Reactions of Cationic Ruthenium Hydrides with 1-Alkynes: Formation of σ-Alkynylruthenium Complexes and Reduction of 1-Alkynes to 1-Alkenes

Antonio M. Echavarren,*[1a] Javier López,[1b] Amelia Santos,*[1b] Antonio Romero,[1b] Juan A. Hermoso,†[1c] and Angel Vegas†[1c]

Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain, Instituto de Ciencia de Materiales de Madrid, Sede D, CSIC, Serrano 113, 28006 Madrid, Spain, and Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain

Received November 7, 1990

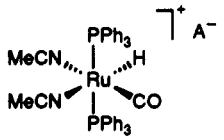
The reaction of $[Ru(CO)H(C_5H_5N)_2(PPh_3)_2]A$ (A = PF_6, ClO_4, BF_4) with 2 equiv of alkynes RC≡CH (R = *n*-C_6H_{13}, *n*-C_8H_{17}, *t*-C_4H_9, *c*-C_6H_{11}, and C_6H_5) gives σ-alkynylruthenium complexes $[Ru(CO)(C{\equiv}CR)(C_5H_5N)_2(PPh_3)_2]A$ and 1-alkenes in a 1:1 ratio. The alkynyl complexes were characterized by IR and NMR spectroscopy and by one X-ray structure. $[Ru(CO)(C{\equiv}C\text{-}C_6H_{13})(C_5H_5N)_2(PPh_3)_2]ClO_4$ crystallizes in the monoclinic space group $P2_1/n$, with a = 11.032 (2) Å, b = 16.734 (6) Å, c = 26.816 (12) Å, β = 96.59 (2)°, Z = 4, and V = 4918 (2) Å^3. However, methyl propynoate affords the coordinatively unsaturated alkenyl complex $[Ru\{C(COOMe){=}CH_2\}(CO)(PPh_3)_2]A$ in low yield. The reaction of $[Ru(CO)(CH{=}CHR)(C_5H_5N)(MeCN)(PPh_3)_2]PF_6$ (R = *t*-Bu, C_6H_5) with 1-alkynes yields the corresponding σ-alkynylruthenium complexes. Hydrogenation of the σ-alkynylruthenium complexes takes place readily under 1 atm of H_2 at 23 °C to regenerate the starting hydrides and 1 equiv of 1-alkene. Heating the ruthenium hydride perchlorate in methanol or ethanol results in reduction of the anion to chloride, yielding the hydride $Ru(CO)H(Cl)(C_5H_5N)(PPh_3)_2$ and, consequently, the reactions of $[Ru(CO)H(C_5H_5N)_2(PPh_3)_2]ClO_4$ with alkynes in these solvents yield alkenyl complexes $Ru(CO)Cl(CH{=}CHR)(C_5H_5N)(PPh_3)_2$.

Introduction

The reaction of alkynes with transition-metal hydride complexes usually results in the formation of a σ-alkenylmetal derivative by an insertion reaction of the acetylene into the metal–hydrogen bond.[2,3] This reaction is a fundamental step in a number of catalytic processes such as the hydrogenation, oligomerization, and polymerization of alkynes.[4] However, in a few instances it has been reported that the reaction of 1-alkynes and metal hydrides gives rise to σ-alkynylmetal complexes.[2b,5-7] Recently, a new pathway for σ-alkynyl formation has been demonstrated with some iron(II) and rhodium(I) complexes in which the initially formed σ-alkenyl complex reacts with a second molecule of alkyne to give the σ-alkynyl complex and a terminal alkene (eq 1).[5f,i]

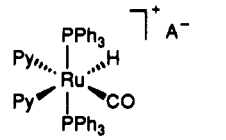
$$M{-}H \xrightarrow{H{-}C{\equiv}C{-}R} M{-}CH{=}CHR \xrightarrow{H{-}C{\equiv}C{-}R} M{-}C{\equiv}C{-}R + RCH{=}CH_2 \quad (1)$$

We have previously shown that the cationic ruthenium(II) hydrides $[Ru(CO)H(MeCN)_2(PPh_3)_2]A$ (1) (**1a**, A = PF_6; **1b**, A = ClO_4) react with alkynes to yield the expected (*E*)-ruthenium alkenyl derivatives resulting from a cis-insertion reaction.[3] In this paper we wish to report that the related ruthenium hydrides $[Ru(CO)H(C_5H_5N)_2(PPh_3)_2]A$ (2) (**2a**, A = PF_6; **2b**, A = ClO_4; **2c**, A = BF_4)[8] react with



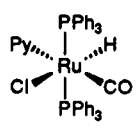
1

A = PF_6 (**1a**), ClO_4 (**1b**)



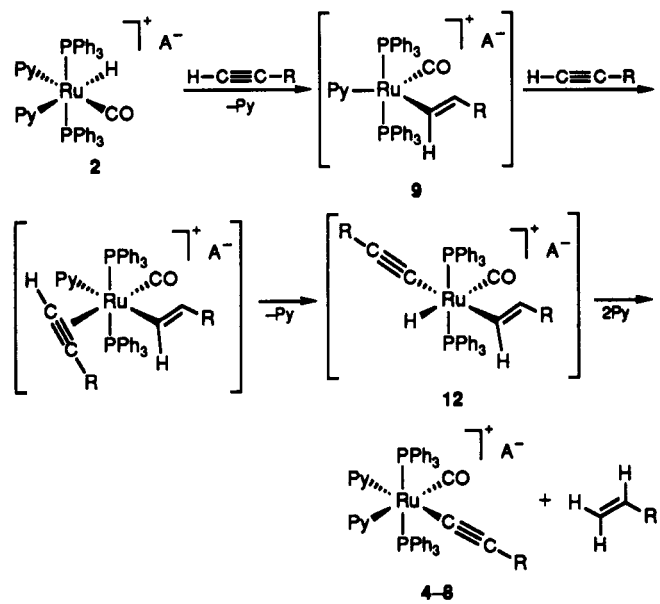
2

A = PF_6 (**2a**), ClO_4 (**2b**), BF_4 (**2c**)



3

Scheme I



†Authors to whom correspondence regarding crystallography should be addressed.

(1) (a) Instituto de Química Orgánica. (b) Instituto de Ciencia de Materiales de Madrid. (c) Instituto de Química Física Rocasolano.

(2) (a) Herberich, G. E.; Barlage, W. *Organometallics* **1987**, *6*, 1924. (b) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (c) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (d) Clark, H. C.; Ferguson, G.; Goel, A. G.; Janzen, E. G.; Ruegger, H.; Siaw, P. Y.; Wang, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. (e) Romero, A.; Santos, A.; López, J.; Echavarren, A. M. *J. Organomet. Chem.* **1990**, *391*, 219 and references cited therein.

