$\overline{CH(CH_2)_3CH_2}$}(CO)($PPr^i_3$) (**6**).

The ^{13}C{^{1}H} NMR spectrum of **6** in benzene-d_6 contains at 141.8 ppm a doublet with a P−C coupling constant of 15.8 Hz, and at 154.6, 149.3, 144.0, 105.2, 79.7, and 57.0 ppm singlets. Figure 2 shows the ^{1}H−^{13}C HETCOR NMR spectrum in benzene-d_6. In this spectrum, the most noticeable correlations are observed at 141.8(^{13}C)−7.39(^{1}H), 105.2(^{13}C)−5.23(^{1}H), and 57.0(^{13}C)−3.94(^{1}H) ppm. On the basis of these correlations, we have assigned the resonances at 141.8, 105.2, and 57.0 ppm to the RuCH=, −CH=, and NCH carbon atoms, respectively. The resonance at 149.3 ppm was assigned to the olefinic =C−N carbon atom of the cyclohexenyl group, whereas the resonances at 154.6, 144.0, and 79.7 ppm were assigned to the N−C=N, =C, and −CPh_2 carbon atoms of the azetidine skeleton, by comparison of the ^{13}C{^{1}H} NMR spectrum of **6** with those of organic methyleneazetidines.[4]

2. Synthesis of Hexahydroquinolinylidenemethyl Complexes. While in organic chemistry much of the effort involving the azetidine nucleus has been directed to its synthesis, few examples of rearrangements of the azetidine ring are known. Dialkyl azetidines afford olefins through a Hoffmann type elimination.[32] Amino alcohols have been obtain by hydrogenolysis of 4-arylazetidines, as well as from bis-azetidines.[5] Different Pd and Pt complexes are known to promote the azetidine ring breakage to yield diamine complexes[33] and aliphatic polyamines.[34] Recently, Alcaide et al.[35] have observed that, in the presence of Et_2AlCl, some azetidines give olefins or alternatively pyrrolidines. It

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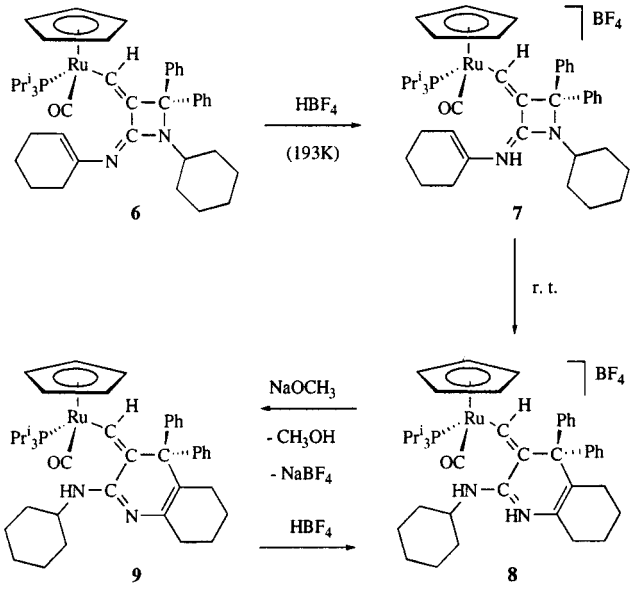
Scheme 2



has been proposed that the key step for the latter reactions is the coordination of the lone electron pair of the azetidine nucleus to the Lewis acid, Et_2AlCl, which promotes the C−N bond breakage. To investigate the possible rearrangements of the azetidine nucleus of **6**, we carried out the reaction of this complex with HBF_4.

Treatment of yellow diethyl ether solutions of **6** with 1 equiv of $HBF_4{\cdot}OEt_2$ at 193 K leads after 1 h to the iminiumazetidinylidenemethyl complex $[Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2N(Cy)C{=}N(H)C{=}CH(CH_2)_3CH_2\}(CO)(PPr^i_3)]BF_4$ (**7**), as a result of the protonation of the exocyclic nitrogen atom of the unsaturated η^1-carbon ligand of **6** (Scheme 2).

Complex **7** was isolated as a yellow solid in 68% yield and characterized by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies. The ^1H NMR spectrum of this complex in chloroform-*d* shows characteristic resonances at 8.78, 8.08, 5.87, and 3.77 ppm. The resonance at 8.78 ppm appears as a doublet with a P−H coupling constant of 7.8 Hz and was assigned to the RuCH= proton, whereas the resonances at 8.08 and 5.87 ppm appear as broad signals and were assigned to the NH and =CH− protons, respectively. The resonance at 3.77 ppm is observed as a broad triplet $J(HH) = 11.4$ Hz) and was assigned to the NCH proton.

