4166 *Organometallics* **2006,** *25,* 4166−4169

Formation of a Half-Sandwich Triscarbene Ruthenium Complex: Oxidative Coupling of 2,7-Nonadiyne Mediated by $[\mathrm{RuCp(IPr^i)(CH_3CN)_2}]^+$ ($\mathrm{IPr^i}$ = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)

Eva Becker,† Verena Stingl,† Kurt Mereiter,‡ and Karl Kirchner*,†

Institute of Applied Synthetic Chemistry and Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

Received April 18, 2006

$[\mathrm{RuCp(IPr^i)(CH_3CN)_2}]\mathrm{PF_6}$, prepared by the reaction of $[\mathrm{RuCp(CH_3CN)_3}]\mathrm{PF_6}$ with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ($\mathrm{IPr^i}$), promotes the oxidative coupling of 2,7-nonadiyne to afford the novel cationic half-sandwich triscarbene complex $[\mathrm{RuCp(IPr^i)({=}C_2(CH_3)_2C_2(CH_2)_3)}]\mathrm{PF_6}$. This compound has been characterized by X-ray crystallography. At elevated temperature in the presence of trace amounts of water the triscarbene undergoes a formal 1,2 hydrogen shift to give the butadienyl carbene complex $[\mathrm{RuCp(IPr^i)({=}C(CH_3)\text{-}C(CH_2)_3C\text{-}\eta^2\text{-}CH{=}CH_2)}]\mathrm{PF_6}$.

Introduction

Studies of the interactions between the $[\mathrm{RuCp(L)}]^+$ (L = $\mathrm{PR_3}$, $\mathrm{SbR_3}$) moiety, derived from labile $[\mathrm{RuCp(L)(CH_3CN)_2}]\mathrm{PF_6}$, and alkynes have revealed a subtle and diverse coordination chemistry.[1] The key intermediate in most reactions is a cationic metallacyclopentatriene[2]—in contrast to a metallacyclopentadiene—featuring two highly electrophilic carbene carbon atoms, giving rise to several interligand transformations. The two main reactions are (i) ligand migration that affords allyl carbenes[3] and (ii) if α-hydrogen atoms are present a 1,2 hydrogen shift resulting in butadienyl carbenes (Scheme 1).[4] Very recently we have shown that ligand migration takes place even in the case where a tertiary phosphine has been replaced by the bulky N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ($\mathrm{IPr^i}$).[5] This was initially surprising since N-heterocyclic carbene ligands are often regarded as "*noninterfering*" supporting ligands,[6] which are much more strongly bound to a metal center than tertiary phosphines and thus less likely to participate in rearrangements within the metal coordination sphere.[7] In the present work we set out to modify the reactants with the aim to impede nucleophilic attack at the α-carbon of the metallacycle and switched over to the internal alkyne 2,7-nonadiyne. We describe here the reaction of $[\mathrm{RuCp(IPr^i)(CH_3CN)_2}]\mathrm{PF_6}$ with 2,7-nonadiyne resulting in the isolation of a novel cationic mixed triscarbene ruthenium complex featuring two electrophilic alkylidene moieties and one nucleophilic N-heterocyclic carbene unit.[8]

Results and Discussion

The reaction of $[\mathrm{RuCp(CH_3CN)_3}]\mathrm{PF_6}$ (**1**) with a slight excess of $\mathrm{IPr^i}$ in toluene/THF (3:2) for 45 min at room temperature affords on workup the cationic complex $[\mathrm{RuCp(IPr^i)(CH_3CN)_2}]\mathrm{PF_6}$ (**2**) in 78% isolated yield (Scheme 2). This complex is air stable in the solid state and in oxygen-free solutions.

