Reaction of Alkynes with $[RuCp(CO)(CH_3CN)_2]^+$ and $[RuCp^*(CO)(CH_3CN)_2]^+$. Convenient Synthesis of Ruthenium Cyclopentadienone Complexes

Eva Rüba,[†] Kurt Mereiter,[‡] Kamran M. Soldouzi,[†] Christian Gemel,[†] Roland Schmid,[†] and Karl Kirchner*[,†,#]

Institute of Inorganic Chemistry and Institute of Mineralogy, Crystallography, and Structural Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

Emilio Bustelo, M. Carmen Puerta,* and Pedro Valerga

Departamento de Ciencias de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real 11510, Spain

Received August 1, 2000

The mono-carbonyl complexes $[RuCp(CO)(CH_3CN)_2]PF_6$ (**1**) and $[RuCp^*(CO)(CH_3CN)_2]PF_6$ (**2**) react with terminal and internal alkynes to afford the cationic complexes [RuCp(η^4-cyclopentadienone)$(CH_3CN)]PF_6$ (**3**) and [RuCp*(η^4-cyclopentadienone)$(CH_3CN)]PF_6$ (**4**), respectively, in high yields. These reactions are highly selective, yielding in the case of terminal alkynes only one regioisomer with the substituents exclusively in the α,α′ positions of the cyclopentadienone moiety. In contrast, the reaction of **1** with PhC≡CPh yields no cyclopentadienone complex but instead the sandwich complex $[RuCp(\eta^6\text{-}C_6H_5PhC{\equiv}CPh)]^+$ and the bis-carbonyl complex $[RuCp(CO)_2(CH_3CN)]^+$ in a 1:1 ratio. X-ray structures of representative complexes are reported.

Introduction

Cyclopentadienones are highly unstable molecules subject to rapid dimerization[1] unless hindered by the presence of bulky substituents or upon coordination to transition metals. The accessibility of such complexes is therefore limited since they have to be arrived at in situ through reactions on suitable precursor complexes. For instance, some transition metal carbonyl complexes have been shown to react with acetylenes giving cyclopentadienone complexes where the metal is in a low oxidation state (0, +I). The first reported cyclopentadienone complex, $Fe(\eta^4\text{-}C_5H_4O)(CO)_3$, has been obtained by treating $Fe(CO)_5$ with excess HC≡CH at high pressure.[2] Other examples are complexes of the types M(η^4-cyclopentadienone)$(CO)_3$ (M = Fe, Ru),[3] MCp(η^4-cyclopentadienone) (M = Co, Rh),[4] and VCp(η^4-cyclopentadienone)(CO)(PMe_3).[5] All these reactions typically proceed via metallacyclopentadiene intermediates according to Scheme 1 for Co and Rh carbonyl complexes.

An alternative approach to cyclopentadienone complexes utilizes oxidative addition of 4-bromo-2-cyclopenten-1-ones to low-valent transition metal complexes. The η^3-cyclopentenoyl intermediate reacts either via hydride abstraction or deprotonation to give a cyclopentadienone complex. Whereas Mo(II) and W(II) cyclopentadienone complexes have been prepared recently via the hydride abstraction route,[6] the deprotonation sequence has been developed by us for the synthesis of Ru(II) cyclopentadienone complexes.

This method is particularly successful for obtaining the parent cyclopentadienone ligand or ones substituted at the 2 and/or 3 position, as illustrated in Scheme 2.[7,8] It should be mentioned that Ru(II) complexes containing the parent cyclopentadienone ligand can also be prepared by the reaction of the Ru(IV) complex $[RuCp_2X]^+$ (X = Cl, Br) with water or Ag_2O albeit in rather low yield (<30%).[9]

We describe here a new and convenient synthesis of both Ru(II) Cp and Cp* complexes containing the parent

[†] Institute of Inorganic Chemistry.
[‡] Institute of Mineralogy, Crystallography, and Structural Chemistry.
[#] E-mail: kkirch@mail.zserv.tuwien.ac.at.

(1) (a) Chapman, O. L.; McIntosh, C. L. *Chem. Commun.* **1971**, 770. (b) Maier, G.; Franz, L. H.; Hartan, H.-G.; Lanz, K.; Reisenauer, H. P. *Chem. Ber.* **1985**, *118*, 3196.

(2) Reppe, W.; Vetter, H. *Justus Liebigs Ann. Chem.* **1953**, *582*, 133.

(3) (a) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1960**, 989. (b) Weiss, E.; Merenyi, R.; Huebel, W. *Chem. Ber.* **1962**, *95*, 1170. (c) Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25. (d) Pearson, A. J.; Shively, R. J.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096.

(4) (a) Markby, R.; Sternberg, H. W.; Wender, I. *Chem. Ind.* **1959**, 1381. (b) Dickson, R. S.; Tailby, G. R. *Aust. J. Chem.* **1970**, *23*, 1531. (c) Bieri, J. H.; Dreiding, A.; Gartenmann, T. C. C.; Gesing, E. R. F.; Kunz, R.; Prewo, R. *J. Organomet. Chem.* **1986**, *306*, 241. (d) Borwieck, H.; Walter, O.; Dinjus, E.; Rebizant, J. *J. Organomet. Chem.* **1998**, *570*, 121. (e) Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem.* **1980**, *92*, 1057.

(5) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925.

(6) (a) Liebeskind, L. S.; Bombrun A. *J. Am. Chem. Soc.* **1991**, *113*, 8736. (b) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 181.

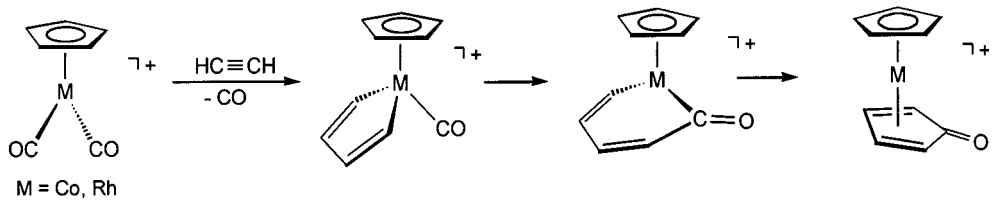
(7) (a) Kirchner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1994**, 161. (b) Kirchner, K.; Mereiter, K.; Umfahrer, A.; Schmid, R. *Organometallics* **1994**, *13*, 1886.

(8) Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1994**, *13*, 5054.