The protonation of the exocyclic nitrogen atom instead of the endocyclic nitrogen atom of **6** was inferred on the basis of a $^1H-^1H$ COSY spectrum, which shows nuclear spin coupling between the resonances at 8.08 and 5.87 ppm (Figure 3).

In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances are observed at 167.5 [d, $J(PC) = 13.8$ Hz], 125.3(s), and 59.3(s) ppm and were assigned to the RuCH=, =CH, and NCH carbon atoms, respectively, on the basis of a $^1H-^{13}C$ HETCOR NMR spectrum.

Complexes **2** and **7** are isomers. Formally, complex **7** is a result of the migration of a $CH_2C{=}N$ proton of the cyclohexylidene group to the exocyclic nitrogen atom of **2**. This isomerization is not spontaneous even at high temperature in chloroform. The isomerization of **7** to **2** is also not observed. In dichloromethane and in chloroform, complex **7** is stable at low temperature. At room

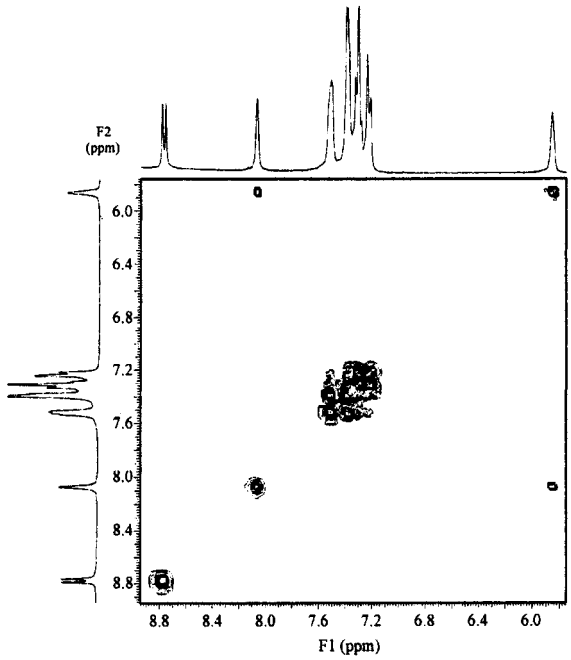


Figure 3. $^1H-^1H$ COSY NMR spectrum of the complex $[Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2N(Cy)C{=}N(H)C{=}CH(CH_2)_3CH_2\}(CO)(PPr^i_3)]BF_4$ (**7**) showing the region between 8.9 and 5.9 ppm.

temperature, it evolves into a 9:1 mixture of a new isomer $[Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2C(CH_2)_4CN(H){=}C\text{-}NHCy\}(CO)(PPr^i_3)]BF_4$ (**8**) and a minor product, which could not be identified.

When a dichloromethane solution of the above -mentioned mixture was passed through an Al_2O_3 (neutral, activity grade V) column, the hexahydroquinolinylidenemethyl complex $Ru(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH{=}CCPh_2C(CH_2)_4C\text{-}N{=}CNHCy\}(CO)(PPr^i_3)$ (**9**) was obtained, as a result of the deprotonation of the endocyclic nitrogen atom of **8**. The protonation of **9** again affords **8**, which was isolated as a pure yellow solid in 65% yield with regard to **7**. This reaction is reversible. Thus, the treatment of **8** with sodium methoxide in tetrahydrofuran at room temperature gives **9** (Scheme 2).

In the ^1H NMR spectrum of **8**, the RuCH resonance appears at 9.04 ppm as a doublet with a P−H coupling constant of 11.4 Hz, whereas the NH resonances are observed at 8.77 and 8.29 ppm. The first one, assigned to the exocyclic NH, appears as a doublet with a H−H coupling of 8.4 Hz. According to the $^1H-^1H$ COSY spectrum, the multiplicity of this signal is due to the spin nuclear coupling with the NCH proton of the cyclohexyl group, which gives rise to a multiplet at 3.79 ppm. The endocyclic NH resonance appears as a broad signal. In the $^{13}C\{^1H\}$ NMR spectrum, the RuCH= resonance is observed at 171.9 ppm as a doublet with a P−C coupling constant of 11.9 Hz, whereas the C_β atom of the RuCH=C unit gives rise to a singlet at 129.3 ppm.