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

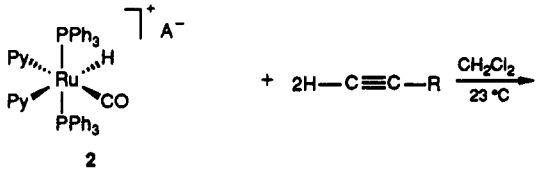
(4) (a) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

0276-7333/91/2310-2371$02.50/0

alkynes to give σ-alkynylruthenium(II) complexes and the corresponding 1-alkenes. Furthermore, these σ-alkynyl complexes react under 1 atm of hydrogen to regenerate the starting hydride and 1 equiv of 1-alkene. During the course of this study we have discovered that in hydride **2b** the perchlorate anion suffers reduction to a chloride ligand to yield the neutral hydride $Ru(CO)H(Cl)(C_5H_5N)(PPh_3)_2$ (**3**).

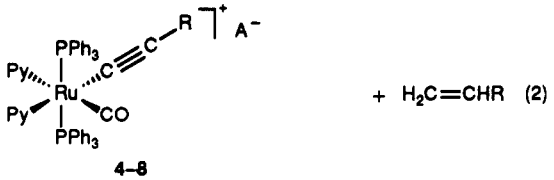
Results and Discussion

Synthesis of Alkynyl Complexes. Reaction of hydrides **2** with 2 equiv of 1-alkyne in dichloromethane solution at 23 °C for 12–24 h gave σ-alkynylruthenium complexes **4–8** in good yield (eq 2). These alkynyl com-



2

A = PF_6 (**2a**), ClO_4 (**2b**), BF_4 (**2c**)



4–8

R = n-C_6H_{13} (**4**) (A = PF_6 (**4a**), ClO_4 (**4b**)), n-C_8H_{17} (**5**) (A = PF_6), t-C_4H_9 (**6**) (A = PF_6), c-C_6H_{11} (**7**) (A = PF_6), C_6H_5 (**8**) (A = PF_6 (**8a**), ClO_4 (**8b**), BF_4 (**8c**)

plexes were stable to air and moisture, although slow decomposition was observed in deuteriochloroform solution to give green uncharacterized products. The structures of **4–8** were assigned on the basis of the spectroscopic data. This assignment was also supported by the determination of the X-ray crystal structure of complex **4b** (Figure 1). The IR spectra showed a weak band between 2120 and 2110 cm^{-1} assigned to the C≡C bond stretching and strong carbonyl absorptions at 1940–1950 cm^{-1}. The pyridine ligands gave rise to broad signals in the ^1H NMR spectra centered around 8.1 ppm (H-2 and H-6) and 6.7 ppm (H-3 and H-5), while the para resonances were overlapping with the phosphine protons. The $^{13}C\{^1H\}$ NMR spectra of complexes **7** and **8** showed the C-1 alkynyl carbon as a triplet coupled with the ^{31}P nuclei at 88.57 and 107.38 ppm, respectively. The C-2 alkynyl carbon appeared at lower field (121.17 and 117.65 ppm, respectively) as singlet resonances.

Monitoring the reaction between hydride **2a** and 1-octyne by ^1H NMR spectroscopy in deuteriochloroform at 23 °C showed slow disappearance of **2a** and formation of alkynyl complex **4a** and 1-octene in an approximate 1:1 ratio. No other ruthenium products or intermediates could be detected. A small amount of the dimer 2-n-hexyl-1-decen-3-yne was also formed in this reaction.[9] Similar reactions of **2a** with 3,3-dimethyl-1-butyne and phenylacetylene were completed in 12–16 h at 23 °C, yielding 3,3-dimethyl-1-butene and styrene, respectively. Hydride **2a** reacts with 3,3-dimethyl-1-butyne in tetrahydrofuran-d_8 solution to give the alkene, although extensive decomposition of the resulting ruthenium complex was observed in this solvent.

Reaction of hydride **2a** with 2 equiv of 1-decyne-*1-d* in benzene-d_6 furnished a 1:1 mixture of the corresponding alkynylruthenium complex **5** and 1-decene-*1-*d_2. On the other hand, the reaction in deuteriochloroform gave a ca. 2:1 mixture of the dideuteriated alkene and (*Z*)-1-decene-*1-d*, even with a carefully dried and acid-free solvent. As suggested by a reviewer, the minor monodeuteriated alkene may derive from insertion of 1-decyne-*d* into the Ru–H bond of **2a**, giving transient **9a**-*d* (see below), which subsequently reacts with residual **2a** by a bimolecular reductive elimination.

The formation of alkynylruthenium complexes **4–8** presumably proceeds through a reactive, and yet undetected, cationic alkenyl complex **9**. Formation of a coordinatively unsaturated 16-electron ruthenium(II) intermediate is supported by the observation that ruthenium hydrides possessing chelating ligands $[Ru(CO)H(bpy)(PPh_3)_2]ClO_4$ (**10**) and $[Ru(CO)H(phen)(PPh_3)_2]ClO_4$ (**11**)[8] do not react with alkynes, even under forcing conditions. A plausible reaction mechanism involves coordination of the 1-alkyne followed by oxidative addition of the C–H bond to Ru(II) to yield Ru(IV) hydride **12**, which leads in a fast step to the σ-alkynylruthenium(II) complex and the 1-alkene by reductive elimination (Scheme I). This process has precedent in the reaction of alkenyliron(II)[5f] and -rhodium(I) complexes[5i] with 1-alkynes and in our recent observation that the alkenylruthenium(II) complex $Ru(CO)Cl(CH{=}CHPh)(Me_2HPz)(PPh_3)_2$ reacts with excess phenylacetylene to form the corresponding alkynylruthenium derivative.[10,11]

In an attempt to ascertain the intermediacy of species like **9**, we tried the reaction of bis(acetonitrile)alkenylruthenium complexes **13–15**[3] with pyridine in the presence

