Migratory Insertion of Acetylene in N-Heterocyclic Carbene Complexes of Ruthenium: Formation of (Ruthenocenylmethyl)imidazolium Salts

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Received October 26, 2006

With the parent acetylene and $[RuCp(IPr)(CH_3CN)_2]PF_6$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) an unusual C−C coupling process takes place involving three acetylene molecules and migration of the NHC ligand to give the formal [2 + 2 + 1] cycloaddition product $[RuCp(\eta^4\text{-}C_5H_5\text{-}\eta^1\text{-}CH\text{-}IPr)]PF_6$. This complex undergoes a facile 1,2-H shift to afford the (ruthenocenylmethyl)imidazolium salt $[RuCp(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}IPr)]PF_6$. The same reaction takes place with $[RuCp(SIPr)(CH_3CN)_2]PF_6$ (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene), giving $[RuCp(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}SIPr)]PF_6$. A conceivable mechanism for this reaction sequence is established by means of DFT/B3LYP calculations. The key step is the facile insertion of acetylene into the Ru−C bond of the NHC ligand, requiring merely 4.1 kcal/mol with 1,3-dimethylimidazol-2-ylidene but 17.2 kcal/mol with 1,3-diphenylimidazol-2-ylidene as model NHC ligands.

Introduction

N-heterocyclic carbenes (NHC) play an important role as "*noninterfering*" supporting ligands in many stoichiometric and catalyzed reactions of transition-metal complexes.[1] The role of the carbene ligands is similar to that of tertiary phosphine ligands, but they are in general much more strongly bound to a metal center than phosphines and thus less likely to be replaced by other ligands.[2] On the other hand, due to the obvious electronic differences between NHC ligands and tertiary phosphines, it is not surprising that NHC ligands are much more likely to participate in rearrangement reactions within the metal coordination sphere. In fact, several recent reports clearly show that NHC−metal bonds are kinetically not inert and are able to participate in various intramolecular reactions.[3] This includes migration of a methyl group to a coordinated NHC ligand[3c] and the reductive elimination of alkylimidazolium salts from NHC alkyl complexes.[3f] Our recent studies of the interactions between the $[RuCp(IPr)]^+$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) moiety, derived from labile $[RuCp(IPr)(CH_3CN)_2]^+$, and various terminal alkynes have revealed that the IPr ligand rapidly migrates onto the carbene carbon atom of a highly electrophilic bis(carbene) intermediate, affording allyl carbene complexes (Scheme 1).[4]

Herein we report the first example of a facile migratory insertion of acetylene into the Ru−C bond of the NHC ligands IPr and SIPr (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene). This behavior strongly contrasts that of tertiary phosphines, where such reactions are, to our knowledge, unknown.

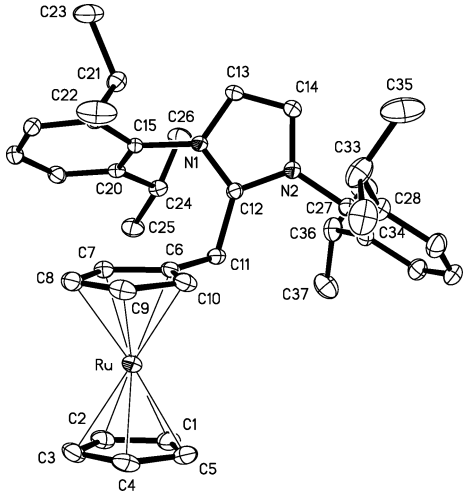

Figure 1. Structural view of $[RuCp(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}IPr)]PF_6$ (**3a**) showing 40% thermal ellipsoids (PF_6^- and hydrogen atoms omitted for clarity). Selected bond lengths (Å): $Ru-C(1-5)_{av}$ = 2.183(2), $Ru-C(6-10)_{av}$ = 2.178(2), C(6)−C(11) = 1.594(2), C(11)−C(12) = 1.501(2), C(12)−N(1) = 1.349(2), C(12)−N(2) = 1.349(2), C(13)−C(14) = 1.354(2).