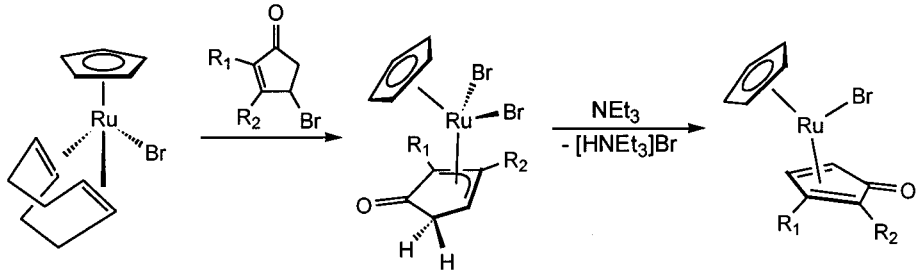
(9) (a) Smith, T. P.; Kwan, K. S.; Taube, H.; Bino, A.; Cohen, S. *Inorg. Chem.* **1984**, *23*, 1943. (b) Kirchner, K.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 7039.

10.1021/om000663p CCC: $19.00
Publication on Web 11/14/2000

Scheme 1



Scheme 2



as well as 2,5-di- and 2,3,4,5-tetrasubstituted cyclopentadienone ligands by the reaction of [RuCp(CO)(CH$_3$CN)$_2$]$^+$ and [RuCp*(CO)(CH$_3$CN)$_2$]$^+$ with various alkynes. X-ray structures of representative complexes are also included.

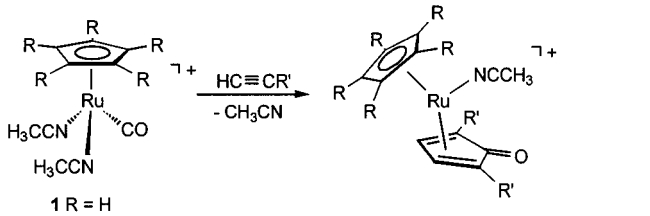
Results and Discussion

[RuCp(CO)(CH$_3$CN)$_2$]$^+$ (**1**) is prepared according to Mann et al.[10] by stirring a solution of [RuCp(CH$_3$CN)$_3$]$^+$ in CH$_3$CN for a few minutes under an atmosphere of CO. The analogous complex [RuCp*(CO)(CH$_3$CN)$_2$]$^+$ (**2**), thus far not reported, is prepared in similar fashion by starting from the corresponding tris-acetonitrile complex [RuCp*(CH$_3$CN)$_3$]$^+$.[11] The transformation is essentially quantitative as monitored by ^{1}H NMR spectroscopy. This product is stable to air in the solid state but decomposes slowly in solution on exposure to air. Characterization was accomplished by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy as well as elemental analysis. The ^{1}H NMR spectrum of **2** bears no unusual features. Thus, the Cp* ligand exhibits a singlet at 1.72 ppm, and the proton resonance of the CH$_3$CN ligands gives a singlet at 2.39 ppm. In the ^{13}C{^{1}H} NMR spectrum the Cp* ring gives rise to singlets at 93.7 and 9.6 ppm, while the CO ligand exhibits a singlet at 200.3 ppm. In the IR spectrum the characteristic CO stretching frequency is observed at 1974 cm^{-1} (cf. 2004 cm^{-1} in **1**[10]).

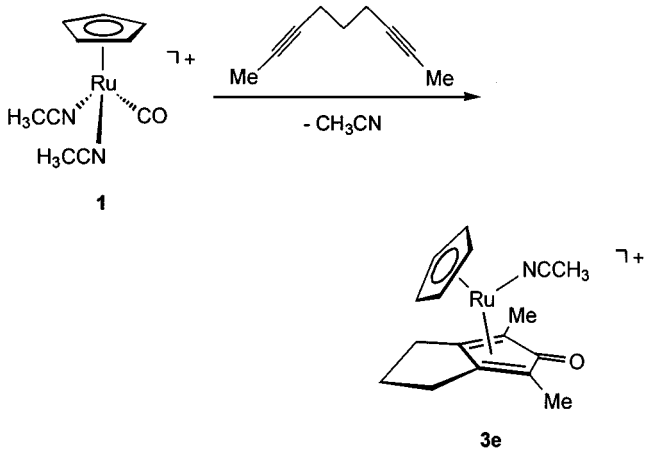
Treatment of **1** with the alkynes HC≡CR (R = Ph, *n*-Bu, C$_6$H$_9$, H) and 2,7-nonadiyne in acetone at 60 °C for 24 h affords, on workup, the cationic cyclopentadienone complexes **3a**−**e** in high yields (Schemes 3 and 4). In a fashion similar to **1**, complex **2** reacts with HC≡CR (R = Ph, *n*-Bu, C$_6$H$_9$) to give the corresponding cyclopentadienone complexes **4a**−**c** in high yields (Scheme 3).

Attempts to prepare the tetracyclone complex [RuCp-(η^4-C$_5$Ph$_4$O)(CH$_3$CN)]$^+$ by treatment of **1** with PhC≡CPh in boiling acetone failed. Instead, the sandwich complex [RuCp(η^6-C$_6$H$_5$-C≡CPh)]$^+$ (**5**)[12,13] together with

Scheme 3



Scheme 4

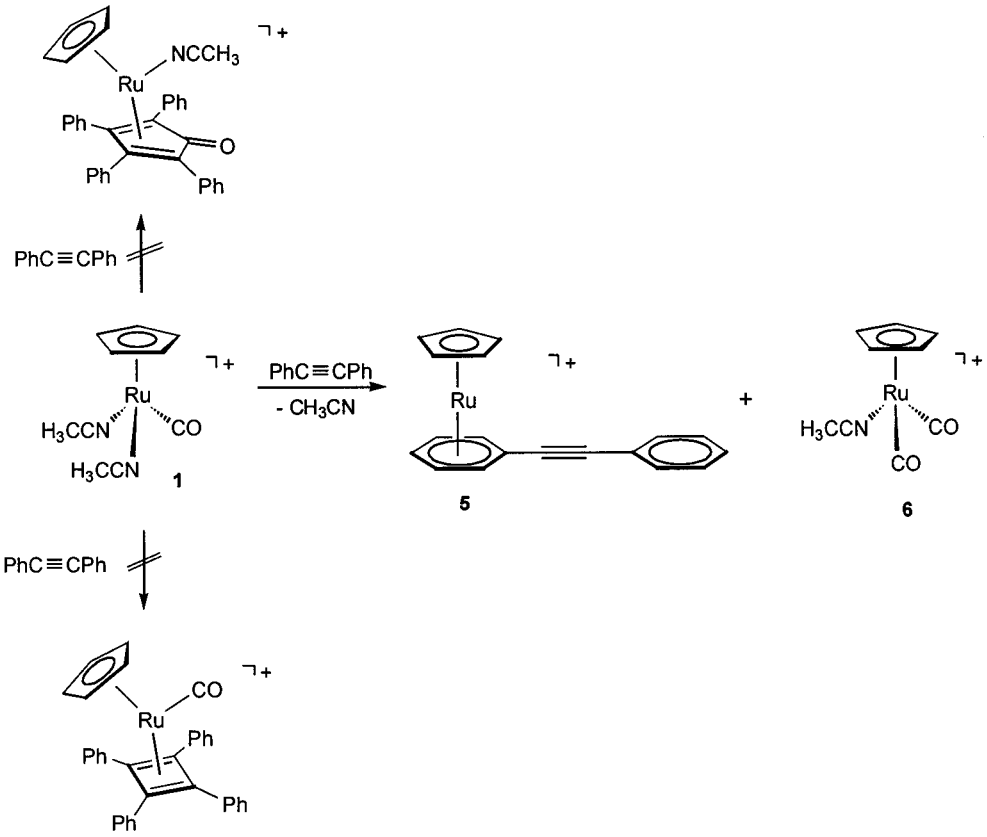


the bis-carbonyl complex [RuCp(CO)$_2$(CH$_3$CN)]$^+$ (**6**)[14] was obtained in a 1:1 ratio (Scheme 5). At room temperature no reaction took place. In contrast, Green et al. have reported[15] that the dimeric complex [RuCp-

(10) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
(11) Steinmetz, B.; Schenk, W. A. *Organometallics* **1999**, *18*, 943.
(12) Chaudret, B.; He, X.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1844.