(5) For the synthesis of σ-alkynylmetal complexes, see: (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143. (b) Critchlow, P. B.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 1902. (c) Ashworth, T. V.; Chalmers, A. A.; Singleton, E. *Inorg. Chem.* **1985**, *24*, 2125. (d) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *349*, C53. (e) Bianchini, C.; Laschi, F.; Ottaviani, F. M.; Peruzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660. (f) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediani, P. *Organometallics* **1989**, *8*, 2080. (g) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179. (h) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Laschi, F.; Zanello, P.; Ottaviani, F. M. *Organometallics* **1990**, *9*, 360. (i) Bianchini, C.; Meli, A.; Peruzzini, H.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146. (j) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans* **1977**, 621. (k) Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1545. (l) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540. (m) Marder, T. B.; Zargarian, D.; Calabrese, J. C.; Herkovitz, T. H.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1484. (n) Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *290*, 99. (o) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187. (p) Werner, H.; Wolf, J.; García-Alonso, F. G.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397. (q) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255. (r) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158. (s) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1990**, *381*, 275. (t) Anderson, G. K.; Lumeta, G. J. *J. Organomet. Chem.* **1985**, *295*, 257. (u) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589. (v) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (w) Habadie, M.; Dartiguenave, M.; Dartiguenave, Y.; Britten, J. F.; Beauchamp, A. L. *Organometallics* **1988**, *8*, 2564. (x) Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382. (y) Field, L. D.; George, A. V.; Hambley, T. W.; Malouf, E. Y.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 931.

(6) For related processes, see: (a) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (b) Appleton, T. G.; Clark, H. C.; Puddephatt, R. *Inorg. Chem.* **1972**, *11*, 2074.

(7) For reviews on the coordination chemistry of metal alkynyl complexes, see: (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (b) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (c) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (d) Dixneuf, P. H. *Pure Appl. Chem.* **1989**, *61*, 1763.

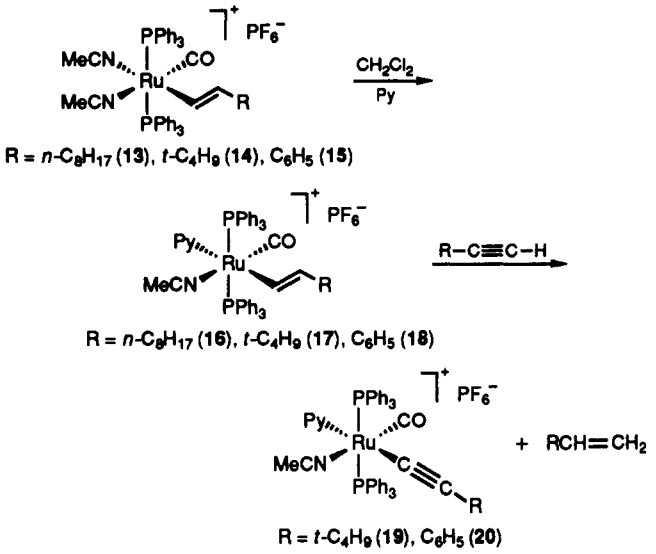
(8) Romero, A.; Vegas, A.; Santos, A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1987**, *319*, 103.

(9) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480.

(10) Romero, A.; Santos, A.; Vegas, A. *Organometallics* **1988**, *7*, 1988.

(11) A related Ru(IV) to Ru(II) reaction has been recently proposed in the orthometalation of a ruthenium enolate: Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234.

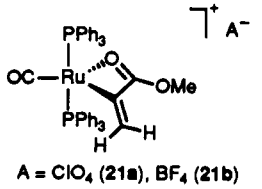
Scheme II



of 1-alkynes. However, very complex reaction mixtures were obtained when these alkenyl complexes were allowed to react with pyridine or 2,6-dimethylpyridine in dichloromethane or deuteriochloroform in the presence of 1 equiv of 1-alkyne. Similar results were obtained when the bis(acetonitrile) hydride **1a** was treated with pyridine and the 1-alkynes. On the other hand, **13–15** could be cleanly transformed into complexes **16–18** by treatment with pyridine in dichloromethane at 23 °C for 15 min (Scheme II). Presumably, the selectivity observed in the exclusive formation of a single stereoisomer arises by coordination of the pyridine ligand away from the more sterically demanding (*E*)-alkenyl ligand. The stereochemistry is assigned from a series of ^{1}H NMR nuclear Overhauser effect (NOE) difference experiments with complex **17**. Irradiation of the H-1 and H-2 alkenyl hydrogens caused a positive NOE on the absorption due to the acetonitrile hydrogens (5 and 3%, respectively). Additionally, irradiation on the acetonitrile hydrogens gave a 2% enhancements on both H-1 and H-2 of the alkenyl ligand, while irradiation on the pyridine ortho hydrogens at 8.10 ppm gave rise to exclusive enhancement on the acetonitrile hydrogens (3%).

Alkenyl complexes **16–18** proved to be reluctant to further substitution of the remaining acetonitrile by a second pyridine ligand. However, **17** reacted almost quantitatively at 23 °C with 3,3-dimethylbutyne and phenylacetylene to give new alkynyl complexes **19** and **20** with concomitant formation of 3,3-dimethyl-1-butene (Scheme II). The stereochemistry of **19** and **20** was assigned tentatively. Phenylacetylene derivative **18** was less reactive and was recovered unchanged after treating with 1-decyne or phenylacetylene, although treatment with the more acidic alkyne methyl propynoate in deuteriochloroform for 72 h gave styrene and uncharacterized ruthenium products.

In contrast with the smooth reaction of hydrides **2** with alkyl- and phenylacetylenes, the reaction with methyl propynoate yielded complex mixtures from which the coordinatively unsaturated complexes **21** could be isolated



A = ClO_4 (**21a**), BF_4 (**21b**)

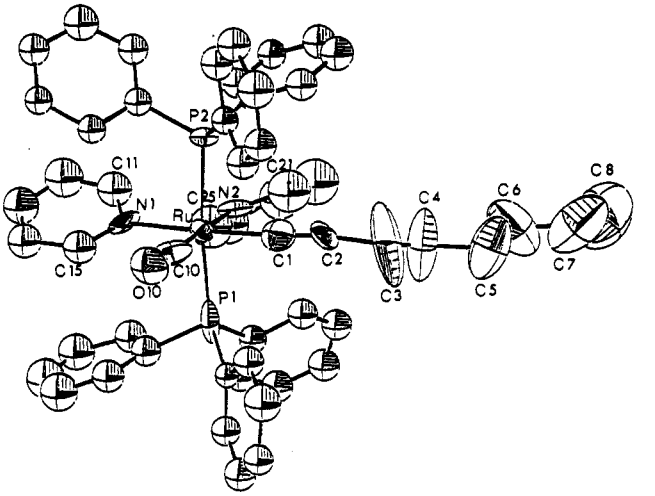


Figure 1. ORTEP drawing of cation $[Ru(CO)(C{\equiv}CC_6H_{13})(C_5H_5N)_2(PPh_3)_2]^+$. Thermal ellipsoids at the 50% level are shown; hydrogen atoms and phenyl carbon numbering are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 4b[a]