† Institute of Applied Synthetic Chemistry.
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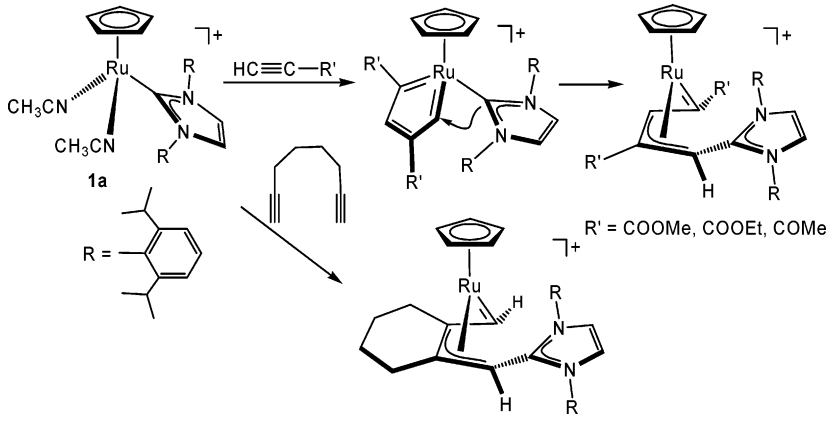
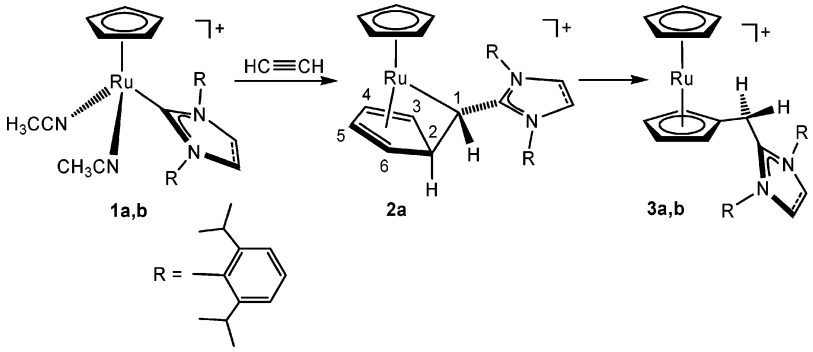
10.1021/om060990i CCC: $37.00
Publication on Web 02/17/2007

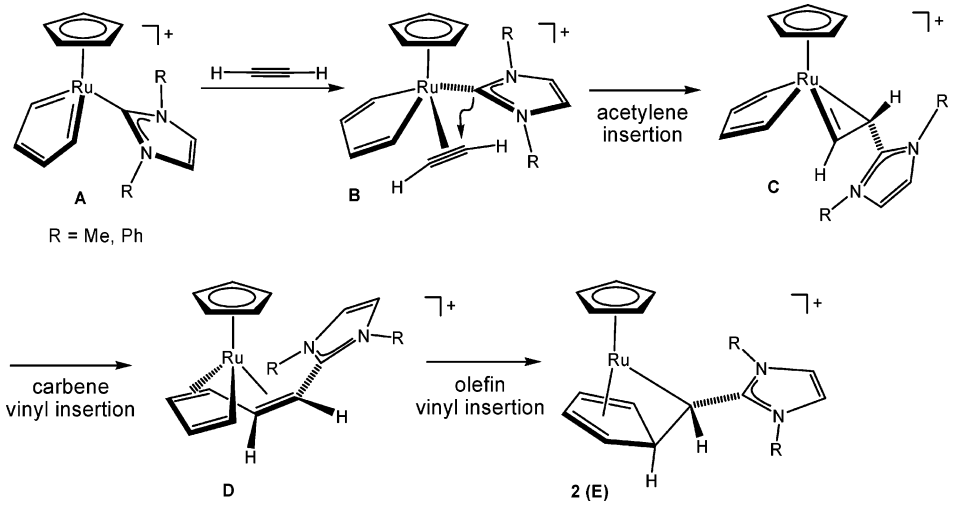
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