(13) The molecular structure of [CpRu(η^6-C$_6$H$_5$-C≡CPh)PF$_6$] (**5**) was determined also by an X-ray structure analysis, which showed the compound to crystallize in space group *P*1 with a = 10.17 Å, b = 10.85 Å, c = 17.49 Å, α = 86.97°, β = 80.21°, γ = 89.75°. Due to twinning and large thermal vibration effects, the crystallographic results were of poor quality (R1 = 0.114 for 3810 reflections) and thus are not reported here but have been deposited with the Cambridge Crystallographic Data Centre, CCDC-148111. In the solid state the compound contains two independent Ru sandwich complexes, the PhC≡CPh moieties of which are not planar but twisted about the C≡C bond axes, by 22° for complex 1 and by 69° for complex 2.
(14) Jungbauer, A.; Behrens, H. *Z. Naturforschung.* **1978**, *33B* 1083.

Scheme 5



$(CO)_2]_2$ reacts with PhC≡CPh in the presence of Ag^+ at room temperature to give, among bis- and tris-carbonyl RuCp complexes, the η^4-cyclobutadiene complex $[RuCp(\eta^4\text{-}C_4Ph_4)(CO)]^+$ rather than **5** or a tetracyclone complex.[16]

All complexes reported are air-stable in the solid state and have been characterized by a combination of elemental analysis, ^1H and $^{13}C\{^1H\}$ NMR, and IR spectroscopy. In addition, the structures of **3b**, **3c**, **3e**, **4a**, **5**, and **6** have been determined by X-ray crystallography.

Both ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** and **4** clearly show that only one regioisomer has been formed with the substituents exclusively in the α,α′ positions of the cyclopentadienone moiety. Accordingly, in the ^1H NMR spectra of **3a**−**c** the Cp ring and the CH_3CN ligand give rise to a singlet at about 5.70 and 2.65 ppm, respectively. The β,β′-hydrogen atoms of cyclopentadienone exhibit a characteristic low-field resonance in the range 7.20−6.28 ppm (2H). Complex **3d**, on the other hand, exhibits the typical AA′XX′ splitting pattern of two apparent multiplets centered at 6.25 and 4.66 ppm assignable to the H_α and H_β protons, respectively, in agreement with the literature.[7] The ^1H NMR spectrum of **3e** is inconspicuous, with the singlet resonances for Cp, the two Me substituents in the α,α′ position, and CH_3CN in the expected ranges. In the $^{13}C\{^1H\}$ NMR spectra the ketonic carbonyl carbon atom displays a characteristic singlet at about 180 ppm, while the C_β and C_α carbon atoms exhibit singlet resonances between 95.8−90.2 and 84.6−80.1 ppm, respectively. The Cp ligand shows a singlet in the range 88.5−86.4 ppm. The overall NMR spectra of complexes **4** are very similar to those of **3** and are not discussed here. In the IR spectra of complexes **3** and **4** the carbonyl stretching frequency is observed between 1691 and 1661 cm^{-1}, consistent with other cyclopentadienone complexes.

A reasonable mechanism that accounts for the formation of cyclopentadienone complexes is shown in Scheme 6. In the first step a bis-acetylene complex (**A**) is formed by the replacement of two CH_3CN ligands (the CH_3CN exchange rate constant of **1** is 6.0×10^{-4} s^{-1} at 40 °C, cf. 29.1×10^{-2} and 3.0×10^{-2} s^{-1}, respectively, in $[RuCp(CH_3CN)_3]^+$ [17] and $[RuCp(PMe_3)(CH_3CN)_2]^+$ [18] at 40 °C). Oxidative coupling affords the unsaturated metallacyclopentadiene (**B**), which may be described also as an 18e metallacyclopentatriene complex (**B′**), a resonance form of **B**. Geometry optimizations and vibrational analyses on **A** and **B** (**B′**) suggest the optimized structures and their relative energies as shown in Figure 1. Accordingly, the oxidative coupling process is strongly exothermic (−36.6 kcal/mol).[19] Moreover, the calculations suggest that the metallacycle exhibits two rather short Ru−C bonds (1.978 and 1.938 Å) and alternating C−C bonds (1.442, 1.394, and 1.451 Å) and may thus be described as metallacyclopentatriene **B′** (cf. the related complex $RuCp(\sigma,\sigma'\text{-}C_4Ph_2H_2)$-

(15) Crocker, M.; Froom, S. F. T.; Green, M.; Nagle, K. R.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2803.

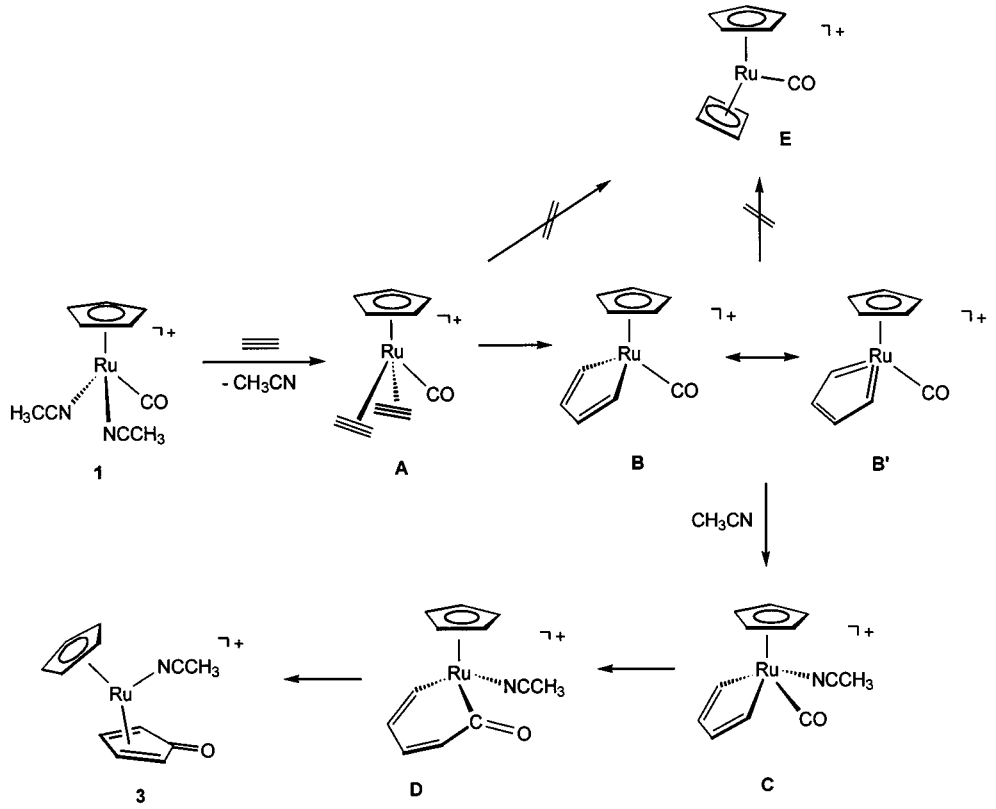
(16) For tetracyclone complexes see: Gupta, H. K.; Rampersad, N.; Stradiotto, M.; McGlinchey, M. J. *Organometallics* **2000**, *19*, 184, and references therein.