Ru-P1	2.36 (1)	C10-O10	1.14 (4)
Ru-P2	2.412 (8)	N1-C11	1.35 (4)
Ru-C10	1.82 (3)	C11-C12	1.48 (5)
Ru-C1	2.01 (3)	C12-C13	1.37 (5)
Ru-N1	2.16 (2)	C13-C14	1.42 (6)
Ru-N2	2.21 (2)	C14-C15	1.48 (6)
C1-C2	1.13 (5)	C15-N1	1.26 (4)
C2-C3	1.54 (5)	N2-C21	1.46 (6)
C3-C4	1.42 (7)	C21-C22	1.46 (8)
C4-C5	1.65 (6)	C22-C23	1.57 (7)
C5-C6	1.36 (8)	C23-C24	1.55 (7)
C6-C7	1.60 (10)	C24-C25	1.52 (7)
C7-C8	1.50 (10)	C25-N2	1.35 (5)
P1-Ru-P2	172.4 (3)	C1-C2-C3	171 (5)
P1-Ru-C10	87 (1)	C2-C3-C4	118 (4)
P1-Ru-C1	87 (1)	C3-C4-C5	114 (4)
P1-Ru-N1	94.3 (8)	C4-C5-C6	106 (4)
P1-Ru-N2	90.2 (8)	C5-C6-C7	99 (5)
P2-Ru-C10	91 (1)	C6-C7-C8	98 (5)
P2-Ru-C1	86 (1)	C11-N1-C15	114 (3)
P2-Ru-N1	93.1 (8)	N1-C11-C12	127 (3)
P2-Ru-N2	92.0 (8)	C11-C12-C13	114 (3)
C1-Ru-C10	94 (1)	C12-C13-C14	123 (3)
C1-Ru-N2	87 (1)	C13-C14-C15	114 (3)
N2-Ru-N1	89.0 (9)	C21-N2-C25	124 (3)
N1-Ru-C10	90 (1)	N2-C21-C22	122 (4)
N1-Ru-C1	176 (1)	C21-C22-C23	109 (4)
N2-Ru-C10	177 (1)	C22-C23-C24	133 (4)
Ru-C10-O10	177 (4)	C23-C24-C25	104 (4)
Ru-C1-C2	175 (3)		

[a] Mean P-C in PPh_3 ligands = 1.85 (3) Å, mean C-C in Ph rings, = 1.40 (5) Å, range of Cl-O bond distances = 1.44 (4)–1.46 (6) Å, mean Cl-O = 1.45 (5) Å; mean C-P-C in PPh_3 ligands = 102 (1)°, mean C-C-C in Ph rings = 120 (3)°, mean Ru-P-C = 116 (1)°, mean O-Cl-O = 109 (3)°.

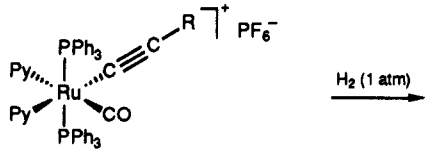
in low yield (**21a**, 13%; **21b**, 32%). The insertion of the alkyne in this complex is inverse to that found in the five-coordinated complex Ru(CO)Cl(HC=CHCOOMe)-$(PPh_3)_2$.[12] Presumably, complexes **21a** and **21b** are stable under the reaction conditions, while the primary insertion

(12) (a) Torres, M. R.; Santos, A.; Solans, X. *Organometallics* **1987**, *6*, 1091. (b) A related six-coordinated complex of Os(II) has been reported recently: Werner, H.; Meyer, U.; Peters, K.; Schnering, H. G. *Chem. Ber.* **1989**, *122*, 2097. (c) The bis-insertion reactions of methyl propynoate with $Ru(CO)H(Cl)(PPh_3)_2$ also proceed by means of an inverse insertion of the alkyne: Castaño, A. M.; Echavarren, A. M.; López, J.; Santos, A. *J. Organomet. Chem.* **1989**, *379*, 171.

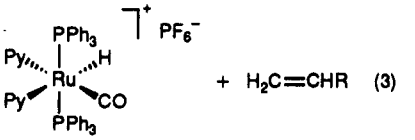
products with structures related to that of **9**, formed in the major pathway, undergo further reactions with the alkyne, leading to uncharacterized products.

Structure of Complex 4b. The structure of **4b** (Figure 1) showed the $[Ru(CO)(C{\equiv}CC_6H_{13})(C_5H_5N)_2(PPh_3)_2]^+$ cations and the ClO_4^- anions held together by electrostatic interaction. Selected bond distances and angles are given in Table I. The Ru atom displays a distorted octahedral coordination with Ru, C1, C10, N1, and N2 in the equatorial plane and the two phosphines in approximately axial positions [P1–Ru–P2 = 172.4 (3)°]. The pyridine ligands in the equatorial plane occupy cis positions. The C1–C2 bond distance (1.13 (4) Å) is within the range observed for the C≡C bond length of σ-alkynylcyclopentadienylruthenium complexes,[4,13] and the Ru–C1 bond distance of 2.01 (3) Å is similar to the Ru–C distance (2.016 (3) Å) in the complex $CpRu(C{\equiv}CPh)(PPh_3)_2$.[13b]

Hydrogenation of σ-Alkynylruthenium Complexes. Hydrogenation of the alkynyl complexes readily takes place at 23 °C under 1 atm of H_2 in dichloromethane or deuteriochloroform solutions for 2–4 h to yield the starting hydride and 1 equiv of 1-alkene (eq 3).[14] The experiments



R = *n*-C_6H_{13} (**4a**), *t*-C_4H_9 (**6**), C_6H_5 (**8a**)

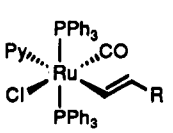


+ $H_2C{=}CHR$ (3)

2a

were carried out with hexafluorophosphate complexes **4a**, **6**, and **8a**, and the process was followed by GC and ^1H NMR spectroscopy. None of the 1-alkynes could be detected. Furthermore, hydride **2a** catalyzed the clean hydrogenation of phenylacetylene to styrene at 23 °C under 1 atm of H_2 in deuteriochloroform, although the reaction is too slow to be useful, affording a 50% conversion after 160 h with a 2% catalyst.