Upon treatment of $[RuCp(IPr)(CH_3CN)_2]^+$ (**1a**)[5] with HC≡CH in CH_2Cl_2 for 10 min at room temperature, $[RuCp(\eta^4\text{-}C_5H_5\text{-}\eta^1\text{-}CH\text{-}IPr)]PF_6$ (**2a**) is obtained in 94% isolated yield (Scheme 2). This compound is air-stable both in solution and in the solid state and was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as well as by elemental analysis. In the course of the overall [2 + 2 + 1] cyclotrimerization[6] the Ru−C(IPr) bond is cleaved and four new C−C bonds are formed, thereby converting two C−C triple bonds into C−C double bonds and one C−C triple bond into a C−C single bond. A similar reaction has been described recently for the reaction of various terminal acetylenes and $[Ru(\eta^5\text{-}C_5H_4CH_2CH_2\text{-}\kappa^1P\text{-}PPh_2)(CH_3CN)_2]PF_6$, featuring a tethered phosphine.[6b] The ^1H NMR spectroscopic data for **2a** include characteristic multiplets in the range of 5.50−3.48 ppm assignable to the diene protons H^{3-6} of the coordinated η^4-cyclopentadiene unit and resonances at 2.18 and 1.83 ppm which correspond to H^2 and the Ru−CH proton H^1. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the sp^3 carbon C^1 is diagnostic, giving rise to an unusually high field shifted resonance at −39.9 ppm. The coordinated sp^2 carbon atoms C^3, C^4, C^5, and C^6 of the cyclopentadiene moiety exhibit resonances at 42.4, 85.2, 85.1, and 69.5 ppm, respectively, while the noncoordinated sp^3 carbon C^2 gives rise to a singlet at 54.4 ppm.

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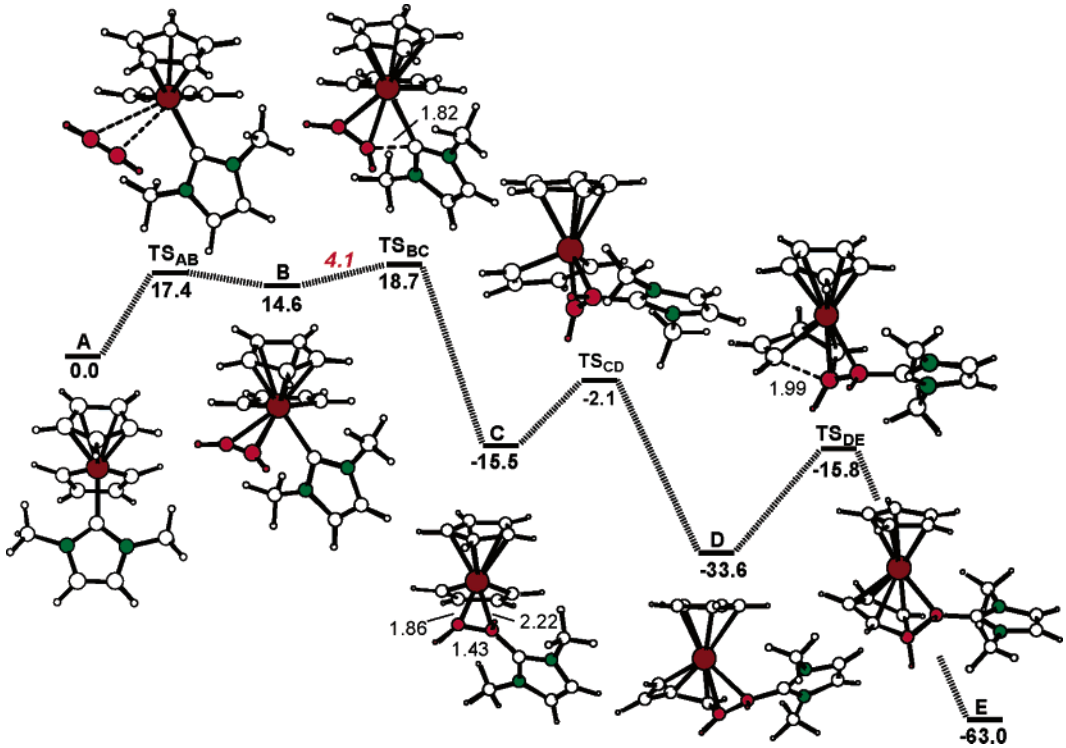

Figure 2. Reaction profile of the computed relative Gibbs free energies (in kcal/mol) for the reaction of the ruthenacyclopentatriene (**A**) with acetylene to give the formal [2 + 2 + 1] cycloadition product (**E**) (bond distances in Å) with 1,3-dimethylimidazol-2-ylidene as the model NHC ligand.