(17) Luginbühl, W.; Zbinden, P.; Pittet, P. A.; Armbruster, T.; Bürgi, H.-B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1991**, *30*, 2350.

(18) Rüba, E.; Mauthner, K.; Simanko, W.; Soldouzi, K. M.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 3843.

(19) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.

Scheme 6



Br adopts a similar bis-carbene structure as established by X-ray crystallography[20]). With CH_3CN, the intermediates **B** (**B′**) may form rapidly the metallacyclopentadiene complex **C**. Finally, insertion of CO into the Ru−C bond yields, via intermediate **D** and a subsequent reductive elimination step, the respective cyclopentadienone complex. It is worth noting that we have not observed the formation of an η^4-cyclobutadiene complex **E** (included in Scheme 6). In fact, DFT calculations show that the formation of such a species should be thermodynamically favorable but apparently does not occur for kinetic reasons. In fact, it has been found that [2+2]

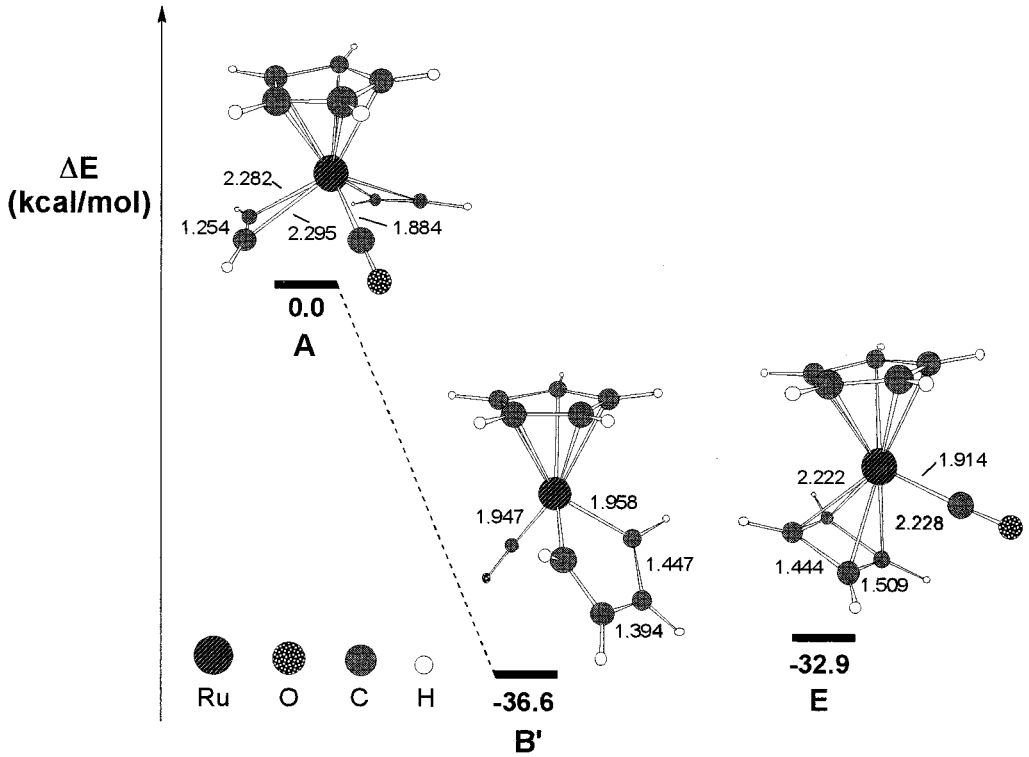


Figure 1. Optimized geometries and relative energies for [RuCp(CO)(η^2-HC≡CH)$_2$]$^+$ (**A**), [RuCp(CO)(σ,σ'-C$_4$H$_4$)]$^+$ (**B′**), and [RuCp(CO)(η^4-C$_4$H$_4$)]$^+$ (**E**) calculated at the B3LYP (Ru sdd; C, H, O d95v) level of theory.

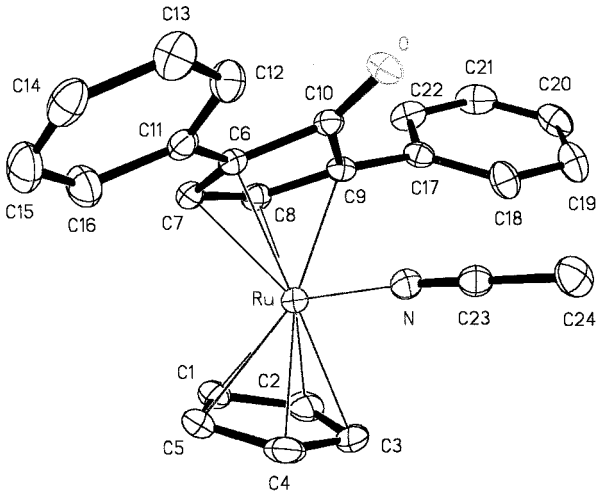


Figure 2. Structural view of [RuCp(η^4-C_5H_2O-2,5-Ph_2)(CH_3-CN)]PF_6 (**3a**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity).