Reduction of Perchlorate Anion. When hydride perchlorate **2b** was heated in the presence of alkynes, variable amounts of σ-alkenyl complexes were also formed. We have recently observed this unexpected reduction of the perchlorate anion in the reaction of hydride **1b** with diphenylacetylene.[3] Performing the reaction in methanol or ethanol yielded alkenylruthenium(II) complexes **22–26**



R = *n*-C_3H_7 (**22**), *n*-C_6H_{13} (**23**), *t*-C_4H_9 (**24**), C_6H_5 (**25**), COOMe (**26**)

in moderate yield (40–60%). The same compounds were previously obtained in good yield by a cis-insertion of 1-alkynes into the Ru–H bond of $Ru(CO)H(Cl)(C_5H_5N)(PPh_3)_2$ (**3**).[2e] Since no reduction of the perchlorate anion of the σ-alkynyl complexes was observed in refluxing ethanol, reduction of the anion seemingly takes place in the starting hydride. Hence, heating of **2b** in methanol or ethanol for 3–6 h afforded hydride **3** in 70% yield. Triphenylphosphine oxide was also isolated in this reaction in 31% yield,[15] as well as uncharacterized ruthenium complexes. The addition of triphenylphosphine, dimethyl sulfide, or cyclohexene does not improve the efficiency of the reduction. That the alcohols are not oxidized in the process was shown by performing the reaction in the presence of benzyl alcohol in toluene or dichloromethane as solvent. In these experiments neither benzaldehyde nor benzoic acid were detected. Although the reduction of perchlorate by Ru(II) has been previously observed in aqueous solutions,[16] this is, to our knowledge, the first example of a reduction in an organic solvent. A coordinated perchlorate ruthenium(II) complex is thought to be involved in the reduction,[17] since in the bipyridine hydride **10** the perchlorate anion does not suffer reduction under identical conditions.

Conclusions

The experimental results reported herein provide evidence for the involvement of σ-alkenyl complexes in the formation of σ-alkynylruthenium complexes from cationic ruthenium hydrides and alkynes. Furthermore, the stepwise hydrogenation of the σ-alkynylruthenium(II) complexes has been shown to yield 1-alkenes and the starting ruthenium hydride. During the course of this study an unexpected reduction of the perchlorate anion to a chloride ligand in organic solvents has been uncovered.

Experimental Section

^1H NMR spectra were recorded on a Bruker AM 200 (200 MHz) or a Varian XL-300 (300 MHz) spectrometer in deuteriochloroform, unless otherwise stated, with tetramethylsilane as an internal standard. The ^1H-decoupled ^{13}C NMR spectra were recorded on a Bruker AM 200 (50 MHz) instrument with the solvent ($CDCl_3$) as internal standard. IR spectra were recorded on a Pye Unicam SP-3-300S spectrophotometer using KBr disks. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC).

Dichloromethane was freshly distilled from calcium hydride. All reactions were carried out under a N_2 or Ar atmosphere.

Synthesis of σ-Alkynylruthenium Complexes 4–8. General Procedure. The 1-alkyne (0.20 mmol) was added to a solution of hydride **2** (0.10 mmol) in dichloromethane (10.0 mL) at 23 °C. The resulting mixture was stirred at this temperature for 12–24 h. The progress of the reaction was monitored by IR or ^1H NMR spectroscopy. The solvent was evaporated, and the resulting solid was triturated with ethyl ether and filtered. The 1-alkenes formed in these reactions were characterized by comparison of their ^1H NMR spectra and GC retention times with authentic samples. The following σ-alkynylruthenium complexes $[Ru(CO)(C{\equiv}CR)(C_5H_5N)_2(PPh_3)_2]A$ were prepared in the stated yields according to this general procedure in a 0.2–1.0-mmol scale.

4a (R = *n*-C_6H_{13}, A = PF_6), 86%: IR (cm^{-1}) ν(C≡C) 2120 (vw), ν(C≡O) 1950 (vs), ν(C=N) 1600 (w), ν(PF_6) 830 (vs); ^1H NMR (300 MHz) δ 8.12 (d, J = 5.2 Hz, 2 H, py), 7.60–7.45 (m, 14 H), 7.34–7.26 (m, 8 H), 7.22–7.14 (m, 12 H), 6.88–6.78 (m, 4 H, py), 2.25–2.17 (m, 2 H), 1.35–1.15 (m, 8 H), 0.86 (t, J = 6.5 Hz, 3 H).

(13) (a) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213. (b) Wisner, J. M.; Batczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, *100*, 115.

(14) For a leading reference on the catalytic chemistry of ruthenium, see: Halpern, J. *Pure Appl. Chem.* **1987**, *59*, 173.

(15) For the catalytic oxidation of triphenylphosphine with Ru(II) complexes, see: Graham, B. W.; Laing, K. R.; O'Connor, C. J.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1237.

(16) (a) Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1962**, *84*, 4984. (b) Endicott, J. F.; Taube, H. *Inorg. Chem.* **1965**, *4*, 437. (c) Mercer, E. E.; Buckley, R. R. *Inorg. Chem.* **1965**, *4*, 1692. (d) Wallace, R. M.; Propst, R. C. *J. Am. Chem. Soc.* **1969**, *91*, 3779. (e) Seewald, D.; Sutin, N.; Watkins, K. O. *J. Am. Chem. Soc.* **1969**, *91*, 7307. (f) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1149. (g) See also: Elder, R. C.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 427.

(17) For the coordination chemistry of perchlorate, see: (a) Johansson, L. *Coord. Chem. Rev.* **1974**, *12*, 241. (b) House, D. A.; Sted, P. J.; Watson, A. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1575 and references cited therein.

Anal. Calcd for $C_{55}H_{53}N_2F_6OP_3Ru$: C, 61.97; H, 5.01; N, 2.63. Found: C, 61.51; H, 5.01; N, 2.32. **4b** (A = ClO_4), 80%: IR (cm^{-1}) ν(C≡C) 2120 (w), ν(C≡O) 1945 (vs), ν(C=N) 1600 (w), $\nu(ClO_4)$ 1090 (vs); the ^1H NMR spectrum is identical with that of **4a**. A crystal of **4b** was suitable for X-ray diffraction study. Small amounts of 2-*n*-hexyl-1-decen-3-yne[9] were also obtained in this reaction: IR (neat, cm^{-1}) 3090 (w), 2200 (w), 1600 (w), 1460 (m); ^1H NMR (200 MHz) δ 5.20 (d, J = 1.8 Hz, 1 H), 5.12 (d, J = 1.8 Hz, 1 H), 2.30 (t, J = 6.8 Hz, 2 H), 2.12 (t, J = 7.2 Hz, 2 H), 1.40–1.22 (m, 16 H), 0.95–0.80 (m, 6 H).

