

# Reactions of $\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$ with Activated Mono- and Disubstituted Acetylenes. Crystal Structure of $[(\text{PPh}_3)_2(\text{CO})(\text{MeO}_2\text{CC}\equiv\text{C})\text{Ru}(\text{MeOOC}=\text{CHCH}=\text{CHCO}_2\text{Me})]$

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The reactions of  $\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$  with the activated acetylenes  $\text{RC}\equiv\text{CR}'$  ( $\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}, \text{C}(\text{O})\text{Me}$  and  $\text{R}' = \text{H}$ ;  $\text{R} = \text{R}' = \text{CO}_2\text{Me}$ ) give rise to three types of products of general formulas  $(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ru}(\text{R}'\text{C}=\text{CHR})$  (I),  $(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ru}(\text{HC}=\text{CRCH}=\text{CHR})$  ( $\text{R} = \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$ ) (II), and  $(\text{CO})(\text{PPh}_3)_2(\text{ROCC}\equiv\text{C})\text{Ru}[\text{R}(\text{O})\text{CC}=\text{CHCH}=\text{CHCOR}]$  ( $\text{R} = \text{OMe}, \text{OEt}, \text{Me}$ ) (III). The four products of the type I are derived from a simple cis insertion of the alkyne into the Ru-H bond, whereas the products of the types II and III can be considered as two different bis-insertion derivatives, with an additional substitution of Cl by an alkynylidene ligand in the type III derivatives. All these compounds have been characterized by analytical and spectroscopic methods (IR and  $^1\text{H}$  NMR). The molecular structure of the type III complex  $(\text{CO})(\text{PPh}_3)_2(\text{MeO}_2\text{CC}\equiv\text{C})\text{Ru}[\text{MeO}(\text{O})\text{CC}=\text{CHCH}=\text{CHCO}_2\text{Me}]$ , determined by X-ray diffraction, can be described as a distorted octahedral species in which both  $\text{PPh}_3$  molecules occupy trans positions, the equatorial positions with respect to the phosphine axis being occupied by the carbonyl, butadienyl (coordinated through C and O atoms), and alkynyl ligands. The additional bond through the ketonic oxygen of the substituent at the alkenylic carbon bonded to Ru gives rise to a higher coordination in the type III complexes.

## Introduction

In an earlier paper we have reported the reactions of  $\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$  with the acetylenes  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{Ph}, n\text{-C}_3\text{H}_5$ ) and  $\text{PhC}\equiv\text{CPh}$ , which lead to alkenyl complexes derived from a simple cis insertion of the alkyne into the H-Ru bond, with elimination of one phosphine molecule.<sup>1</sup> In this work we describe the reactivity of  $\text{Ru}(\text{CO})\text{HCl}(\text{PPh}_3)_3$  toward the activated mono- and disubstituted acetylenes  $\text{RO}_2\text{CC}\equiv\text{CH}$  ( $\text{R} = \text{Me}, \text{Et}$ ),  $\text{MeCOC}\equiv\text{CH}$ , and  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ .

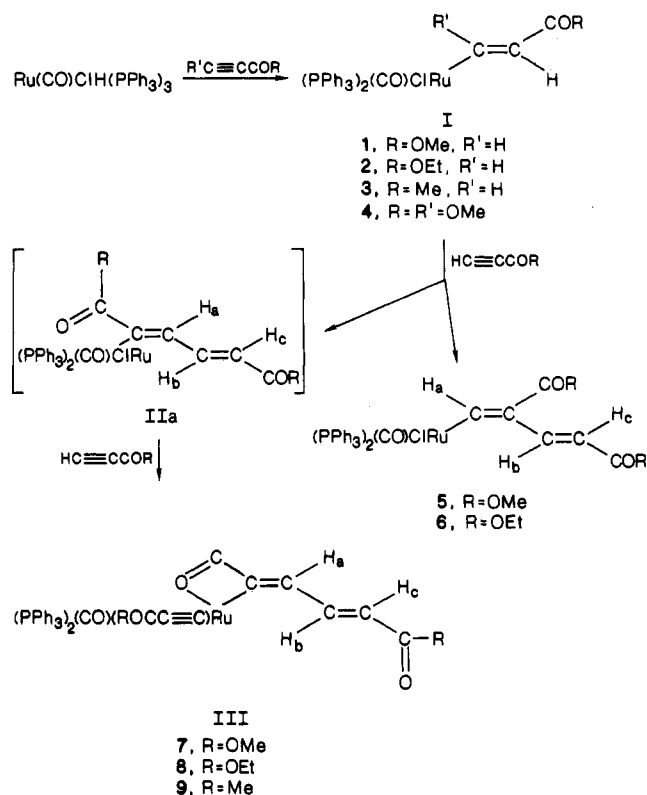
Several different reaction types of these acetylenes with metal hydride complexes have been described. Besides the simple insertion reactions in its different modes,<sup>2</sup> the carboxylate groups of the alkenyl ligands formed can coordinate to the metal through the ketonic oxygen atom, giving rise generally to five-membered metallacycles.<sup>3-6</sup> Several examples of bis insertion also have been described in which an additional  $\pi$  bond with the olefinic system is formed, as in the case of the reaction of  $\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$  with methyl propiolate.<sup>7</sup> The addition of a third molecule of the acetylene to the earlier compound leads to formation of an allene complex.<sup>7</sup> Sometimes metallacycles are formed, as in the reaction of  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  with dimethyl acetylenedicarboxylate, which leads to two five-membered alkenylmetallacycles each containing two acetylene units.<sup>8</sup>  $\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3$  also reacts with methyl propiolate to give a six-membered metallacycle resulting from a tris insertion of the alkyne, the complex also containing a five-membered metallacycle derived from the coordination of the ketonic oxygen of one  $\text{CO}_2\text{Me}$  group.<sup>9</sup>

Only reactions of the ruthenium hydrides  $\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ ,<sup>3,7,10</sup>  $\text{HRu}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)$ ,<sup>11</sup> and  $\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3$ <sup>9</sup> with acetylenes containing alkyl carbox-

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## Scheme I



ylate groups as substituents have been previously described.

(1) Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* 1986, 309, 169.

(2) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* 1976, 14, 245.

(3) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1974, 106.

(4) Booth B. L.; Hargreaves, G. *J. Chem. Soc. A* 1969, 2766.

(5) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* 1979, 101, 508.

(6) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, M. *Organometallics* 1986, 5, 72.

## Results and Discussion

The reactions of  $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_3$  with an excess of the activated acetylenes  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{MeO}_2\text{C}^-$ ,  $\text{EtO}_2\text{C}^-$ ,  $\text{MeCO}^-$ ) give rise to a mixture of products, from which compounds containing one, two, or three alkyne molecules could be isolated and characterized. The solvent used and the reaction time seem to affect the proportion of the different complexes in the reaction mixture. We indicate in the Experimental Section the best conditions for the isolation of each of these products. The same probably occurs in the reaction with dimethyl acetylenedicarboxylate, but in this case only a mono insertion derivative was isolated and characterized. Scheme I summarizes the different products obtained from these reactions.

**Simple Insertion Derivatives.** The reactions of  $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_3$  in  $\text{CH}_2\text{Cl}_2$  with the alkynes earlier mentioned yield in all cases a product of general formula  $[\text{Ru}(\text{CO})\text{Cl}(\text{R}'\text{C}=\text{CHR})(\text{PPh}_3)_2]$  (compounds 1–4, type I, Scheme I), which can be considered as resulting from a simple cis insertion of the alkyne into the Ru–H bond with elimination of one phosphine molecule. These products can be isolated by precipitation with  $\text{Et}_2\text{O}$ . IR bands assignable to  $\nu(\text{C}\equiv\text{C})$  vibrations are absent. Strong  $\nu(\text{C}=\text{O})$  bands between 1915 and 1940  $\text{cm}^{-1}$  indicate the presence of the carbonyl ligand.  $\nu(\text{C}=\text{O})$  (1600–1700  $\text{cm}^{-1}$ ) and  $\nu(\text{COC})$  (1160–1250  $\text{cm}^{-1}$ ) bands are also observed in all cases. One band in the range 1507–1560  $\text{cm}^{-1}$  has been assigned to a  $\nu(\text{C}=\text{C})$  stretching vibration.