Characterization was accomplished by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy as well as elemental analysis. The ^{1}H NMR spectrum bears no unusual features. Thus, the Cp ligand exhibits a singlet at 3.85 ppm, and the proton resonance of the $\mathrm{CH_3CN}$ ligands gives a singlet at 2.23 ppm. In the ^{13}C{^{1}H} NMR

---

* To whom correspondence should be addressed. E-mail: kkirch@mail.zserv.tuwien.ac.at.

† Institute of Applied Synthetic Chemistry.

‡ Institute of Chemical Technologies and Analytics.

(1) Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **2004**, 2609.

(2) For metallacyclopentatriene complexes see: Ruthenium: (a) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143. (b) Ernst, C.; Walter, O.; Dinjus, E.; Arzberger, S.; Görls, H. *J. Prakt. Chem.* **1999**, *341*, 801. (c) Gemel, C.; LaPensée, A.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 1189. (d) Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. Osmium: Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712. Cobalt: Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925. Molybdenum: Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. Tungsten: Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

(3) (a) Rüba, E.; Mereiter, K.; Schmid, R.; Sapunov, V. N.; Kirchner, K.; Schottenberger, H.; Calhorda, M. J.; Veiros, L. F. *Chem. Eur. J.* **2002**, *8*, 3948. (b) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Chem. Commun.* **2001**, 1996. (c) Mauthner, K.; Soldouzi, K. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4681.

(4) (a) Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K. *Organometallics* **2003**, *22*, 2124. (b) Becker, E.; Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **2001**, *20*, 3851.

(5) Becker, E.; Stingl, V.; Dazinger, G.; Puchberger, M.; Mereiter, K.; Kirchner, K. *J. Am. Chem. Soc.* **2006**, *128*, 6572.

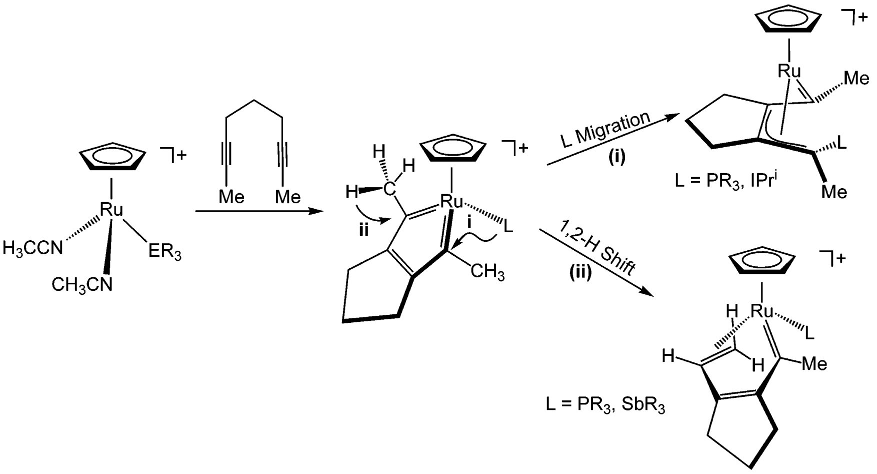
(6) For reviews see: (a) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (d) Herrmann, W. A. *Angew.* Chem., *Int. Ed.* **2002**, *41*, 1290. (e) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69. (f) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951.

(7) For recent examples of the "*noninnocent*" behavior of NHC ligands see: (a) Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 15702. (b) Allen, D. P.; Crudden, C. M.; Calhoun, L. A.; Wang, R. Y. *J. Organomet. Chem.* **2004**, *689*, 3203. (c) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756. (d) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944. (e) McGuiness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K, J. *J. Am. Chem. Soc.* **2001**, *123*, 4029. (f) McGuiness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918.