5 (R = *n*-C_8H_{17}, A = PF_6), 84%: IR is almost superimposable to that of **4a**; ^1H NMR (300 MHz) δ 8.12 (d, J = 5.2 Hz, 2 H, py), 7.60–7.45 (m, 14 H), 7.34–7.26 (m, 8 H), 7.22–7.14 (m, 12 H), 6.76–6.63 (m, 4 H, py), 2.25–2.17 (m, 2 H), 1.35–1.13 (m, 12 H), 0.88 (t, J = 6.5 Hz, 3 H). Anal. Calcd for $C_{54}H_{57}F_6N_2OP_3Ru$: C, 62.58; H, 5.25; N, 2.56. Found: C, 62.61; H, 5.43; N, 2.70.

6 (R = *t*-C_4H_9, A = PF_6), 80%: IR (cm^{-1}) ν(C≡C) 2100 (w), ν(C≡O) 1950 (vs), ν(C=N) 1600 (m), $\nu(PF_6)$ 830 (vs); ^1H NMR (300 MHz) δ 8.07 (d, J = 5.3 Hz, 2 H, py), 7.55–7.50 (m, 14 H), 7.35–7.31 (m, 8 H), 7.22–7.17 (m, 12 H), 6.69–6.65 (m, 4 H, py), 1.01 (s, 9 H). Anal. Calcd for $C_{53}H_{49}F_6N_2OP_3Ru$: C, 61.32; H, 4.76; N, 2.70. Found: C, 61.05; H, 4.74; N, 2.69.

7 (R = *c*-C_6H_{11}, A = PF_6), 82%: IR (cm^{-1}) ν(C≡C) 2110 (vw), ν(C≡O) 1940 (vs), ν(C=N) 1600 (m), $\nu(PF_6)$ 850 (vs); ^1H NMR (200 MHz) δ 8.09 (d, J = 5.1 Hz, 2 H), 7.46–7.47 (m, 14 H), 7.35–7.22 (m, 20 H), 6.70–6.67 (m, 4 H), 2.47–2.31 (m, 1 H), 1.66–1.42 (m, 5 H), 1.32–1.10 (m, 5 H); ^{13}C NMR δ 204.67 (t, J = 15.2 Hz), 154.24 (py), 154.15 (py), 137.73 (py), 137.05 (py), 134.02 (t, J = 4.8 Hz, PPh_3), 131.07 (t, J = 21.0 Hz, PPh_3), 130.17, 128.35 (t, J = 4.4 Hz, PPh_3), 125.33 (py), 124.50 (py), 121.27, 88.57 (t, J = 18.2 Hz), 33.62, 32.15, 26.13, 24.90. Anal. Calcd for $C_{55}H_{51}F_6N_2OP_3Ru$: C, 62.09; H, 4.83; N, 2.63. Found: C, 61.76; H, 5.02; N, 2.80.

8a (R = C_6H_5, A = PF_6), 71%: IR (cm^{-1}) ν(C≡C) 2100 (m), ν(C≡O) 1948 (vs), ν(C=N) 1600 (m), $\nu(PF_6)$ 850 (vs); ^1H NMR (300 MHz) δ 8.12 (d, J = 5.8 Hz, 2 H), 7.83–7.46 (m, 10 H), 7.40–7.26 (m, 12 H), 7.25–7.06 (m, 15 H), 6.92 (d, J = 7.3 Hz, 2 H), 6.73–6.80 (m, 4 H); ^{13}C NMR δ 204.13 (t, J = 14.9 Hz), 154.26 (py), 153.97 (py), 137.81 (py), 137.31 (py), 133.83 (t, J = 5.0, PPh_3), 130.31 (s, PPh_3), 130.30 (t, J = 27.3 Hz, PPh_3), 129.90 (s, PPh_3), 128.52 (t, J = 5.1 Hz, PPh_3), 127.93, 125.50 (py), 125.38, 124.79 (py), 117.65, 107.58 (t, J = 18 Hz) (one carbon signal overlaps). **8b** (A = ClO_4) 71%: IR (cm^{-1}) ν(C≡C) 2100 (m), ν(C≡O) 1948 (vs), ν(C=N) 1602 (m), $\nu(ClO_4)$ 1085 (vs); the ^1H NMR spectrum is identical with that of **8a**. Anal. Calcd for $C_{55}H_{45}ClN_2O_5P_2Ru$: C, 65.25; H, 4.48; N, 2.77. Found: C, 65.07; H, 4.62; N, 2.76. **8c** (A = BF_4) 34%: IR (cm^{-1}) ν(C≡C) 2100 (m), ν(C≡O) 1948 (vs), ν(C=N) 1602 (m), $\nu(BF_4)$ 1602 (vs), 1055 (br); the ^1H NMR spectrum is identical with that of **8a**. Anal. Calcd for $C_{55}H_{45}BF_4N_2OP_2Ru$: C, 66.07; H, 4.54; N, 2.80. Found: C, 66.21; H, 4.55; N, 2.65.

1-Decyne-*1-d*. To a solution of 1-decyne (1.53 mg, 11.1 mmol) in tetrahydrofuran (10 mL) at −60 °C was added *n*-BuLi (9.0 mL, 1.4 M solution in hexane, 12.60 mmol). After warming to 23 °C (ca. 1 h), the mixture was treated with D_2O (99.8% D, 3.0 mL). The mixture was extracted with diethyl ether, dried ($MgSO_4$), and evaporated to yield 1-decyne-*1-d* (1.50 g, 97%): ^1H NMR (200 MHz) δ 2.17 (t, J = 6.9 Hz, 2 H), 1.60–1.16 (m, 12 H), 0.82 (t, J = 7.0 Hz, 3 H); ^{13}C δ 84.29 (1:1:1 t, J = 7.5 Hz), (1:1:1 t, J = 37.9 Hz), 31.82, 29.16. 29.06, 28.76, 28.51, 22.63, 18.36, 14.04.

Reaction of Hydride 2a with 1-Decyne-*1-d*. To a suspension of hydride **2a** (15 mg, 0.02 mmol) in benzene-d_6 (1.5 mL) was added 1-decyne-*1-d* (8 μL, 0.04 mmol). The mixture was stirred at 23 °C for 10 h. The mixture was filtered to yield alkynyl complex **5**. The benzene-d_6 solution contained pure 1-decene-*1-d*$_2$: ^1H NMR (200 MHz, benzene-d_6) δ 5.31–5.27 (m, 1 H), 2.24–2.16 (m, 2 H), 1.41–1.18 (m, 12 H), 0.87 (t, J = 7.1 Hz, 3 H).