The  $^1\text{H}$  NMR spectra of the  $\text{RC}\equiv\text{CH}$  derivatives show two alkenyl proton signals as doublets with  $J = 16$ –22 Hz, which are characteristic of a trans configuration of the alkenyl group. Signals corresponding to the Me or Et groups are also observed. The phosphine proton signals appear as one or two multiplets, which correspond in total to 30 H (2 $\text{PPh}_3$ ). The  $^1\text{H}$  NMR spectrum of the dimethyl carboxylate derivative shows the expected signal for one alkenyl proton. In this case we suppose also a cis insertion of the  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  ligand into the Ru–H bond. Two methyl singlets and the usual phosphine phenyl multiplets are also present.

The yield in the formation of the simple insertion products increases in the series  $\text{MeO}_2\text{CC}\equiv\text{CH}$  (30–40%) <  $\text{EtO}_2\text{CC}\equiv\text{CH}$  (50–60%) <  $\text{MeCOC}\equiv\text{CH}$  (60%) <  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  (60–70%).

The complexes are nonelectrolytes, stable to air, soluble in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , and insoluble in  $\text{Et}_2\text{O}$ .

**Bis-Insertion Derivatives.** Two types of bis-insertion derivatives have been isolated, which correspond to the general formulations  $[(\text{PPh}_3)_2(\text{CO})\text{ClRu}\{\text{H}_a\text{C}=\text{C}(\text{CO}_2\text{R})\text{CH}_b=\text{CH}_c\text{CO}_2\text{R}\}]$  (type IIb, compounds 5 and 6, Scheme I) and  $[(\text{PPh}_3)_2(\text{CO})(\text{ROCC}\equiv\text{C})\text{Ru}\{\text{R}(\text{O})\text{CC}=\text{CH}_a\text{CH}_b=\text{CH}_c\text{COR}\}]$  (type III, compounds 7–9, Scheme I), respectively.

In the reaction with  $\text{MeO}_2\text{CC}\equiv\text{CH}$  in  $\text{CH}_2\text{Cl}_2$ , by chromatographing the yellow solution resulting after precipitation and separation of 1, the crystalline complex 7 was obtained in moderate yield (50%). The crystals were adequate for an X-ray structure determination. The  $^1\text{H}$  NMR spectrum of this complex shows three alkenylic

proton signals corresponding to an  $-\text{RCCH}_a\text{CH}_b=\text{CH}_c\text{R}$  system ( $\delta(\text{H}_a) > \delta(\text{H}_b) > \delta(\text{H}_c)$ ), three methyl singlets and two phenyl multiplets (30 H, 2 $\text{PPh}_3$ ), whereas in the IR spectrum, besides a medium  $\nu(\text{C}=\text{C})$  band at 1618  $\text{cm}^{-1}$ , a sharp  $\nu(\text{C}\equiv\text{C})$  band at 2100  $\text{cm}^{-1}$ , characteristic of an alkynyl ligand, is observed. The strong  $\nu(\text{C}=\text{O})$  absorptions, with maxima at 1720, 1685, and 1576  $\text{cm}^{-1}$ , are indicative of the presence of several different carboxylate groups, the band at 1685  $\text{cm}^{-1}$  being assigned to the  $\nu(\text{C}=\text{O})$  of the alkynyl ligand. The band at 1576  $\text{cm}^{-1}$  could be due to the presence of a  $\text{C}=\text{ORu}$  bond, as occurs in the case of  $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ru}(\text{MeO}_2\text{CC}=\text{CHC}(\text{O})\text{OMe})$ .<sup>3</sup> On the basis of all these spectral data, together with the analytical results, we have assigned to this complex a structure of the type III. This complex and its homologues 8 and 9 can be considered as derived from a bis cis,cis insertion of the alkyne in an antiparallel relative orientation of both molecules, with substitution of Cl by an alkynyl  $\text{RC}\equiv\text{C}^-$  group and elimination of one phosphine molecule. This cis-insertion mode is clearly deduced from the coupling of the alkenyl proton signals observed in the  $^1\text{H}$  NMR spectrum ( $J_{\text{H}_a\text{H}_c} = 16$  Hz; no coupling between  $\text{H}_a$  and  $\text{H}_b$  was observed). The possibility of an additional coordination through a  $\text{C}=\text{O}$  group prompted us to determine the crystal structure of 7, presented below, which confirms the presence of such coordination.