If a solution of **2a** is kept at 40 °C for 12 h, the (ruthenocenylmethyl)imidazolium salt [RuCp(η^5-C_5H_4-CH_2-IPr)]PF_6 (**3a**) is formed in essentially quantitative yield as a result of a facile 1,2-hydrogen shift. The driving force for this rearrangement is obviously ligand aromatization. A structural view of **3a** is depicted in Figure 1. The same reaction takes place with acetylene and [RuCp(SIPr)$(CH_3CN)_2$]PF_6 (**1b**) (a structural view of this compound is given in the Supporting Information), bearing the slightly more basic saturated NHC ligand 1,3-bis-(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene. In this case, however, no intermediate could be detected and only the formation of the imidazolinium salt [RuCp(η^5-C_5H_4-CH_2-SIPr)]-PF_6 (**3b**) was observed (a structural view of **3b** is given in the Supporting Information).

In this context it has to be mentioned that Ru(*p*-cymene)-(NHC)Cl_2 (NHC = 1-butyl-3-methylimidazol-2-ylidene) was found to catalyze the oligomerization of HC≡CPh, where the linear oligomers contain a positively charged imidazolium endgroup.[7] This observation seems to be related to our observations and may suggest that insertion of HC≡CPh into the Ru−C bond of the NHC ligand initiates the oligomerization process.

DFT/B3LYP calculations have been performed to shed light on the mechanism of this unusual transformation. The result of this study is shown in Scheme 3. A free energy profile for the conversion of **A** to the [2 + 2 + 1] cycloaddition product **2** (**E** in the model) is depicted in Figure 2 with 1,3-dimethylimidazol-2-ylidene (R = Me) as the model NHC ligand. Additionally, the free energy profile for the most crucial conversion of **A** to **C** has been calculated with the bulkier NHC ligand 1,3-diphenylimidazol-2-ylidene (R = Ph) (Figure 3), since it has been shown that that aromatic and aliphatic imidazolium compounds exhibit different electronics and particularly significant steric differences.[8] On the basis of our experimental findings, the starting point and key intermediate is the ruthenacyclopentatriene complex **A**, which is able to accommodate a third acetylene molecule to afford the metallacyclopentadiene acetylene complex **B**. This is the rate-determining step both for R = Me and for R = Ph. The most remarkable step is the insertion of acetylene into the Ru−C bond of **B**, resulting in the formation of the novel metallacyclopentadiene 1-metallacyclopropene complex **C**. The free activation energy for this intramolecular process is very low for R = Me, requiring merely 4.1 kcal/mol, but 17.2 kcal/mol is needed for R = Ph, which may be largely attributed to the increased steric bulk of the 1,3-diphenylimidazol-2-ylidene ligand. In fact, Nolan et al. have demonstrated that the electronic differences for NHC ligands are relatively small when moving from alkyl- to aryl-substituted ligands, especially in comparison to the substantial electronic differences seen in phosphine ligands.[8] It should be noted that coupling reactions between a coordinated alkyne and coordinated phosphines to yield 1-metallacyclopropenes have been reported in the literature.[9,10] In all of these cases, however, the "formal"