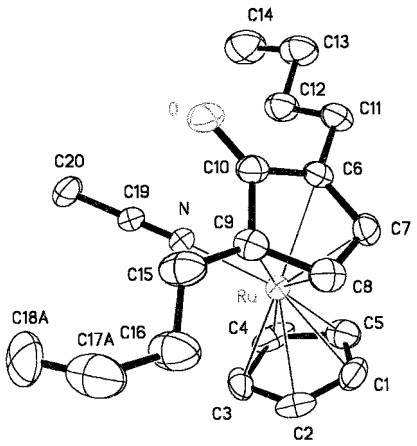


Figure 3. Structural view of [RuCp(η^4-C_5H_2O-2,5-*n*-Bu_2)(CH_3CN)]PF_6 (**3b**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity).

cycloadditions of coordinated acetylenes are symmetry forbidden, implying a large energy barrier.[21]

Structural views of complexes **3a**, **3b**, **3e**, and **4a**·CH_2Cl_2 are depicted in Figures 2−5. In all of them cyclopentadienone is *exo* oriented with respect to the CH_3CN ligand. A main feature comprises the envelope conformation of the cyclopentadienone ring, which can be subdivided into two planes, one defined by C_2, C_3, C_4, and C_5 (butadiene fragment) and the other by C_1, C_2, C_5, and O. The angles between these planes are 18.5°, 20.4°, 21.9°, and 19.8° for **3a**, **3b**, **3e**, and **4a**·CH_2Cl_2, respectively. The diene C−C bonds in all complexes adopt a short−long−short pattern, as is the case for most cyclopentadienone complexes reported thus far. The bond distances between Ru and the butadiene fragment for C_3 and C_4 are shorter than that for C_2 and C_5 by about 0.1 Å (see Table 1), a feature that is also characteristic of η^4-cyclopentadienone complexes in general. Selected bond distances and angles are given in Table 1.

(20) Albers, M. O.; deWaal, P. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.
(21) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055.

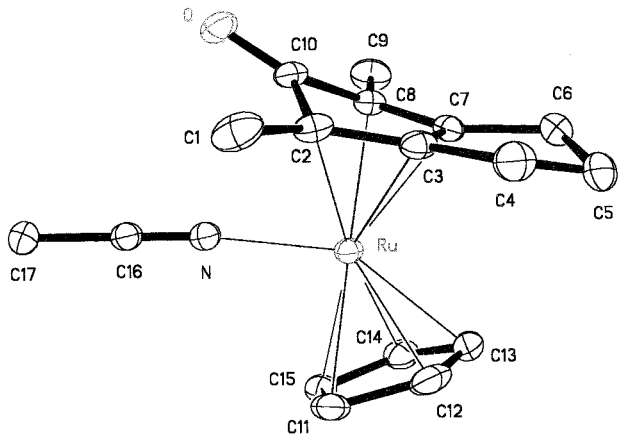


Figure 4. Structural view of [RuCp(η^4-$OC_5Me_2C_3H_6$)(CH_3-CN)]PF_6 (**3e**) showing 20% thermal ellipsoids (PF_6^- omitted for clarity).

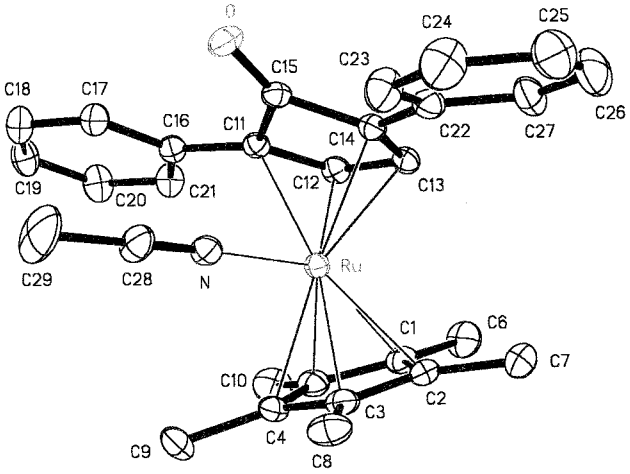
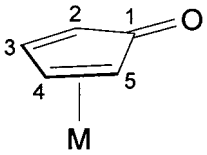


Figure 5. Structural view of [RuCp*(η^4-C_5H_2O-2,5-Ph_2)(CH_3CN)]PF_6·CH_2Cl_2 (**4a**·CH_2Cl_2) showing 20% thermal ellipsoids (PF_6^- and CH_2Cl_2 omitted for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) and Ring Dihedral Angles (deg) for Complexes 3a, 3b, 3d, 3e, and 4a·CH_2Cl_2



	3a	**3b**	**3d**[a]	**3e**	**4a**·CH_2Cl_2
Ru−Cp(av)	2.201(2)	2.178(6)	2.19(1)	2.209(3)	2.217(3)
Ru−C_2	2.289(2)	2.252(6)	2.25(1)	2.254(2)	2.274(3)
Ru−C_3	2.168(2)	2.146(6)	2.15(1)	2.190(2)	2.167(2)
Ru−C_4	2.162(2)	2.148(6)	2.167(8)	2.195(2)	2.153(2)
Ru−C_5	2.255(2)	2.278(7)	2.276(7)	2.268(4)	2.255(3)
C_2−C_3	1.410(3)	1.403(9)	1.40(1)	1.392(4)	1.406(4)
C_3−C_4	1.432(3)	1.44(1)	1.43(1)	1.448(4)	1.435(4)
C_4−C_5	1.409(3)	1.41(1)	1.379(9)	1.414(4)	1.410(4)
Ru−N	2.070(2)	2.059(5)	2.057(5)	2.076(2)	2.063(2)
Ru−N−C	175.1(1)	176.0(5)	175.5(6)	170.0(2)	174.5(3)
C=O	1.207(2)	1.209(8)	1.221(7)	1.217(3)	1.211(3)
dihedral angle[b]	18.5(1)	20.4(5)	18.0(5)	21.9(2)	19.8(2)

[a] Ref 7b. [b] Angle formed between the planes defined by C_2, C_3, C_4, C_5, and C_1, C_2, C_5, O.

The solid-state structure of **6** has also been determined by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Figure 6, with important bond

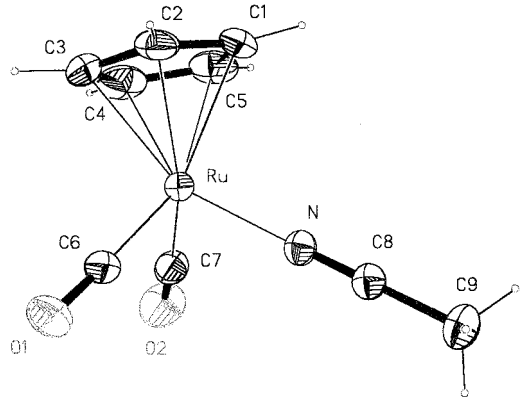


Figure 6. Structural view of [RuCp(CO)$_2$(CH$_3$CN)]PF$_6$ (**6**)-showing 20% thermal ellipsoids (PF$_6^-$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ 2.200(4), Ru−C(6) 1.899(4), Ru−C(7) 1.894(4), Ru−N 2.056-(3), O(1)−C(6) 1.130(4), O(2)−C(7) 1.120(4), C(6)−Ru−C(7) 91.6(1), C(6)−Ru−N 89.3(1), C(7)−Ru−N 93.9(1), Ru−N−C(8) 175.0(3), Ru−C(6)−O(1) 177.7(3), Ru−C(7)−O(2) 174.0-(4).

distances and angles reported in the caption. The complex adopts a typical three-legged piano stool conformation with the CO and CH$_3$CN ligands as the legs. There are no structural features pointing to unusual deviations or distortions.