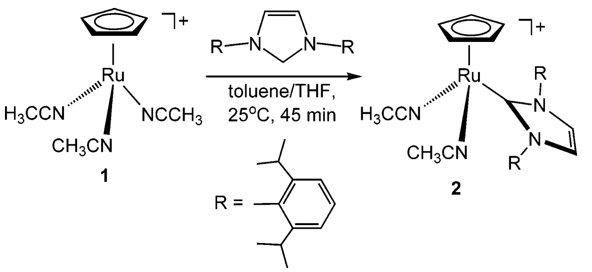
(8)) For other triscarbene and related polycarbene complexes see: (a) Lin, G.; Jones, N. D.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem.* **2003**, *115*, 4188. (b) Fränkel, R.; Kernbach, U.; Bakola-Christianopoulou, Plaia, U.; Suter, M.; Ponikwar, W.; Nöth, H.; Moinet, C.; Fehlhammer, W. P. *J. Organomet. Chem.* **2001**, *617*−*618*, 530.

10.1021/om060345b CCC: \$33.50

Scheme 1



Scheme 2



spectrum the carbene carbon atom of the IPr^i ligand gives rise to a signal at 185.2 ppm. The Cp ligand exhibits a singlet at 73.0 ppm. In addition, the structure of **2** has been determined by X-ray crystallography. A structural view is depicted in Figure 1, with selected bond distances reported in the caption. The complex adopts a typical three-legged piano stool conformation with structural features very similar to those reported for the related phosphine complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me, Ph, Cy).[9]

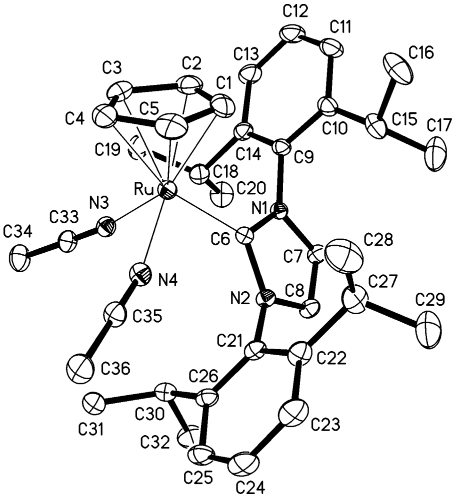


Figure 1. Structural view of $[RuCp(IPr^i)(CH_3CN)_2]PF_6{\cdot}CH_3CN$ ($\mathbf{2}{\cdot}CH_3CN$) showing 30% thermal ellipsoids (PF_6^-, CH_3CN, and H atoms omitted for clarity). Selected bond lengths (Å): Ru−C(1−5)$_{av}$ 2.174(2), Ru−C(6) 2.100(2), Ru−N(3) 2.067(2), Ru−N(4) 2.062(2).

Treatment of **2** with 1 equiv of 2,7-nonadiyne in CH_2Cl_2 for 48 h results in the formation of the deep purple mixed triscarbene complex $[RuCp(IPr^i)(=C_2(CH_3)_2C_2(CH_2)_3)]^+$ (**3**) in essentially quantitative yield, as monitored by ^1H NMR spectroscopy (Scheme 3). For comparison, the half-sandwich mixed dicarbene complex $RuCp(=CPh_2)(NHC)Cl$ (NHC = 1,3-dicyclohexylimidazolin-2-ylidene) has been described recently.[10] The identity of **3** was established by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by elemental analysis. The most characteristic features in the $^{13}C\{^1H\}$ NMR spectrum are low-field resonances at 304.1 and 182.5 ppm assignable to the two carbene carbon atoms of the ruthenacyclopentatriene moiety and the carbene carbon of the IPr^i ligand, respectively. It has to be mentioned that only in a few cases, namely, from the reactions of $[RuCp(SbPh_3)(CH_3CN)_2]^+$ and $[RuCp(PCy_3)(CH_3CN)_2]^+$ with 2,8-decadiyne[3b,4b] and the reaction of $[RuCp(IPr^i)(CH_3CN)_2]^+$ with 1,7-octadiyne,[5] has a ruthenacyclopentatriene intermediate been identified by means of $^{13}C\{^1H\}$ NMR spectroscopy. The characteristic carbene resonances were observed at 330.0, 325.6, and 298.0 ppm, respectively. These shifts correlate roughly with the σ-donor properties of the respective co-ligands increasing in the order $SbPh_3 < PCy_3 < IPr^i$.[11]