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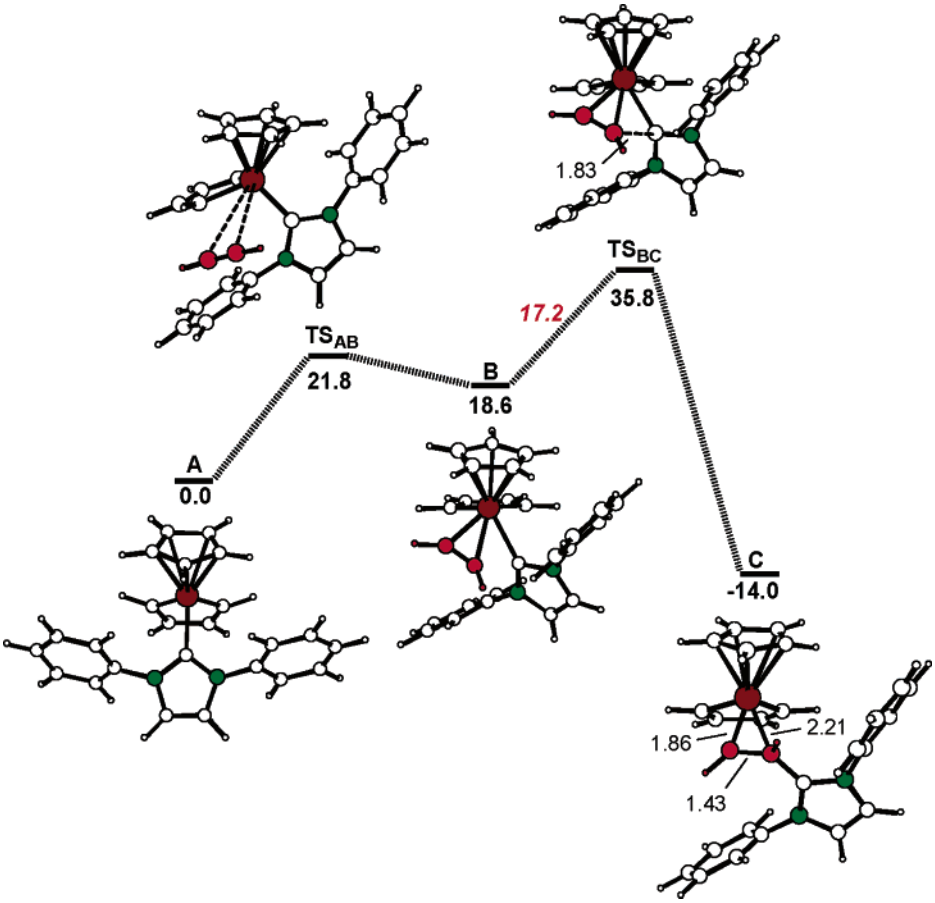

Figure 3. Reaction profile of the computed relative Gibbs free energies (in kcal/mol) for the reaction of the ruthenacyclopentatriene (**A**) with acetylene to give the 1-metallacyclopropene intermediate (**C**) (bond distances in Å) with 1,3-diphenylimidazol-2-ylidene as the model NHC ligand.

insertion of alkynes into metal−P bonds appears to be a nucleophilic addition at the coordinated alkyne, requiring prior dissociation of the phosphine. In fact, intermolecular nucleophilic additions of phosphines and phosphites to alkyne ligands are feasible and well established.[11] Complex **C** is prone to C−C coupling between the carbene carbon atom of the 1-metallacyclopropene moiety and the α-carbon of the metallacyclopentadiene unit to give **D**. This reaction requires a free activation energy of 13.4 kcal/mol and is energetically very favorable, releasing 35.0 kcal/mol. The final and rate-determining step is the insertion of the vinyl moiety into the η^2-olefin unit to give **E**, thus completing the [2 + 2 + 1] cyclotrimerization. The overall reaction from **A** to **E** is strongly exergonic by −63.0 kcal/mol.

In conclusion, our experimental and theoretical data provide for the first time clear evidence that acetylene is able to undergo facile migratory insertion into the Ru−C bond of NHC ligands, which has not been observed before in N-heterocyclic carbene complexes. This process is accompanied by Ru−C bond cleavage and is another example of the finding that an N-heterocyclic carbene ligand is not necessarily just a spectator ligand. This behavior is in contrast with that of related phosphine systems.

Experimental Section

General Techniques. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[12] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [RuCp(CH$_3$CN)$_2$(IPr)]PF$_6$ (**1a**) was prepared according to the literature.[13] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to SiMe$_4$. ^{1}H and ^{13}C{^{1}H} NMR signal assignments were confirmed by ^{1}H-COSY, 135-DEPT, and HSQC(^{1}H−^{13}C) experiments.