Synthesis of Alkenyl Complexes [Ru(CO)(CH=CHR)(MeCN)(C_5H_5N)(PPh_3)$_2$]PF_6. General Procedure. Pyridine (1.2 mmol) was added to a solution of alkenyl complex [Ru(CO)(CH=CHR)(MeCN)$_2$(PPh_3)$_2$]PF_6[3] (0.50 mmol) in dichloromethane (10 mL) at 23 °C. After stirring for 15 min, the mixture was evaporated and the residue was triturated with diethyl ether to yield a white solid. The following alkenyl complexes were prepared in the stated yields according to this procedure in a 0.5–1.0-mmol scale.

16 (R = *n*-C_6H_{17}), 79%: IR (cm^{-1}) ν(C≡N) 2284 (vw), ν(C≡O) 1930 (vs), ν(C=N) 1600 (w), $\nu(PF_6)$ 835 (vs); ^1H NMR (200 MHz) δ 8.10 (d, J = 4.9 Hz, 2 H, py), 7.45–7.18 (m, 31 H), 6.86–6.79 (m, 2 H, py), 6.26 (dt, J = 16.3, 3.7 Hz, 1 H), 4.74 (dt, J = 16.3, 6.4 Hz, 1 H), 1.95–1.86 (m, 2 H), 1.67 (t, J = 1.4 Hz, 3 H), 1.32–1.04 (m, 12 H), 0.88 (t, J = 6.7 Hz, 3 H). Anal. Calcd for $C_{54}H_{57}F_6N_2OP_3Ru$: C, 61.30; H, 5.43; N, 2.65. Found: C, 61.50; H, 5.35; N, 2.60.

17 (R = *t*-C_4H_9), 84%; IR (cm^{-1}) ν(C≡N) 2290 (vw), ν(C≡O) 1940 (vs), ν(C=N) 1600 (w), $\nu(PF_6)$ 850 (vs); ^1H NMR (200 MHz) δ 8.10 (d, J = 5.8 Hz, 2 H, py), 7.41–7.24 (m, 31 H), 6.85–6.78 (m, 2 H, py), 6.13 (dt, J = 16.7, 3.6 Hz, 1 H), 4.84 (d, J = 16.7 Hz, 1 H), 1.68 (s, 3 H), 0.75 (s, 9 H); ^{13}C δ 205.99 (t, J = 14.5 Hz), 153.55 (py), 151.30 (t, J = 3.5 Hz), 136.18 (py), 133.84 (t, J = 5.1 Hz, PPh_3), 130.56 (t, J = 21.6 Hz, PPh_3), 130.06 (PPh_3), 128.13 (t, J = 4.5 Hz, PPH_3), 125.89, 125.49 (py), 36.41, 29.46, 2.74 (one alkenyl carbon signal overlaps). Anal. Calcd for $C_{50}H_{49}F_6N_2OP_3Ru$: C, 59.94; H, 4.93; N, 2.80. Found: C, 59.64; H, 5.20; N, 2.99.

18 (R = C_6H_5), 94%: IR (cm^{-1}) ν(C≡N) 2290 (vw), ν(C≡O) 1950 (vs), ν(C=N) 1595 (m), $\nu(PF_6)$ 850 (vs); ^1H NMR (300 MHz) δ 8.17–8.15 (m, 2 H, py), 7.57 (dt, J = 17.0, 3.7 Hz, 1 H), 7.52–7.28 (m, 16 H), 7.28–7.16 (m, 18 H), 7.06–7.00 (m, 2 H), 6.81 (d, J = 7.3 Hz, 2 H), 7.58 (d, J = 17.0 Hz, 1 H), 1.56 (s, 3 H). Anal. Calcd for $C_{52}H_{45}F_6N_2OP_3Ru$: C, 61.12; H, 4.44; N, 2.74. Found: C, 61.37; H, 4.44; N, 3.00.

Reaction of Alkenyl Complex [Ru(CO)(CH=CH-*t*-C_4H_9)(MeCN)(C_5H_5N)(PPh_3)$_2$]PF_6 (17) with 1-Alkynes. To a solution of alkenyl complex **16** (455 mg, 0.45 mmol) in dichloromethane (15 mL) was added *tert*-butylacetylene (100 μL, 0.81 mmol). The resulting solution was stirred at 23 °C for 35 h. The solvent was evaporated, and the residue was triturated with 1:1 hexane–diethyl ether to yield [Ru(CO)(C≡C-*t*-C_4H_9)(MeCN)(C_5H_5N)(PPh_3)$_2$]PF_6 (**19**) (380 mg, 84%) as a white solid: IR (cm^{-1}) ν(C≡C) 2100 (vw), ν(C≡O) 1960 (vs), ν(C=N) 1600 (w), $\nu(PF_6)$ 850 (vs); ^1H NMR (200 MHz) δ 8.45–8.43 (m, 2 H, py), 7.69–7.58 (m, 12 H), 7.34–7.24 (m, 21 H), 1.49 (s, 3 H), 1.08 (s, 9 H); ^{13}C δ 202.34 (t, J = 14.2 Hz), 152.34 (py), 137.07 (py), 133.85 (t, J = 5.4 Hz, PPh_3), 131.03 (t, J = 22.5 Hz, PPh_3), 130.09 (s, PPh_3), 128.22 (t, J = 4.8 Hz, PPh_3), 124.94 (py), 124.28, 122.89 (t, J = 1.8 Hz), 89.23 (t, J = 17.1 Hz), 31.76, 29.44, 2.20. Anal. Calcd for $C_{50}H_{47}F_6N_2OP_3Ru$: C, 60.06; H, 4.74; N, 2.80. Found: C, 60.36; H, 4.39; N, 2.50.

Similarly, the reaction of **16** with phenylacetylene (1.4 equiv, 21 h) yields alkynyl complex [Ru(CO)(C≡CC_6H_5)(MeCN)(C_5H_5N)(PPh_3)$_2$]PF_6 (**20**) as a white solid (82%): IR (cm^{-1}) ν(C≡C) 2100 (m), ν(C≡O) 1975 (vs), ν(C=N) 1590 (m), $\nu(PF_6)$ 850 (vs); ^1H NMR (300 MHz) δ 8.43 (d, J = 5.3 Hz, 2 H, py), 7.64–7.60 (m, 12 H), 7.37–7.26 (m, 21 H), 7.26–7.13 (m, 3 H), 7.03–7.01 (m, 2 H), 1.56 (s, 3 H); ^{13}C NMR δ 201.78 (t, J = 13.8 Hz), 152.56 (py), 137.25 (py), 133.74 (t, J = 5.3 Hz, PPh_3), 130.25 (t, J = 22.3 Hz, PPh_3), 130.25 (PPh_3), 128.45 (t, J = 4.5 Hz, PPh_3), 128.05, 125.42, 125.08, 115.53, 109.24 (t, J = 16.8 Hz), 2.31 (three phenyl carbon signals overlap). Anal. Calcd for $C_{52}H_{43}F_6N_2OP_3Ru$: C, 61.24; H, 4.25; N, 2.75. Found: C, 61.22; H, 4.35; N, 3.02.