The structure of **3** has been confirmed by X-ray crystallography (Figure 2). Obviously C−C coupling had occurred between the internal sp carbons of the 2,7-nonadiyne ligand, forming a five-membered ring system. The metallacycle has a rms aplanarity of only 0.019 Å and is inclined to the Cp ring at

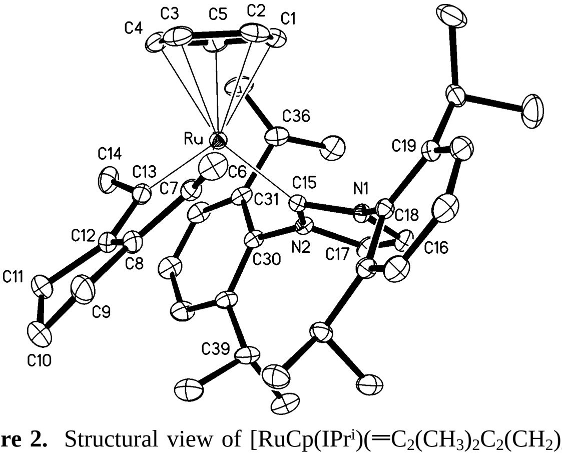
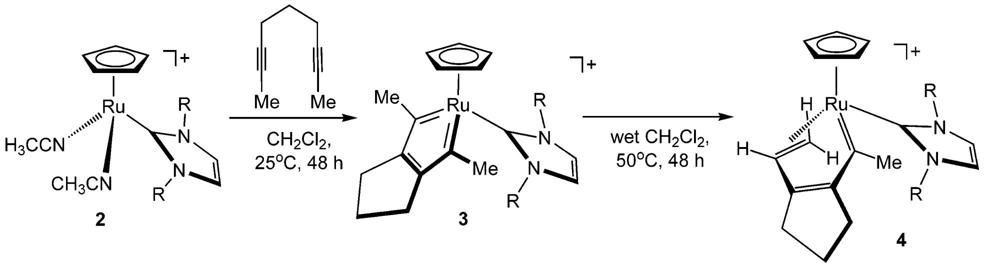


Figure 2. Structural view of $[RuCp(IPr^i)(=C_2(CH_3)_2C_2(CH_2)_3)]$-$PF_6{\cdot}CH_2Cl_2$ ($\mathbf{3}{\cdot}CH_2Cl_2$) showing 30% thermal ellipsoids (PF_6^-, CH_2Cl_2, and H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ 2.293(2), Ru−C(7) 1.945(2), Ru−C(13) 1.942(2), Ru−C(15) 2.100(2), C(7)−C(8) 1.437(2), C(8)−C(12) 1.358(2), C(12)−C13) 1.435(2); C(7)−Ru−C(13) 80.84(7).

Scheme 3



40.8(1)°. The coordinated C4 ring is nearly planar, with a torsion angle C(7)−C(8)−C(12)−C(13) of −0.6(2)°, and strong alternation of the C−C bonds is observed.

The C−C bond lengths of the ruthenacycle C(7)−C(8), C(8)−C(12), and C(12)−C13) are 1.437(2), 1.358(2), and 1.435(2) Å, respectively. The Ru−C(7) and Ru−C(13) bonds are very short (1.945(2) and 1.942(2) Å), clearly suggesting that C(7) and C(13) are alkylidene carbons doubly bonded to the ruthenium center, while the Ru−C(15) bond distance is significantly longer (2.100(2) Å), being typical for a heteroatom-stabilized carbene. Thus, **3** is clearly better formulated as metallacyclopentatriene rather than metallacycopentadiene.