In an attempt to obtain a simple bis-insertion product of methyl propiolate, we have reacted the starting compounds in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . From the red solution formed, red crystals of 5 appeared after some days. In the  $^1\text{H}$  NMR spectrum of this complex three alkenylic proton signals are observed, which are different from those found for the yellow complex 7 and correspond also to a butadienyl system but of the type  $-\text{H}_a\text{C}=\text{CRCH}_b=\text{CH}_c\text{R}$  ( $\text{R} = \text{CO}_2\text{Me}$ ). In this case  $\delta(\text{H}_b) > \delta(\text{H}_a)$ , and some coupling between  $\text{H}_a$ ,  $\text{H}_b$ , and the P atoms of both  $\text{PPh}_3$  molecules is observed ( $J = 1.2$  Hz). Two methyl singlets and two phenyl multiplets of the  $\text{PPh}_3$  molecules are also present. No  $\nu(\text{C}\equiv\text{C})$  absorption was observed, and a strong band at 1550  $\text{cm}^{-1}$  was assigned to  $\nu(\text{C}=\text{C})$ . Only a strong  $\nu(\text{C}=\text{O})$  band at 1695  $\text{cm}^{-1}$  with a shoulder at 1655  $\text{cm}^{-1}$  appears, and the absence of bands toward 1580  $\text{cm}^{-1}$  excludes  $-\text{C}=\text{ORu}$  bonding. On the basis of these spectral data, together with the analytical results, we can assign to this complex a structure of the type IIa or IIb.

In the reaction with  $\text{EtO}_2\text{CC}\equiv\text{CH}$  in  $\text{CH}_2\text{Cl}_2$ , from the reddish solution resulting after filtration of the principal greenish product 2, a crystalline red complex 6 can be isolated by addition of MeOH, concentration, and recrystallization from MeOH (yield 10%). The  $^1\text{H}$  NMR spectrum is similar to that of 5 and shows two methylene quadruplets and two methyl triplets of the Et groups while the IR spectrum is completely similar to that of 5.

The yellow complex 8 can be isolated from the reaction with  $\text{EtO}_2\text{CC}\equiv\text{CH}$  in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . The complex is totally similar to 7 on the basis of analytical and spectral data. It is to be noted that the  $^1\text{H}$  NMR spectrum of 8 in  $\text{CDCl}_3$  always shows the signals corresponding to the complex 6 together with those of 8. An anion exchange of  $\text{EtO}_2\text{CC}\equiv\text{C}^-$  by  $\text{Cl}^-$  by interaction with the solvent could explain the presence of the signals of the red complex 6, but complex 6 also could be present as an impurity. However, no change in color has been observed in a solution of 8 in  $\text{CHCl}_3$  for several days. This lends more probable the IIb structure for the bis-insertion complexes 5 and 6, and IIa could be the structure of an intermediate bis-insertion species in the formation of the type III complexes (Scheme I).

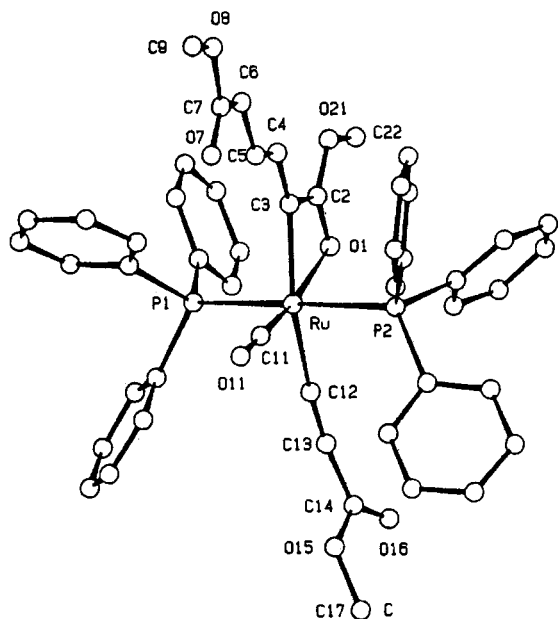
(7) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P.; *J. Chem. Soc., Dalton Trans.* 1977, 621.

(8) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* 1968, 7, 1298.

(9) Yamazaki, H.; Aoki, K. *J. Organomet. Chem.* 1976, 122, C54.

(10) Blackmore, T.; Bruce, M. I.; Stone, F. G. A.; Davis, R. E.; Garza, A. *J. Chem. Soc. D.* 1971, 852.

(11) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1979, 906.