In summary, we have shown that the readily available mono-carbonyl complexes **1** and **2** are valuable precursors for the synthesis of a variety of Ru(II) cyclopentadienone complexes of types [RuCp(η^4-cyclopentadienone)(CH$_3$CN)]$^+$ and [RuCp*(η^4-cyclopentadienone)-(CH$_3$CN)]$^+$. In the case of terminal alkynes, exclusively the 2,5-disubstituted cyclopentadienone complexes are formed.

Experimental Section

General Information. 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.[22] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [RuCp(CO)(CH$_3$CN)$_2$]PF$_6$ (**1**) was prepared according to the literature.[10] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 101.26 MHz, respectively, and were referenced to SiMe$_4$. IR spectra where recorded on a Perkin-Elmer 16PC FTIR spectrometer.

[RuCp*(CO)(CH$_3$CN)$_2$]PF$_6$ (2). A solution of [RuCp*(CH$_3$-CN)$_3$]PF$_6$ (300 mg; 0.594 mmol) in acetonitrile (5 mL) was stirred for 1 h at room temperature under an atmosphere of CO. The color of the solution changed from dark orange to yellow. The solvent was then removed under reduced pressure, and the residue was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 260 mg (89%). Anal. Calcd for C$_{15}$H$_{21}$F$_6$N$_2$OPRu: C, 36.67; H, 4.31. Found: C, 36.69; H, 4.33. ^{1}H NMR (δ, CD$_2$Cl$_2$, 20 °C): 2.39 (s, 6H, CH$_3$CN), 1.72 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 200.3 (1C, CO), 126.4 (2C, CH$_3$*C*N), 93.7 (5C, Cp*), 9.6 (5C, Cp*), 3.6 (2C, *C*H$_3$CN). IR (KBr, cm^{-1}): 2318, 2265 (m, ν_{CN}), 1974 (s, ν_{CO}).

[RuCp(η^4-C$_5$H$_2$O-2,5-Ph$_2$)(CH$_3$CN)]PF$_6$ (3a). A solution of **1** (163 mg, 0.387 mmol) in acetone (5 mL) was treated with HC≡CPh (87 μL, 0.774 mmol), and the mixture was stirred for 24 h at 60 °C. The color of the solution changed from yellow to orange. Slow addition of diethyl ether (15 mL) led to the precipitation of an orange microcrystalline solid, which was collected on a glass frit, washed twice with diethyl ether, and dried under vacuum. Yield: 208 mg (92%). Anal. Calcd for C$_{24}$H$_{20}$F$_6$NOPRu: C, 49.32; H, 3.45. Found: C, 49.40; H, 3.38. ^{1}H NMR (δ, acetone-d_6, 20 °C): 7.96 (m, 4H, Ph), 7.35 (m, 6H, Ph), 7.20 (s, 2H$_\beta$), 5.70 (s, 5H, Cp), 2.78 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 180.7 (1C, CO), 132.9 (1C, CN), 130.3 (2C, Ph), 130.1 (4C, Ph), 129.9 (4C, Ph), 128.2 (2C, Ph), 90.2 (2C, C$_\beta$), 88.5 (5C, Cp), 82.7 (2C, C$_\alpha$), 5.2 (1C, NC*C*H$_3$). IR (KBr, cm^{-1}): 2321, 2291 (m, ν_{CN}), 1673 (s, ν_{CO}).

[RuCp(η^4-C$_5$H$_2$O-2,5-*n*-Bu$_2$)(CH$_3$CN)]PF$_6$ (3b). This complex has been prepared analogously to **3a** with **1** (125 mg, 0.297 mmol) and HC≡CBu^n (53 μL, 0.594 mmol) as the starting materials. Yield: 145 mg (90%). Anal. Calcd for C$_{20}$H$_{28}$F$_6$NOPRu: C, 44.12; H, 5.18. Found: C, 44.28; H, 5.22. ^{1}H NMR (δ, acetone-d_6, 20 °C): 6.28 (s, 2H$_\beta$), 5.72 (s, 5H, Cp), 2.69 (s, 3H, C*H*$_3$CN), 1.97 (m, 4H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.36 (m, 8H, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.88 (m, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 182.9 (1C, CO), 133.0 (1C, *C*N), 95.8 (2C, C$_\beta$), 87.6 (5C, Cp), 84.6 (2C, C$_\alpha$), 33.2 (2C, CH$_2$), 25.8 (2C, CH$_2$), 23.9 (2C, CH$_2$), 14.8 (2C, CH$_3$), 5.2 (1C, NC*C*H$_3$). IR (KBr, cm^{-1}): 2332, 2297 (m, ν_{CN}), 1690 (s, ν_{CO}).

[RuCp(η^4-C$_5$H$_2$O-2,5-(C$_6$H$_9$)$_2$)(CH$_3$CN)]PF$_6$ (3c). This complex has been prepared analogously to **3a** with **1** (150 mg, 0.356 mmol) and 1-ethynyl cyclohexene (88 μL, 0.748 mmol) as the starting materials. Yield: 190 mg (90%). Anal. Calcd for C$_{24}$H$_{28}$F$_6$NOPRu: C, 48.65; H, 4.76. Found: C, 48.69; H, 4.72. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 6.97 (m, 2H, C$_6$H$_9$), 6.14 (s, 2H$_\beta$), 5.54 (s, 5H, Cp), 2.65 (s, 3H, C*H*$_3$CN), 2.07 (m, 8H, C$_6$H$_9$), 1.58 (m, 8H, C$_6$H$_9$). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 181.6 (1C, CO), 132.9 (1C, *C*N), 130.8 (2C, C$_6$H$_9$), 129.7 (2C, C$_6$H$_9$), 92.9 (2C, C$_\beta$), 86.4 (5C, Cp), 80.1 (2C, C$_\alpha$), 26.8 (2C, C$_6$H$_9$), 26.7 (2C, C$_6$H$_9$), 23.2 (2C, C$_6$H$_9$), 22.5 (2C, C$_6$H$_9$), 4.9 (1C, NC*C*H$_3$). IR (KBr, cm^{-1}): 2330, 2301 (m, ν_{CN}), 1691 (s, ν_{CO}).