If **2** is treated with 1 equiv of 2,7-nonadiyne in wet CH_2Cl_2 for 48 h at 40 °C, the butadienyl carbene complex $[RuCp(IPr^i)({=}C(CH_3)\text{-}C(CH_2)_3C\text{-}\eta^2\text{-}CH{=}CH_2)]PF_6$ (**4**) is obtained (Scheme 3). The nature of this compound is readily apparent from NMR spectroscopy. In the $^{13}C\{^1H\}$ NMR the characteristic resonance of the carbene carbon occurs at 316.5 ppm. The uncoordinated and coordinated sp^2 carbon atoms C^2, C^3, C^4, and C^5 of the butadienyl unit exhibit resonances at 187.4, 172.6, 75.3, and 55.9 ppm, respectively, while the resonance of the methyl carbon atom is observed at 50.5 ppm. Complex **4** is also formed by keeping a CH_2Cl_2 solution of **3** in the presence of small (catalytic) amounts of water for 48 h at 40 °C. In rigorously dried CH_2Cl_2, however, **3** is stable even at elevated temperatures. Water apparently serves as proton transfer reagent, facilitating the 1,2-H shift, and may suggest that this is an intermolecular process. This is in contrast to the reaction of $[RuCp(SbR_3)(CH_3CN)_2]PF_6$ (R = Ph, *n*-Bu) with 2,8-decadiyne, where a metallacyclopentatriene−butadienyl carbene transformation occurs at room temperature but in an intramolecular fashion, where no base or acid is required. Noteworthy, Taube and co-workers reported the conversion of the dicationic osmacyclopentatriene complex $[Os(en)_2({=}C_2(CH_3)_2C_2(CH_3)_2)]^{2+}$ to a butadienyl carbene in the presence of *tert*-butylamine, a process clearly related to our findings.[12]

In conclusion, we have shown that the carbene complex $[RuCp(IPr^i)(CH_3CN)_2]PF_6$ mediates the oxidative coupling of 2,7-nonadiyne to afford a novel cationic half-sandwich triscarbene complex of the type $[RuCp(IPr^i)({=}C_2(CH_3)_2C_2(CH_2)_3)]^+$ featuring two different types of carbene carbon atoms, viz., two alkylidene moieties and one heteroatom-stabilized carbene. This complex is surprisingly stable taking into account the high electrophilicity of related compounds containing biscarbene ligands.[1]

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 used without further purification. The solvents were purified according to standard procedures.[13] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ (**1**), 2,7-nonadiyne, and IPr^i·HCl were prepared according to the literature.[14−16] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H−COSY, 135-DEPT, and HSQC(^1H−^{13}C) experiments.

$[RuCp(IPr^i)(CH_3CN)_2]PF_6$ (2). A suspension of IPr^i·HCl (690 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 **1** (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 column chromatography (neutral Al_2O_3, eluent: CH_3CN). **2** was isolated as a yellow microcrystalline solid. Yield: 78% (486 mg). Anal. Calcd for $C_{36}H_{47}F_6N_4PRu$: C, 55.24; H, 6.05; N, 7.16. Found: C, 55.44; H, 6.21; N, 7.35. ^1H NMR (δ, acetone-d_6, 20 °C): 7.56 (s, 2H, IPr^{i}C*H*), 7.55 (t, J_{HH} = 8.1 Hz, 2H, Ar^4), 7.43 (d, J_{HH} = 8.1, 4H, Ar^{3,5}), 3.85 (s, 5H, Cp), 2,92 (m, J_{HH} = 6.9 Hz, 4H, Pr^i-C*H*), 2.23 (s, 6H, CH_3CN), 1.35 (d, J_{HH} = 6.9 Hz, 12H, Pr^i-CH_3), 1.18 (d, J_{HH} = 6.9 Hz, 12H, Pr^i-CH_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 185.2 (IPr^{i-1}), 146.3 (Ar^{2,6}), 137.9 (Ar^1), 130.4 (Ar^4), 125.9 (Pr$^{i-3,4}$), 123.8 (Ar^{3,5}), 73.0 (Cp), 28.4 (Pr^i-*C*H), 24.9 (Pr^i-*C*H_3), 21.8 (Pr^i-*C*H_3).