[RuCp(CH$_3$CN)$_2$(SIPr)]PF$_6$ (1b). A suspension of SIPr·HCl (692 mg, 1.62 mmol) in 20 mL of toluene was cooled to −40 °C, and *n*-BuLi (0.65 mL of a 2.6 M solution in *n*-hexane) was added via syringe. The mixture was stirred for 30 min at room temperature. LiCl was removed by filtration. This solution was then slowly added to a stirred solution of [RuCp(CH$_3$CN)$_3$]PF$_6$ (350 mg, 0.81 mmol) in THF (10 mL). The solution was stirred at room temperature for 30 min. After removal of the solvent under vacuum the remaining brown solid was dissolved in 2 mL of acetonitrile and purified by

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column chromatography (neutral Al_2O_3, eluent CH_3CN). **1b** was isolated as a yellow microcrystalline solid. Yield: 76% (480 mg). Anal. Calcd for $C_{36}H_{49}F_6N_4PRu$: C, 55.16; H, 6.30; N, 7.15. Found: C, 55.09; H, 6.40; N, 7.25. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.46−7.26 (m, 6H, Ar[4]), 3.99 (s, 4H, SIPr CH_2), 3.80 (s, 5H, Cp), 3.33 (m, J_{HH} = 6.8 Hz, 4H, Pr^i CH), 2.09 (s, 6H, CH_3CN), 1.34 (d, J_{HH} = 6.8 Hz, 12H, Pr^i CH_3), 1.33 (d, J_{HH} = 6.8 Hz, 12H, Pr^i CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 214.7 (NCN), 147.0 (Ar^{2,6}), 138.8 (Ar^1), 131.6 (Ar^4), 126.3 (*C*N), 124.4 (Ar^{3,5}), 74.4 (Cp), 54.9 (SIPr *C*H$_2$), 28.5 (Pr^i *C*H), 25.9 (Pr^i *C*H$_3$), 23.1 (Pr^i *C*H$_3$), 4.2 (*C*H$_3$CN).

[RuCp(η^4-C$_5$H$_5$-η^1-CH-IPr)]PF$_6$ (2a). A solution of **1a** (100 mg, 0.13 mmol) in 5 mL of CH_2Cl_2 was stirred under an atmosphere of acetylene for 10 min at room temperature. Then the solvent was removed and **2a** was isolated as a pure, air-stable red-brown solid. Yield: 94% (93 mg). Anal. Calcd for $C_{38}H_{47}F_6N_2PRu$: C, 58.68; H, 6.09; N, 3.60. Found: C, 58.83; H, 6.19; N, 3.53. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.75−7.38 (m, 6H, Ar), 7.21 (s, 2H, IPr CH), 5.50 (m, 1H, H^5), 5.37 (m, 1H, H^6), 5.24 (m, 1H, H^4), 4.59 (s, 5H, Cp), 3.48 (m, 1H, H^3), 2.87−2.63 (m, 4H, Pr^i CH), 2.18 (m, 1H, H^2), 1.78 (m, 1H, H^1), 1.39 (d, J_{HH} = 6.7 Hz, 12H, Pr^i CH_3), 1.23 (d, J_{HH} = 6.5 Hz, 12H, Pr^i CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 163.9 (NCN), 145.8 (Ar^{2,6}), 145.1 (Ar^{2,6}), 132.3 (Ar^4), 132.2 (Ar^1), 132.0 (Ar^4), 125.5 (Ar^{3,5}), 125.2 (Ar^{3,5}), 124.8 (IPr *C*H), 123.6 (IPr *C*H), 85.2 (C^4), 85.1 (C^5), 78.2 (Cp), 69.5 (C^6), 54.4 (C^2), 42.4 (C^3), 29.5 (Pr^i *C*H), 29.3 (Pr^i *C*H), 26.9 (Pr^i *C*H), 25.2 (Pr^i *C*H), 22.3 (Pr^i *C*H$_3$), 21.6 (Pr^i *C*H$_3$), −39.9 (C^1).

[RuCp(η^5-C$_5$H$_4$-CH$_2$-IPr)]PF$_6$ (3a). A solution of **2a** (90 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was heated to 40 °C for 12 h. After the solvent was removed, the remaining solid was purified by column chromatography (neutral Al_2O_3, eluent 1/1 Et_2O/CH_2Cl_2). Yield: 96% (86 mg). Anal. Calcd for $C_{38}H_{47}F_6N_2PRu$: C, 58.68; H, 6.09; N, 3.60. Found: C, 58.77; H, 6.11; N, 3.72. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.41−7.72 (m, 8H, Ar, IPr CH), 4.33 (s, 5H, Cp), 4.29 (bs, 2H, H^{3,4}), 3.78 (bs, 2H, H^{2,5}), 3.54 (s, 2H, CH_2), 2.48 − 2.17 (m, 4H, Pr^i CH), 1.29 (d, J_{HH} = 6.0 Hz, 12H, Pr^i CH_3), 1.23 (d, J_{HH} = 5.7 Hz, 12H, Pr^i CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 146.2 (NCN), 145.0 (Ar^{2,6}), 132.7 (Ar^4), 129.2 (Ar^1), 125.4 (Ar^{3,5}), 124.8 (IPr *C*H), 78.5 (C^1), 71.7 (C^{2,5}), 71.3 (Cp), 70.9 (C^{3,4}), 29.3 (Pr^i *C*H), 29.1 (Pr^i *C*H), 26.6 (*C*H$_2$), 25.2 (Pr^i *C*H$_3$), 22.4 (Pr^i *C*H$_3$).