Complex **9** was obtained as pale yellow crystals in 68% yield, with regard to **7**, and characterized by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction. A view of the

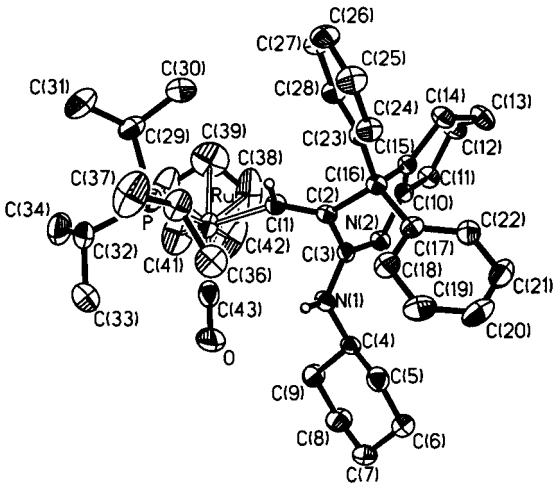


Figure 4. Molecular diagram of the complex Ru(η^5-C_5H_5)-{(*Z*)-CH=CCPh$_2$C(CH$_2$)$_4$CN=CNHCy}(CO)(PPr$^i_3$) (**9**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of the Complex Ru(η^5-C_5H_5){(*Z*)-CH=CCPh$_2$C(CH$_2$)$_4$CN=CNHCy}(CO)(PPr$^i_3$) (9)

Ru−P	2.3234(11)	C(16)−C(17)	1.556(5)
Ru−C(43)	1.829(5)	C(16)−C(15)	1.544(5)
Ru−C(1)	2.113(4)	C(15)−C(10)	1.344(5)
C(1)−C(2)	1.339(5)	C(10)−N(2)	1.418(4)
C(2)−C(3)	1.499(5)	C(10)−C(11)	1.515(5)
C(3)−N(1)	1.368(5)	C(11)−C(12)	1.526(5)
C(3)−N(2)	1.300(5)	C(12)−C(13)	1.518(6)
N(1)−C(4)	1.465(5)	C(13)−C(14)	1.536(5)
C(2)−C(16)	1.558(5)	C(14)−C(15)	1.519(5)
C(16)−C(23)	1.545(5)		

P−Ru−C(43)	90.17(14)	C(2)−C(3)−N(2)	122.8(3)
P−Ru−C(1)	90.27(10)	C(3)−N(1)−C(4)	123.3(3)
P−Ru−G(1)[a]	127.9(2)	C(3)−C(2)−C(16)	107.7(3)
C(43)−Ru−C(1)	93.04(17)	C(3)−N(2)−C(10)	116.4(3)
C(43)−Ru−G(1)[a]	128.0(3)	N(2)−C(10)−C(11)	113.1(3)
C(1)−Ru−G(1)[a]	117.1(2)	N(2)−C(10)−C(15)	123.2(3)
Ru−C(1)−C(2)	131.2(3)	C(10)−C(11)−C(12)	112.9(3)
C(1)−C(2)−C(3)	125.9(3)	C(10)−C(15)−C(14)	121.7(3)
C(1)−C(2)−C(16)	126.4(3)	C(10)−C(15)−C(16)	118.5(3)
C(2)−C(16)−C(15)	106.6(3)	C(11)−C(10)−C(15)	123.5(3)
C(2)−C(3)−N(1)	117.4(3)	C(14)−C(15)−C(16)	119.6(3)

[a] G(1) is the midpoint of the C(38)−C(42) Cp ligand.

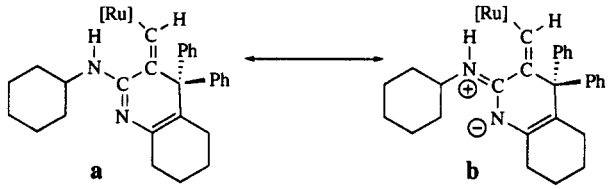
molecular geometry is shown in Figure 4. Selected bond distances and angles are listed in Table 2.

As for **2a**, the geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying one face of the octahedron, and the angles formed by the triisopropylphosphine, the carbonyl group, and the hexahydroquinolinylidenemethyl ligand are close to 90°.

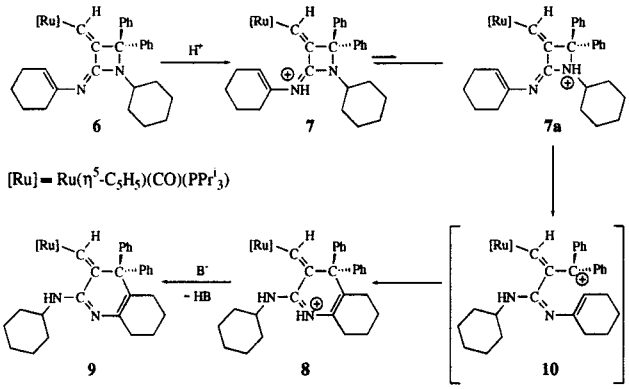
The Ru−C(1) distance [2.113(4) Å] is about 0.04 Å longer than the related parameter in **2a**, while the C(1)−C(2) distance [1.339(5) Å] is statistically identical with the related bond length in **2a**.