[RuCp(η^4-C$_5$H$_4$O)(CH$_3$CN)]PF$_6$ (3d). A solution of **1** (100 mg, 0.237 mmol) in acetone (4 mL) was stirred under an atmosphere of acetylene for 12 h at room temperature. The orange solution was evaporated to dryness, and the residue was washed with diethyl ether and dried under vacuum. Yield: 87 mg (85%). The NMR spectra were in agreement with those reported in the literature.[7]

[RuCp(η^4-C$_5$Me$_2$OC$_3$H$_6$)(CH$_3$CN)]PF$_6$ (3e). This complex has been prepared analogously to **3a** with **1** (100 mg, 0.237 mmol) and 2,7-nonadiyne (41 μL, 0.260 mmol) as the starting materials. Yield: 95 mg (80%). Anal. Calcd for C$_{17}$H$_{20}$F$_6$-NOPRu: C, 40.81; H, 4.03. Found: C, 40.79; H, 4.00. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 5.08 (s, 5H, Cp), 3.19−3.04 (m, 2H, CH$_2$), 2.82−2.65 (m, 2H, CH$_2$), 2.51 (s, 3H, C*H*$_3$CN), 2.41−2.13 (m, 2H, CH$_2$), 1.62 (s, 6H, Me). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 184.3 (1C, CO), 133.3 (1C, *C*N), 88.6 (5C, Cp), 82.1 (2C, C$_\beta$), 81.9 (2C, C$_\alpha$), 28.2 (2C, CH$_2$), 24.7 (1C, CH$_2$), 9.7 (2C, Me), 4.6 (1C, NC*C*H$_3$). IR (KBr, cm^{-1}): 2320, 2291 (m, ν_{CN}), 1687 (s, ν_{CO}).

[RuCp*(η^4-C$_5$H$_2$O-2,5-Ph$_2$)(CH$_3$CN)]PF$_6$ (4a). A solution of **2** (100 mg, 0.204 mmol) and HC≡CPh (49 μL, 0.448 mmol) in acetone (3 mL) was stirred at room temperature for 12 h. After that time the solvent was removed under reduced pressure and the residue washed with diethyl ether. The dark red solid was dried under vacuum. Yield: 106 mg (80%). Anal. Calcd for C$_{29}$H$_{30}$F$_6$NOPRu: C, 53.21; H, 4.62. Found: C, 53.30; H, 4.69. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 7.92−7.59 (m, 4H, Ph), 7.52−7.18 (m, 6H, Ph), 6.02 (s, 2H, H$_\beta$), 2.90 (s, 3H, CH$_3$CN), 1.72 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 178.8 (1C, CO), 133.5 (1C, CN), 129.7 (2C, Ph), 129.4 (4C, Ph), 128.8 (4C, Ph), 127.4 (2C, Ph), 101.4.2 (2C, C$_\beta$), 87.0 (5C, Cp), 83.4 (2C, C$_\alpha$), 9.9 (5C, Cp*), 5.1 (1C, NC*C*H$_3$). IR (KBr, cm^{-1}): 2320, 2284 (m, ν_{CN}), 1661 (s, ν_{CO}).

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

Table 2. Crystallographic Data for 3a, 3b, 3e, 4a·CH_2Cl_2, and 6

	3a	3b	3e	4a·CH_2Cl_2	6
formula	$C_{24}H_{20}F_6NOPRu$	$C_{20}H_{28}F_6NOPRu$	$C_{17}H_{20}F_6NOPRu$	$C_{30}H_{32}Cl_2F_6NOPRu$	$C_9H_8F_6NO_2PRu$
fw	584.45	544.47	500.38	739.51	408.20
cryst. size, mm	0.55 × 0.40 × 0.16	0.34 × 0.30 × 0.03	0.70 × 0.40 × 0.08	0.84 × 0.26 × 0.20	0.60 × 0.16 × 0.07
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Cc* (No. 9)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	10.853(3)	10.516(3)	14.381(7)	16.826(6)	23.707(5)
b, Å	10.922(4)	10.704(4)	7.779(4)	11.172(4)	10.526(3)
c, Å	11.772(5)	11.651(5)	17.680(9)	17.217(6)	11.954(4)
α, deg	101.45(2)	68.61(2)			
β, deg	101.94(2)	87.40(2)	103.07(1)	90.59(2)	114.19(2)
γ, deg	116.78(2)	80.71(2)			
V, Å^3	1148.8(7)	1205.0(8)	1927(2)	3236(2)	2721(1)
Z	2	2	4	4	8
ρ_{calc}, g cm^{-3}	1.690	1.501	1.725	1.518	1.993
T, K	295(2)	295(2)	297(2)	297(2)	295(2)
μ, mm^{-1} (Mo Kα)	0.818	0.773	0.959	0.758	1.338
F(000)	584	552	1000	1496	1584
abs corr	multiscan	multiscan	multiscan	multiscan	multiscan
F(000)	584	552	1000	1496	1584
transmn factor min/max	0.74/0.86	0.91/0.98	0.63/0.80	0.72/0.86	0.78/0.93
θ_{max}, deg	30	25	30	30	27
index ranges	$-15 \le h \le 14$	$-12 \le h \le 12$	$-19 \le h \le 20$	$-23 \le h \le 23$	$-30 \le h \le 30$
	$-15 \le k \le 15$	$-12 \le k \le 12$	$-10 \le k \le 10$	$-15 \le k \le 15$	$-13 \le k \le 13$
	$-16 \le l \le 16$	$-13 \le l \le 13$	$-24 \le l \le 24$	$-23 \le l \le 23$	$-15 \le l \le 15$
no. of rflns measd	16 359	12 417	16 882	46 221	15 761
no. of unique rflns	6495	4231	5521	9345	2971
no. of rflns $I > 2\sigma(I)$	5665	3210	5387	6867	2378
no. of params	347	282	248	407	220
R1 ($I > 2\sigma(I)$)	0.028	0.053	0.023	0.038	0.030
R1 (all data)	0.034	0.076	0.024	0.059	0.044
wR2 (all data)	0.074	0.145	0.060	0.115	0.074
diff Fourier peaks min/max, e Å^{-3}	−0.31/0.53	−0.37/0.61	−0.28/0.28	−0.37/0.60	−0.32/0.31

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

[RuCp*(η^4-C_5H_2O-2,5-*n*-Bu_2)(CH_3CN)]PF_6 (4b). This complex has been prepared analogously to **4a** with **2** (77 mg, 0.153 mmol) and 1-hexyne (40 μL, 0.351 mmol) as the starting materials. Yield: 65 mg (70%). Anal. Calcd for $C_{25}H_{38}F_6NOPRu$: C, 48.86; H, 6.23. Found: C, 48.91; H, 6.20. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 5.23 (s, 2H, H_β), 2.70 (s, 3H, CH_3CN), 2.14−1.62 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.91 (s, 15H, Cp*), 1.46−1.18 (m, 8H, $CH_2CH_2CH_2CH_3$), 0.99−0.82 (m, 6H, $CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 181.7 (1C, CO), 131.4 (1C, *C*N), 100.8 (2C, C_β), 92.5 (2C, C_α), 89.8 (5C, Cp*), 32.9 (2C, CH_2), 24.7 (2C, CH_2), 23.3 (2C, CH_2), 13.9 (2C, CH_3), 9.4 (5C, Cp*), 4.8 (1C, NCCH_3). IR (KBr, cm^{-1}): 2323, 2289 (m, ν_{CN}), 1672 (s, ν_{CO}).