[RuCp(η^5-C$_5$H$_4$-CH$_2$-SIPr)]PF$_6$ (3b). A solution of **1b** (100 mg, 0.13 mmol) in 5 mL of CH_2Cl_2 was stirred under an atmosphere of acetylene for 30 min at room temperature. Then the solvent was removed and **3b** was isolated as a pure, air-stable brown solid. Yield: 96% (96 mg). Anal. Calcd for $C_{38}H_{49}F_6N_2PRu$: C, 58.53; H, 6.33; N, 3.59. Found: C, 58.60; H, 6.24; N, 3.52. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.60 (t, J_{HH} = 7.5 Hz, 2H, Ar^4), 7.39 (d, J_{HH} = 7.5 Hz, 4H, Ar^{3,5}), 4.56 (bs, 2H, H^{3,4}), 4.40 (s, 4H, SIPr CH_2), 4.27 (s, 5H, Cp), 4.84 (bs, 2H, H^{2,5}), 3.26 (s, 2H, CH_2), 2.85 (m, J_{HH} = 6.8 Hz, 4H, Pr^i CH), 1.36 (d, J_{HH} = 6.8 Hz, 12H, Pr^i CH_3), 1.34 (d, J_{HH} = 6.8 Hz, 12H, Pr^i CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 167.7 (N*C*N), 146.0 (Ar^{2,6}), 131.8 (Ar^4), 129.2 (Ar^1), 125.6 (Ar^{3,5}), 77.2 (C^1), 72.0 (C^{2,5}), 71.3 (Cp), 70.9 (C^{3,4}), 52.8 (SIPr *C*H), 29.3 (Pr^i *C*H), 28.0 (*C*H$_2$), 25.8 (Pr^i *C*H$_3$), 23.2 (Pr^i *C*H$_3$).

X-ray Structure Determination. X-ray data were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and 0.3° ω-scan frames. Corrections for absorption, λ/2 effects, and crystal decay were applied.[14] The structures were solved by direct methods using the program SHELXS97.[15] Structure refinement on F^2 was carried out with the program SHELXL97.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. For **1b** and **3b** see Supporting Information.

Crystal data for **3a**: $C_{38}H_{47}F_6N_2PRu$, M_r = 777.82, triclinic, space group $P\bar{1}$ (No. 2), T = 100(2) K, a = 10.3126(9) Å, b = 10.9150(10) Å, c = 16.9277(15) Å, V = 1776.2(3) Å,^{3} Z = 2, μ = 0.548 mm^{-1}. Of 16 177 reflections collected, 10 035 were independent. Final R indices: R1 = 0.036 (all data), wR2 = 0.081 (all data).

Computational Details. All calculations were performed using the Gaussian03 software package on the Silicon Graphics Origin 2000 computer of the Vienna University of Technology.[16] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[17] with the Stuttgart/Dresden ECP (SDD) basis set[18] to describe the electrons of the ruthenium atom. For the C, N, and H atoms the 6-31g** basis set was employed.[19] A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. The vibrational eigenvectors corresponding to the reaction coordinate (with imaginary frequency) of all transition states were visually checked to confirm the connectivity of transition states with the reactants and the products. Crucial transition states (**TS$_{BC}$**) have been confirmed by IRC calculations. All geometries were optimized without symmetry constraints.

Acknowledgment. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged (Project No. P16600-N11).

Supporting Information Available: CIF files giving complete crystallographic data and technical details for **1b**, **3a**, and **3b** and text, figures, and tables giving additional details of the crystal structures of **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060990I

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