With regard to the aminohexahydroquinolinylidene skeleton, the difference between the C(3)−N(1) and N(1)−C(4) distances is noticeable. The separation between the exocyclic nitrogen atom N(1) and the C(4) atom of the cyclohexyl group [1.464(5) Å] agrees well with a C−N single bond and is similar to the separation

Scheme 3



Scheme 4



found between the exocyclic nitrogen atom N(1) and the cyclohexyl group in **2a** [1.482(5) Å]. However, the C(3)−N(1) distance is 1.368(5) Å, the same as the separation found between the atoms N(2) and C(37) of **2a**. This suggests that for an adequate description of the bonding situation in the aminohexahydroquinolinylidenemethyl ligand a second resonance form such as **b** (Scheme 3) should be considered. This is also supported by the value of the C(3)−N(2) distance [1.300(5) Å], which is slightly longer than the N−C double bond found in Schiff bases, hydrazones, and related compounds (about 1.29 Å), and by the value of the C(3)−N(1)−C(4) angle, which is 123.3(3)°.

In the ^{1}H NMR spectrum of **9**, the most noticeable resonance is that corresponding to the NH proton, which appears at 5.37 ppm as a doublet with a H−H coupling constant of 8.1 Hz, by nuclear spin coupling with the NCH proton of the cyclohexyl group, according to the ^{1}H−^{1}H COSY spectrum. In the ^{13}C{^{1}H} NMR spectrum, the RuCH= resonance is observed at 136.2 ppm as a doublet with a P−C coupling constant of 11.5 Hz, whereas the C_β atom of the RuCH=C unit and the N−C=N carbon atom give rise to singlets at 116.3 and 158.2 ppm, respectively.

In a similar manner to **2**, **7**, and **8**, complexes **9** and **6** are isomers. Although the isomerization of **6** into **9** is not spontaneous, the sequence of reactions shown in Scheme 2 indicates that it can be easily carried out by protonation of **6** and subsequent deprotonation of **8**. In addition, it should be noted that during the process the stereochemistry at the C−C double bond of the RuCH= C unit is retained.

Scheme 4 shows a possible mechanism for the isomerization of **6** to **9**, where the species **7** and **8** are intermediates. The process involves the split of the N−CPh$_2$ bond of the azetidine skeleton and the subsequent electrophilic attack of the resulting carbocation to the olefin of the cyclohexenyl group. Although, as a result of the protonation of **6**, we have isolated only **7**, in solution, this compound should be in equilibrium with a nondetectable concentration of its tautomer **7a**, which

is produced by hydrogen transfer from the exocyclic nitrogen atom to the endocyclic nitrogen atom. Thus, the coordination of the lone electron pair of the azetidine nitrogen atom to the proton should promote the N−CPh_2 bond breakage to form the carbocation, in agreement with Alcaide's proposal.[35]

With regard to the result of the attack of the carbocation to the olefin of the cyclohexenyl group, it should be mentioned that the formation of the six-membered heterocycles of **8** and **9** is determined by the disposition of the substituents at the nitrogen atom of the imine group, during the process. Thus, using a molecular model, it can be easily established that a change in the position of the substituents at this nitrogen atom does not allow the formation of **8**. In other words, the rearrangement of the azetidine skeleton to the six-membered heterocycle is due not only to the presence of the cyclohexenylimino substituent in the azetidine but also to the stereochemistry at the C=N double bond.

Concluding Remarks

This study has revealed that the transition-metal allenylidene compounds are useful substrates to generate an azetidine skeleton. Thus, the addition of dicyclohexylcarbodiimide to the complex [Ru(η^5-C_5H_5)(C=C=CPh_2)(CO)(PPr^i_3)]BF_4, followed by the deprotonation of the resulting cation, affords the cyclohexenyliminoazetidinylidenemethyl complex Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$N(Cy)C=NC=CH(CH$_2$)$_3$CH$_2$}(CO)(PPr^i_3), as a result of a formal [2+2] cycloaddition of one of the two carbon−nitrogen double bonds of the dicyclohexylcarbodiimide to the C_β−C_γ double bond of the allenylidene ligand, and an Alder-ene reaction, where the C_α−C_β double bond acts as an enophile.