[Ru{C(COOMe)=CH$_2$}(CO)(PPh_3)$_2$]BF_4 (21b). To a solution of hydride **2c** (200 mg, 0.22 mmol) in dichloromethane (10 mL) was added methyl propynoate (38 μL, 0.45 mmol). The mixture was stirred at 23 °C for 3 h. The solvent was evaporated, and the residue was triturated with ethanol to yield **21b** (59 mg, 32%) as a gray-white solid: IR (cm^{-1}) ν(C≡O) 1940 (vs), ν(C=O) 1550 (s), $\nu(BF_4)$ 1060 (br, vs); ^1H NMR (300 MHz) δ 7.45–7.38 (m, 30 H), 6.71 (t, J = 2.2 Hz, 1 H), 6.08 (t, J = 1.6 Hz, 1 H), 2.84 (s, 3 H). An ^1H NOEDIFF experiment showed enhancements at δ 6.08 (36%) and 2.84 (2%) after irradiation at 6.71 and an enhancement at δ 6.71 (17%) after irradiation at δ 6.08. The perchlorate complex (**21a**) was prepared from hydride **1b** in 13% yield: IR (cm^{-1}) ν(C≡O) 1920 (vs), ν(C=O) 1550 (S), $\nu(ClO_4)$ 1090 (vs); the ^1H NMR spectrum was identical with that of **21b**. Anal. Calcd for $C_{41}H_{35}ClO_7P_2Ru$: C, 58.75; H, 4.21. Found: C, 59.31; H, 4.38.

Reduction of the Perchlorate Anion. A suspension of ruthenium hydride **2b** (100 mg, 0.11 mmol) in ethanol (10 mL) was heated under reflux for 6 h. After cooling to room temperature, the solid was filtered to yield hydride **3**[2e] (63 mg, 75%). The

Table II. Summary of Crystallographic Data and Details of the Structure Determination of 4b

Crystal Data	
formula	$C_{55}H_{53}ClN_2O_5P_2Ru$
fw	1020.46
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.032 (2)
b, Å	16.734 (6)
c, Å	26.816 (12)
β, deg	96.59 (2)
V, Å^3	4918 (2)
Z	4
d_{calcd}, g cm^{-3}	1.38
$F(000)$	2112
μ, cm^{-1}	4.8
Data Collection Parameters	
diffractometer	Enraf-Nonius CAD4
radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
scan technique	$\omega/2\theta$
no. of unique reflns	9225
no. of ind reflns	8598
no. of obsd reflns	2291 ($I \geq 3\sigma$ criterion)
internal consistency	R_{int} = 0.009
cryst decay	no
Structure Determination and Refinement	
unit weight assigned to every reflection	
R, % $[R = \sum(\|F_o\| - \|F_c\|/\sum\|F_o\|]$	9.8

ethanol solution contained a 1:1 mixture of hydrides **2b** and **3** (determined by ^{1}H NMR integration of the triplet hydride resonances at −13.00 and −13.52 ppm, respectively).

The reaction of hydride **2b** with 1-alkynes yielded neutral alkenylruthenium complexes Ru(CO)Cl(CH=CHR)(C_5H_5N)(PPh_3)$_2$ identical with those prepared before from Ru(CO)H(Cl)(C_5H_5N)(PPh_3)$_2$.[2e] The following complexes were prepared from **2b** under different conditions in the stated yields: **22** (R = n-C_3H_7) was prepared in methanol under reflux for 3 h (60%); **23** (R = n-C_6H_{13}) was prepared in methanol under reflux for 3 h (40%); **24** (R = t-C_4H_9) was prepared in dichloromethane under reflux for 6 h (50%); **25** (R = C_6H_5) was prepared in ethanol under reflux for 14 h (52%); **26** (R = CO_2Me) was prepared in methanol under reflux for 3 h (46%).

X-ray Data Collection, Structure Determination, and Refinement of 4b. A single pale yellow crystal of **4b** of 0.30 × 0.24 × 0.12 mm was selected for structure determination. The determination of the cell constants and the intensity data collection were carried out at room temperature. Unit cell dimensions were determined by least-squares refinement of 25 accurately centered reflections. Pertinent crystal data and data collection parameters can be found in Table II. The data collection was limited up to θ = 25° because no significant intensity was observed above this limit. In addition only 2291 reflections of the 8598 measured were considered observed. The structure was solved by Patterson and Fourier synthesis. An empirical absorption correction[18] was applied after the isotropic refinement. Maximum and minimum corrections applied were 1.106 and 0.849, respectively (mean 0.999). The refinement was made in the mixed mode, anisotropic only for Ru, P, and N atoms, as well as for the CO group and the octynyl ligand, and isotropic for other atoms (a total of 345 parameters were refined, data to parameter ratio = 5.64). There were some unexpected bond lengths (i.e. C4–C5 and C5–C6 distances of 1.65 and 1.36 Å, respectively) and a great dispersion in phenyl and pyridine C–C bond distances, reflecting limitations in the quality of the data. The final Fourier difference map showed a largest differential peak and hole of 1.5 and −0.79 e/Å^3, respectively. Scattering factors and anomalous dispersion factors were taken from the literature.[19] All calculations were performed on a VAX 11/750 computer by using the following programs: XRAY80 System,[20a] DIRDIF,[20b] and PARST.[20c]

Acknowledgment. We gratefuly acknowledge support of this work by the Dirección General de Investigación Científica y Técnica (DGICYT), Project No. PB87-0201-C03-02. We also thank Julio Montoya and Dr. Pedro Noheda for some of the perchlorate reduction experiments.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters (4 pages); a listing of F_o vs F_c (35 pages). Ordering information is given on any current masthead page.

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1987**, *39*, 158.
(19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(20) (a) Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. *The XRAY 80 System of Crystallographic Programs*; Computer Science Center, University of Maryland, College Park, MD. (b) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van Der Hark, T. E. M.; Prick, P. A.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C. *DIRDIF System of Computer Programs*. Technical Report 1983/1; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983. (c) Nardelli, M. *PARST*; Università di Parma: Parma, Italy.