[RuCp*(η^4-C_5H_2O-2,5-(C_6H_9)$_2$)(CH_3CN)]PF_6 (4c). This complex has been prepared analogously to **4a** with **2** (100 mg, 0.204 mmol) and 1-ethynyl cyclohexene (52.7 μL, 0.448 mmol) as the starting materials. Yield: 108 mg (80%). Anal. Calcd for $C_{29}H_{38}F_6NOPRu$: C, 52.56; H, 5.78. Found: C, 52.58; H, 5.72. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 6.54 (m, 2H, C_6H_9), 5.35 (s, 2H$_\beta$), 2.74 (s, 3H, CH_3CN), 2.33−1.40 (m, 16H, C_6H_9), 1.86 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 179.6 (1C, CO), 131.6 (1C, *C*N), 129.8 (2C, C_6H_9), 129.5 (2C, C_6H_9), 100.5 (2C, C_β), 91.7 (2C, C_α), 86.0 (5C, Cp), 27.4 (2C, C_6H_9), 26.6 (2C, C_6H_9), 23.3 (2C, C_6H_9), 22.8 (2C, C_6H_9), 10.2 (5C, Cp*), 5.0 (1C, NCCH_3). IR (KBr, cm^{-1}): 2320, 2286 (m, ν_{CN}), 1669 (s, ν_{CO}).

Reaction of 1 with Diphenylacetylene. Formation of [RuCp(η^6-C_6H_5-C≡CPh)]PF_6 (5) and [RuCp(CO)$_2$(CH_3CN)]PF_6 (6). A solution of **1** (134 mg, 0.318 mmol) in acetone (5 mL) was treated with PhC≡CPh (119 mg, 0.668 mmol), and the mixture was stirred for 24 h at 60 °C. Addition of diethyl ether (15 mL) led to the precipitation of a pale yellow solid, which was collected on a glass frit, washed twice with diethyl ether, and dried under vacuum. The ^{1}H NMR spectrum showed two products in a 1:1 ratio. The mixture could not be separated by column chromatography. **5**: ^{1}H NMR (δ, CD_3NO_2, 20 °C): 7.63−7.33 (m, 5H, Ph), 6.53−6.41(m, 2H, η^6-Ph), 6.35−6.12 (m, 3H, η^6-Ph), 5.47 (s, 5H, Cp). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 133.0 (2C, Ph), 131.0 (1C, Ph), 129.8 (2C, Ph), 122.0 (1C, Ph), 92.1 (1C, η^6-Ph), 89.1 (2C, η^6-Ph), 87.0 (1C, C≡C), 86.8 (2C, η^6-Ph), 86.3 (1C, η^6-Ph), 84.4 (1C, C≡C), 82.3 (2C, η^6-Ph). IR (KBr, cm^{-1}): 2229 (m, $\nu_{C\equiv C}$). The NMR and IR spectra of **6** were in agreement with those reported in the literature.[23]

NMR Spectroscopic Studies. A 5 mm NMR tube was charged with a solution of **1** (31 mg, 0.074 mmol) and PhC≡CPh (28 mg, 0.115 mmol) in neat CD_3NO_2 and was capped with a septum. The tube was then heated at 60 °C, and ^{1}H NMR spectra were recorded every 4 h. The reaction was complete after approximately 24 h, indicating the formation of **5**, **6**, and free CH_3CN in a 1:1:3 ratio.

Acetonitrile Exchange Kinetics on 1 in CD_3NO_2. The CH_3CN exchange in **1** was measured at 40 °C by monitoring the increase in intensity of the proton NMR signal of free CH_3CN (at 1.97 ppm) and the decrease of the bound CH_3CN (at 2.63 ppm) following the methodology described elsewhere.[18,24] Accordingly, 10 mg of **1** was dissolved in 0.5 mL of CD_3NO_2, deuterated acetonitrile (41 μL) was added by syringe, and spectra were taken at regular intervals.

$$[RuCp(CO)(CH_3CN)_2]PF_6 + 2\ CD_3CN \rightarrow [RuCp(CO)(CD_3CN)_2]PF_6 + 2\ CH_3CN \quad (1)$$

X-ray Structure Determination for 3a, 3b, 3e, 4a·CH_2Cl_2, and 6. Crystals of **3a**, **3b**, **3e**, **4a**·CH_2Cl_2, and **6** were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. Crystal data and experimental details are given in Table 2. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ =

(23) Jungbauer, A.; Behrens, H. *Z. Naturforsch.* **1978**, *33b*, 1083.
(24) Rüba, E.; Simanko, W.; Mereiter, K. Schmid, R., Kirchner, K. *Inorg. Chem.* **2000**, *39*, 382.
(25) Sheldrick, G. M. *SHELXS97*: Program for the Solution of Crystal Structures; University of Göttingen: Germany, 1997.
(26) Sheldrick, G. M. *SHELXL97*: Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.

0.71073 Å, 0.3° ω-scan frames covering complete spheres of the reciprocal space). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. All structures were solved by direct methods using the program SHELXS97.[25] Structure refinement on F^2 was carried out with the program SHELXL97.[26] 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. Orientation disorder of PF_6 groups (**3a**, **4a**·CH_2Cl_2, **6**) and one *n*-butyl chain (**3b**) was taken into account.

Computational Details. All calculations were performed using the Gaussian98 software package[27] on the Silicon Graphics Power Challenge of the Vienna University of Technology. The geometry and energy of the complexes [RuCp(η^2-CH≡CH)$_2$(CO)]$^+$ (**A**), [RuCp(σ,σ'-C$_4$H$_4$)(CO)]$^+$ (**B′**), and [RuCp(η^4-C$_4$H$_4$)(CO)]$^+$ (**E**) were optimized at the B3LYP level[28] with the Stuttgart/Dresden ECP (SDD) basis set[29] to describe the electrons of the ruthenium atom. For C, H, and O the Dunning−Huzinaga valence double-ζ basis set (D95v) was used.[30] A vibrational analysis was performed for all structures to confirm that they have no imaginary frequency. The geometries were optimized without constraints (C_1 symmetry).

Acknowledgment. Financial support by the "Österreichischer Akademischer Austauschdienst" (Acciones Integradas Project 6/99 and HU 1998-0026) is gratefully acknowledged.

Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for **3a**, **3b**, **3e**, **4a**·CH_2Cl_2, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000663P

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 9*8, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.

(29) (a) Haeusermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *78*, 1211. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535. (c) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1996**, *105*, 1052.

(30) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*, Schäfer, H. F., III, Ed.; Plenum Press: New York, 1976; p 1.