In solution and in the solid state, this azetidinylidenemethyl derivative is stable. However, in the presence of acid, it rearranges to the thermodynamically more stable hexahydroquinolinylidenemethyl isomer Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$C(CH$_2$)$_4$CN=CNHCy}(CO)(PPr^i_3), as a consequence of the split of the N−CPh_2 bond of the azetidine skeleton and the subsequent attack of the CPh_2 carbon atom to the olefin of the cyclohexenyl group. The formation of the six-membered heterocycle is the result of two factors: (i) the presence of a cyclohexenylimino group bonded to the azetidine skeleton and (ii) the stereochemistry at the C=N double bond.

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.[15]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of [Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$N(Cy)C=N=C(CH$_2$)$_4$CH$_2$}(CO)(PPr^i_3)]BF_4 (2a) and [Ru(η^5-C_5H_5){*(E)*-CH=CCPh$_2$N(Cy)C=N=C(CH$_2$)$_4$CH$_2$}(CO)(PPr^i_3)]BF_4 (2b) at a 4 to 1 Molar Ratio. A solution of **1** (300 mg, 0.47 mmol) in 10 mL of dichloromethane at room temperature was treated with *N*,*N*′-dicyclohexylcarbodiimide (99 mg, 0.48 mmol). The mixture was stirred for 5 h, and the color changed from dark red to orange. Solvent was evaporated in vacuo, and the residue was washed with tetrahydrofuran, to afford a yellow solid. Yield: 349 mg (88%). Anal. Calcd for $C_{43}H_{58}BF_4N_2OPRu$: C, 61.64; H, 6.98; N, 3.34. Found: C, 61.61; H, 6.97; N, 3.45. IR (Nujol, cm^{-1}): ν(CO) 1927 (vs), ν(C=N) 1679 (s), ν(C=C) 1528 (s), ν(Ph) 1607 (w), ν(BF_4) 1053 (vs, br).

Spectroscopic Data for 2a. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 9.71 (d, 1H, *J*(PH) = 5.9, Ru−CH=), 7.60−7.10 (m, 10H, Ph), 5.23 (s, 5H, Cp), 3.43 (m, 1H, NCH), 2.60 (m, 4H, CH_2), 2.10−1.60 (m, 19H, CH_2 + PC*H*CH_3), 0.96 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.7, PCHC*H*$_3$), 0.85 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.5, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 68.3 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus HETCOR): δ 206.1 (d, *J*(PC) = 17.6, CO), 185.5 (s, N=C=N), 182.9 (d, *J*(PC) = 13.9, Ru−CH=), 172.0 (s, C=N), 142.4 (s, Ru−CH=*C*), 138.1, 136.9, (both s, C_{ipsoPh}), 129.9, 129.4, 128.8, 128.3, 125.9 (all s, Ph), 86.7 (s, Cp), 86.4 (s, CPh_2), 56.8 (s, NCH), 38.2, 38.1, 32.2, 30.0, 26.5, 26.3, 25.1, 25.0, 24.8, 23.9 (all s, CH_2), 27.2 (d, *J*(PC) = 23.8, P*C*HCH$_3$), 19.4, 18.8 (both s, PCH*C*H$_3$).

Spectroscopic Observed Data for 2b. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 10.27 (d, 1H, *J*(PH) = 6.2, Ru−CH=), 7.60−7.10 (m, 10H, Ph), 4.77 (s, 5H, Cp), 3.25 (m, 1H, NCH). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 69.2 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus HETCOR): δ 205.6 (d, *J*(PC) = 16.8, CO), 188.2 (s, N=C=N), 180.4 (d, *J*(PC) = 12.7, Ru−CH=), 161.4 (s, C=N), 144.1 (s, Ru−CH=*C*), 135.9, 135.8, (both s, C_{ipsoPh}), 129.5, 129.0, 128.7, 128.4 (all s, Ph), 89.0 (s, CPh_2), 86.3 (s, Cp), 55.9 (s, NCH), 37.9, 31.4, 31.2, 28.2, 24.9, 24.5, 24.0 (all s, CH_2), 29.0 (d, *J*(PC) = 23.2, P*C*HCH$_3$), 19.5, 19.2 (both s, PCH*C*H$_3$).