$[RuCp(IPr^i)({=}C_2(CH_3)_2C_2(CH_2)_3)]PF_6$ (3). A solution of **2** (100 mg, 0.13 mmol) and 2,7-nonadiyne (28 μl, 0.19 mmol) in CH_2Cl_2 (5 mL) was stirred at 25 °C for 48 h. The solvent was then removed under reduced pressure, and the remaining deep purple solid was washed with Et_2O and dried under vacuum. Yield: 87% yield (92 mg). Anal. Calcd for $C_{41}H_{53}F_6N_2PRu$: C, 59.76; H, 6.48; N, 3.40. Found: C, 59.84; H, 6.21; N, 3.36. ^1H NMR (δ, CD_2Cl_2, 20 °C): 7.85−7.29 (m, 8H, IPr^i), 5.08 (s, 5H, Cp), 2.56 (m, J_{HH} = 6.6 Hz, 4H, Pr^i-C*H*), 2.33−1.39 (m, 6H, −(CH_2)$_3$−), 1.42 (d, J_{HH} = 6.6 Hz, 12H, Pr^i-CH_3), 1.13 (d, J_{HH} = 6.6 Hz, 12H, Pr^i-CH_3), 0.21 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 304.1 (Ru=C1), 182.5 (IPr^{i-1}), 174.7 (C2), 145.6 (Ar^{2,6}), 145.1 (Ar^{2,6}), 137.1 (Ar^1), 136.0 (Ar^1), 132.3 (Ar^4), 131.1 (Ar^4), 128.4 (Pr^{i-3}), 126.2 (Pr^{i-4}),

---

(9) (a) Rüba, E.; Simanko, W.; Mauthner, K.; Soldouzi, K. M.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 3843. (b) Slugovc, C.; Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **2000**, *131*, 1241.

(10) Baratta, W.; Herdtweck, E.; Herrmann, W. A.; Rigo, P.; Schwarz, J. *Organometallics* **2002**, *21*, 2101.

(11) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815, and references therein.

(12) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 7609.

(13) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

(14) (a) Kündig, E. P.; Monnier, F. R. *Adv. Synth. Catal.* **2004**, *346*, 901. (b) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(15) Anderson, B. A.; Bao, J.; Brandvold, T. A.; Challener, C. A.; Wulff, W. D.; Xu, Y.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 10671.

(16) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49.

124.8 ($Ar^{3,5}$), 124.3 ($Ar^{3,5}$), 92.0 (Cp), 20.8 ($\mathit{C}H_3$), 29.1 (Pr^i-*C*H), 28.9 (Pr^i-*C*H), 28.7 ($\mathit{C}H_2$), 28.2 ($\mathit{C}H_2$), 26.2 (Pr^i-$\mathit{C}H_3$), 21.8 (Pr^i-$\mathit{C}H_3$).