Preparation of Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$N(Cy)C=NC=CH(CH$_2$)$_3$CH$_2$}(CO)(PPr^i_3) (6). A suspension of **2** (324 mg, 0.41 mmol) in 15 mL of tetrahydrofuran at room temperature was treated with sodium methoxide (22 mg, 0.41 mmol), and the mixture was stirred for 1 h. The color turned from yellow to pale yellow, and the solvent was removed in vacuo. A 15 mL portion of toluene was added, and the mixture was filtered to eliminate sodium tetrafluoroborate. The solution was concentrated to ca. 1 mL, and 20 mL of pentane was carefully added. The mixture was stored at 241 K to afford **6** as white crystals. Yield: 216 mg (74%). Anal. Calcd for $C_{43}H_{57}N_2OPRu$: C, 68.86; H, 7.66; N, 3.74. Found: C, 68.40; H, 7.52; N, 3.63. IR (Nujol, cm^{-1}): ν(CO) 1909 (vs), ν(C=N) 1673 (vs), ν(C=C) 1599 (s). ^{1}H NMR (300 MHz, 293 K, CD_2Cl_2): δ 7.60-7.20 (m, 10H, Ph), 7.02 (d, 1H, *J*(PH) = 3.3, Ru−CH=), 5.33 (s, 5H, Cp), 4.89 (t, 1H, *J*(HH) = 3.7, C=CH), 3.68 (tt, 1H, *J*(HH) = 12.0, *J*(HH) = 3.6, NCH), 2.14 (m, 4H, CH_2), 1.80-0.58 (m, 17H, CH_2 + PC*H*CH_3), 0.92 (dd, 9H, *J*(HH) = 7.4, *J*(PH) = 14.6, PCHC*H*$_3$), 0.89 (dd, 9H, *J*(HH) = 7.4, *J*(PH) = 12.8, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CD_2Cl_2): δ 73.7 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus HETCOR): δ 208.1 (d, *J*(PC) = 18.9, CO), 154.6 (s, N−C=N), 149.3 (s, N*C*=CH), 145.2, 145.1 (both s, C_{ipsoPh}), 144.0 (s, Ru−CH=*C*), 141.8 (d, *J*(PC) = 15.8, Ru−CH=), 130.9, 127.9, 127.7, 127.6, 127.5, 126.0 (all s, Ph), 105.2 (s, NC=*C*H), 86.8 (s, Cp), 79.7 (s, CPh_2), 57.0 (s, NCH), 32.1, 30.8, 30.3 27.2 (all s, CH_2), 27.0 (d, *J*(PC) = 23.3, P*C*HCH$_3$), 26.7, 26.1, 25.3, 23.9, 23.4 (all s, CH_2), 20.1, 19.1 (both s, PCH*C*H$_3$). MS (FAB$^+$): m/z = 751 ([M + 1]$^+$).

Preparation of [Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$N(Cy)C=N(H)C=CH(CH$_2$)$_3$CH$_2$}(CO)(PPr^i_3)]BF_4 (7). A pale yellow solution of **6** (102 mg, 0.14 mmol) in 15 mL of diethyl ether at 193 K was treated with tetrafluoroboric acid (19 μL, 57% in Et_2O, 0.14 mmol). The mixture was stirred for 1 h, while temperature was slowly increased to 233 K, to afford a pale

yellow solid, which was washed with cold diethyl ether. Yield: 80 mg (68%). Anal. Calcd for $C_{43}H_{58}BF_4N_2OPRu$: C, 61.64; H, 6.98; N, 3.34. Found: C, 61.38; H, 6.59; N, 3.42. IR (Nujol, cm^{-1}): ν(NH) 3296 (w), ν(CO) 1921 (vs), ν(C=C) 1677 (w), ν(C=N) 1643 (s), ν(Ph) 1594 (m), $\nu(BF_4)$ 1050 (vs, br). ^{1}H NMR (300 MHz, 253 K, $CDCl_3$): δ 8.78 (d, 1H, J(PH) = 7.8, Ru−CH=), 8.08 (br, 1H, NH), 7.52−7.22 (m, 10H, Ph), 5.87 (br, 1H, NC=CH), 5.22 (s, 5H, Cp), 3.77 (br t, 1H, J(HH) = 11.4, NCH), 2.30−0.33 (m, 18H, CH_2), 1.60 (m, 3H, PC*H*CH_3), 0.85 (dd, 9H, J(HH) = 7.2, J(PH) = 14.4, PCHC*H*$_3$), 0.83 (dd, 9H, J(HH) = 6.7, J(PH) = 13.6, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 253 K, CD_2Cl_2): δ 68.3 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 253 K, $CDCl_3$, plus HETCOR): δ 208.3 (d, J(PC) = 18.0, CO), 167.5 (d, J(PC) = 13.8, Ru−CH=), 162.8 (s, N−C=N), 140.4 (s, N*C*=CH), 138.8, 137.1, (both s, C_{ipsoPh}), 131.2 (s, Ru−CH=*C*), 130.0, 129.5, 128.6, 128.3, 127.8, 126.0 (all s, Ph), 125.3 (s, NC=*C*H), 86.8 (s, CPh_2), 86.4 (s, Cp), 59.3 (s, NCH), 32.0, 28.6, 28.0 (all s, CH_2), 26.5 (d, J(PC) = 23.9, P*C*HCH$_3$), 25.4, 25.2, 24.5, 24.2, 21.8, 21.0 (all s, CH_2), 19.4 (s, PCH*C*H$_3$), 18.6 (d, J(PC) = 1.9, PCH*C*H$_3$).

Preparation of [Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$C(CH$_2$)$_4$CN(H)=CNHCy}(CO)(PPr$^i_3$)]BF_4 (8). A pale yellow diethyl ether solution of **9** (57 mg, 0.08 mmol) at room temperature was treated with tetrafluoroboric acid (14 μL, 54% in Et_2O, 0.08 mmol). Immediately, a pale yellow solid precipitated, which was washed with diethyl ether. Yield: 59 mg (93%). Anal. Calcd for $C_{43}H_{58}BF_4N_2OPRu$: C, 61.64; H, 6.98; N, 3.34. Found: C, 61.54; H, 6.49; N, 3.16. IR (Nujol, cm^{-1}): ν(NH) 3315, 3287 (both w), ν(CO) 1917 (vs), ν(C=N) 1628 (s), ν(C=C) 1537 (m), $\nu(BF_4)$ 1074, 1051, 1013 (all s). ^{1}H NMR (300 MHz, 273 K, $CDCl_3$): δ 9.04 (d, 1H, J(PH) = 11.4, Ru−CH=), 8.77 (d, 1H, J(HH) = 8.4, CHN*H*), 8.29 (br s, 1H, NH), 7.26−6.88 (10H, Ph), 4.95 (s, 5H, Cp), 3.79 (m, 1H, C*H*NH), 2.58−0.79 (m, 18H, CH_2), 1.97 (m, 3H, PC*H*CH_3), 0.96 (dd, 9H, J(HH) = 7.2, J(PH) = 12.9, PCHC*H*$_3$), 0.95 (dd, 9H, J(HH) = 7.5, J(PH) = 15.9, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 273 K, $CDCl_3$): δ 68.4 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 273 K, $CDCl_3$, plus HETCOR): δ 206.2 (d, J(PC) = 20.4, CO), 171.9 (d, J(PC) = 11.9, Ru−CH=), 155.1 (s, N−C=N), 144.5 (s, N*C*=C), 142.6, 141.5 (both s, C_{ipsoPh}), 129.3 (s, Ru−CH=*C*), 130.4, 128.7, 128.2, 127.6, 126.9, 126.5 (all s, Ph), 121.6 (s, NC=*C*), 86.0 (s, Cp), 62.2 (s, CPh_2), 50.5 (s, NCH), 32.2, 31.0, 28.6 (all s, CH_2), 26.4 (d, J(PC) = 23.0, P*C*HCH$_3$), 25.6, 25.0, 23.9, 23.7, 22.7, 21.8 (all s, CH_2), 19.8 (s, PCH*C*H$_3$), 18.8 (d, J(PC) = 1.9, PCH*C*H$_3$).

Preparation of Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$C(CH$_2$)$_4$CN=CNHCy}(CO)(PPr$^i_3$) (9). **7** (134 mg, 0.17 mmol) was solved in 40 mL of dichloromethane at 203 K, and the yellow solution was kept at 293 K for 5 days. The solution was concentrated to ca. 1 mL and chromatographed on alumina. A dichloromethane/tetrahydrofuran mixture (1:1) eluted a pale yellow fraction. Solvent was removed in vacuo, and the residue was extracted with three fractions of 20 mL of diethyl ether. Solvent was removed in vacuo from the diethyl ether solution, and the residue was washed with pentane to afford **9** as a white solid. Yield: 80 mg (68%). Anal. Calcd for $C_{43}H_{57}N_2OPRu$: C, 68.86; H, 7.66; N, 3.74. Found: C, 68.63; H, 7.82; N, 3.98. IR (Nujol, cm^{-1}): ν(NH) 3447 (w), ν(CO) 1909 (vs), ν(C=N) 1585 (s), ν(C=C) 1501 (m). ^{1}H NMR (300 MHz, 273 K, $CDCl_3$): δ 7.18−7.02 (11 H, Ph + RuCH), 5.37 (d, 1H, J(HH) = 8.1, NH), 5.00 (s, 5H, Cp), 3.70 (m, 1H, NCH), 2.31−0.79 (18H, CH_2), 2.02 (m, 3H, PC*H*CH_3), 1.02 (dd, 9H, J(HH) = 6.6, J(PH) = 13.8, PCHC*H*$_3$), 1.00 (dd, 9H, J(HH) = 5.1, J(PH) = 12.6, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 273 K, $CDCl_3$): δ 71.4 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 273 K, $CDCl_3$, plus HETCOR): δ 208.5 (d, J(PC) = 20.7, CO), 158.2 (s, N−C=N), 148.9 (s, N*C*=C), 146.2, 145.7, (both s, C_{ipsoPh}), 141.8 (s, NC=*C*), 136.2 (d, J(PC) = 11.5, Ru−CH=), 130.6, 130.1, 127.1, 127.0, 125.4, 125.1 (all s, Ph), 116.3 (s, Ru−CH=*C*), 86.3 (s, Cp), 63.4 (s, CPh_2), 48.9 (s, NCH), 32.8, 32.3, 31.4, 30.3 (all s, CH_2), 26.0 (d, J(PC) = 22.1, P*C*HCH$_3$), 25.9, 25.0, 24.9, 23.6, 23.5 (all s, CH_2), 19.9, 19.1 (both s, PCH*C*H$_3$).