[RuCp(IPr^i)(=C(CH$_3$)C(CH$_2$)$_3$C-η^2-CH=CH$_2$)]PF$_6$ (4). A solution of **1** (100 mg, 0.13 mmol) and 2,7-nonadiyne (28 μl, 0.19 mmol) in CH_2Cl_2 (5 mL) containing traces of water was stirred at 40 °C for 48 h. The volume of the dark red solution was then reduced to about 0.5 mL. Upon addition of Et_2O, a precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 93 mg (89%). Anal. Calcd for $C_{41}H_{53}F_6N_2PRu$: 59.76; H, 6.48; N, 3.40. Found: C, 60.01; H, 6.09; N, 3.54. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.65−7.35 (m, 6H, Ar), 7.24 (s, 2H, IPr^i-C*H*), 4.74−4.49 (m, 1H, H^4), 4.59 (s, 5H, Cp), 3.53 (d, J_{HH} = 11.1 Hz, 1H, H^{5cis}), 2.85−2.03 (m, 11H, Pr^i-C*H*, −(CH_2)$_3$−, H^{5trans}), 1.67 (s, 3H, CH_3), 1.38 (t, J_{HH} = 6.0 Hz, 12H, Pr^i-CH_3), 1.14 (d, J_{HH} = 6.3 Hz, 12H, Pr^i-CH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20°C): 316.6 (Ru=C1), 187.4 (C2), 180.4 (IPr^{i-1}), 172.6 (C3), 146.5 ($Ar^{2,6}$), 146.4 ($Ar^{2,6}$), 145.0 (Ar^1), 136.5 (Ar^1), 132.3 ($Ar^{3,5}$), 131.3 ($Ar^{3,5}$), 127.7 (Ar^4), 126.2 (Ar^4), 124.8 (Pr^{i-3}), 88.6 (Cp), 75.3 (C4), 55.9 (C5), 50.5 ($\mathit{C}H_3$), 36.5 ($\mathit{C}H_2$), 29.1 (Pr^i-*C*H), 29.0 (Pr^i-*C*H), 27.6 ($\mathit{C}H_2$), 27.5 ($\mathit{C}H_2$), 26.8 (Pr^i-$\mathit{C}H_3$), 26.3 (Pr^i-$\mathit{C}H_3$), 24.0 (Pr^i-$\mathit{C}H_3$), 23.5 (Pr^i-$\mathit{C}H_3$).

X-ray Structure Determination. X-ray data for [RuCp(IPr^i)(CH$_3$CN)$_2$]PF$_6$·CH$_3$CN (**2**·CH$_3$CN) and [RuCp(IPr^i)(=C$_2$(CH$_3$)$_2$C$_2$(CH$_2$)$_3$)]PF$_6$·CH$_2$Cl$_2$ (**3**·CH$_2$Cl$_2$) were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space (θ_{max} = 30°). Corrections for absorption, λ/2 effects, and crystal decay were applied.[17] The structures were solved by direct methods using the program SHELXS97.[18] Structure refinement on F^2 was carried out with the program SHELXL97.[13] 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.

Crystal data of **2**·CH$_3$CN: $C_{38}H_{50}F_6N_5PRu$, M_r = 822.87, monoclinic, space group $P2_1/c$ (no. 14), T = 173(2) K, a = 11.7140(6) Å, b = 13.5611(7) Å, c = 25.5245(12) Å, β = 97.550(1)°, V = 4019.5(3) Å^3, Z = 4, μ = 0.490 mm^{-1}. Of 58 742 reflections collected, 11 666 were independent; final R indices: R_1 = 0.038 (all data), wR_2 = 0.090 (all data). Crystal data of **3**·CH$_2$Cl$_2$: $C_{42}H_{55}Cl_2F_6N_2PRu$, M_r = 904.82, monoclinic, space group $P2_1/n$ (no. 14), T = 100(2) K, a = 12.6022(6) Å, b = 25.3077(12) Å, c = 13.2930(6) Å, β = 100.426(1), V = 4169.6(3) Å^3, Z = 4, μ = 0.602 mm^{-1}. Of 49 622 reflections collected, 12 061 were independent; final R indices: R_1 = 0.034 (all data), wR_2 = 0.078 (all data).

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

Supporting Information Available: Complete crystallographic data and technical details in CIF format for **2**·CH$_3$CN and **3**·CH$_2$Cl$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060345B

---

(17) Bruker programs: *SMART*, version 5.629; *SAINT*, version 6.54; *SADABS*, version 2.10; *XPREP*, version 6.14; *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2003.

(18) Sheldrick, G. M. *SHELX97*: *Program System for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.