Table 3. Crystal Data and Data Collection and Refinement for Complexes [Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$N(Cy)=C=N=C(CH$_2$)$_4$CH$_2$}(CO)(PPr$^i_3$)]BF_4 (2a) and Ru(η^5-C_5H_5){*(Z)*-CH=CCPh$_2$C(CH$_2$)$_4$CN=CNHCy}(CO)(PPr$^i_3$) (9)

	2a	9
formula	$C_{43}H_{58}BF_4N_2OPRu$	$C_{43}H_{57}N_2OPRu$
mol wt	837.76	749.95
color, habit	yellow, irregular prism	yellow, rectangular plate
cryst size, mm	0.83 × 0.55 × 0.29	0.53 × 0.33 × 0.10
space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	11.165(1)	9.870(1)
b, Å	21.762(2)	13.770(1)
c, Å	17.577(2)	16.110(2)
α, deg	90	99.194(7)
β, deg	101.295(7)	102.323(8)
γ, deg	90	109.343(6)
V, Å^3	4188.0(7)	1954.2(3)
Z	4	2
D(calcd), g cm^{-3}	1.329	1.274
μ, mm^{-1}	0.465	0.476
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
temp, K	200.0(2)	223.0(2)
no. of data collected	9096	9697
no. of unique data	7363 (R_{int} = 0.0175)	6825 (R_{int} = 0.0219)
no. of params refined	517	436
R_1[a] ($F^2 > 2\sigma(F^2)$)	0.0488	0.0489
wR_2[b] (all data)	0.1834	0.1528
S[c] (all data)	0.966	0.800

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$ (**2a**, a = 0.0824, b = 10.99; **9**, a = 0.1249, b = 5.38). [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of refined parameters.

Crystal Data for 2a and 9. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **2** in dichloromethane, or **9** in dichloromethane/pentane. A summary of crystal data and refinement parameters is reported in Table 3. The yellow crystals (0.83 × 0.55 × 0.29 (**2a**) and 0.53 × 0.33 × 0.10 (**9**)) were glued on a glass fiber and mounted on a Siemens P4 four-circle diffractometer, with graphite-monochromated Mo Kα radiation. A group of 29 reflections in the range 20° ≤ 2θ ≤ 30° (**2a**) or 60 reflections in the range 20° ≤ 2θ ≤ 40° (**9**) were carefully centered at 200 (**2a**) or 223 K (**9**) and used to obtain by least-squares methods the unit cell dimensions. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[36] The structures were solved by direct methods[37] and conventional Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL93 (**2a**) or SHELXL97 (**9**)).[38] The BF_4^- anion of **2a** was found to be disordered. It was modeled on the basis of two different moieties sharing the central boron atom with complementary occupancy factors refined to final values of 0.62(2) and 0.38(2). After anisotropic refinement of **9**, only two peaks of high electron density were observed (>1 e/Å^3). The relative intensity

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and geometry of these residuals (see Experimental Section) suggested the presence of a second Ru and P atom corresponding to a situation of static disorder affecting the molecule. The small intensity of these peaks prevents finding a proper model for this disorder. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were calculated and refined riding on their respective carbon atoms with a common isotropic thermal parameter (**2a**) or thermal parameters related to bonded atoms (**9**). Atomic scattering factors, corrected for anomalous dispersion for Ru and P, were implemented by the program. The refinement converge to $R_1 = 0.0488$ (**2a**) or 0.0489 (**9**) [$F^2 > 2\sigma(F^2)$] and wR_2 (all data) = 0.1834 (**2a**) or 0.1528 (**9**), with weighting parameters $x = 0.0824$, $y = 10.99$ (**2a**) and $x = 0.1249$, $y = 5.38$ (**9**).

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Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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