**Figure 1.** Drawing of the molecular structure of  $[(\text{PPh}_3)_2(\text{CO})(\text{MeO}_2\text{CC}\equiv\text{C})\text{Ru}(\text{MeOOC}=\text{CHCH}=\text{CHCO}_2\text{Me})]$ . The atom numbering is the same as that used in Table II; numbering of the carbons of the phenyl rings is omitted for clarity as are all the H atoms.

It is to be noted the appreciable higher proportion of **6** in the reaction mixture in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ , which is red after filtration of **2**, whereas in the reactions with ethyl propiolate the  $\text{CH}_2\text{Cl}_2$  solution after filtration of **1** is yellow, as corresponding to a higher proportion of the complex **7**.

In the reaction with  $\text{MeCOC}\equiv\text{CH}$  in  $\text{CH}_2\text{Cl}_2$  only a bis-insertion derivative of the type III was isolated by concentration, precipitation, and separation of **3**, as can be deduced from analytical and spectral data.

All these complexes are nonelectrolytes stable to air, soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{Me}_2\text{CO}$ ,  $\text{Et}_2\text{O}$ , and insoluble in petroleum ether and hexane.

**Description of the Structure of Complex 7.** The structure of **7** consists of discrete molecules (Figure 1) linked by van der Waals forces. Selected bond distances and angles are given in Table I. The Ru atom displays a distorted octahedral coordination, with Ru, O(1), C(11), C(3), and C(12) atoms in the equatorial plane (largest deviation from mean plane  $-0.013$  (2) Å in Ru atom), and two P atoms of  $\text{PPh}_3$  ligands are in the apical sites. The compression of the C(3)–Ru–O(1) angle to  $63.5$  (1)° produces an increase of the remaining equatorial angles C(12)–Ru–O(1) =  $97.2$  (1)°, C(12)–Ru–C(11) =  $93.6$  (1)°, and C(11)–Ru–C(3) =  $105.7$  (1)°. The Ru–C bond lengths vary in the order Ru–C(11) [ $1.817$  (4) Å] < Ru–C(12) [ $2.064$  (4) Å] < Ru–C(3) [ $2.114$  (4) Å], which can be related to the  $\pi$ -acceptor character of the ligands decreasing in the order  $\text{C}\equiv\text{O} > \text{C}\equiv\text{C} > \text{C}=\text{C}$ . The longer Ru–O(1) bond length with respect to the Ru–C distances earlier mentioned can be attributed to the poorer donor nature of the oxygen— with respect to the carbon—donor molecules. The coordination of O(1) to Ru atom produces an increase in the C(2)–O(1) bond length [ $1.240$  (1) Å], while the C(14)–O(16) bond length is equal to  $1.196$  (4) Å. This fact is favored by the planarity of the  $\text{C}_6\text{H}_4\text{O}_4$  butadienyl ligand, while the C(12)–C(13)–C(14)–O(16) torsion angle is equal to  $-106.3$  (2)°.

In the butadienyl ligand a clear alternation of short and long C–C distances is observed, the double bonds being localized between C(3)–C(4) [ $1.348$  (5) Å] and C(5)–C(6) [ $1.344$  (5) Å]. The bond length C(4)–C(5) [ $1.44$  (6) Å] is

**Table I.** Selected Bond Lengths (Å) and Angles (deg) for Compound **7** (Esd's Given in Parentheses)

Bond Lengths <sup>a</sup>			
Ru–P(1)	2.387 (1)	O(21)–C(22)	1.458 (6)
Ru–P(2)	2.382 (1)	C(2)–C(3)	1.469 (6)
Ru–C(3)	2.114 (4)	C(3)–C(4)	1.348 (5)
Ru–C(12)	2.064 (4)	C(4)–C(5)	1.445 (6)
Ru–C(11)	1.817 (4)	C(5)–C(6)	1.344 (5)
Ru–O(1)	2.245 (3)	C(6)–C(7)	1.467 (6)
C(101)–P(1)	1.817 (5)	C(7)–O(7)	1.205 (8)
C(111)–P(1)	1.835 (4)	C(7)–O(8)	1.335 (6)
C(121)–P(1)	1.837 (3)	O(8)–C(9)	1.455 (7)
C(201)–P(2)	1.834 (4)	C(12)–C(13)	1.203 (5)
C(211)–P(2)	1.826 (4)	C(13)–C(14)	1.444 (6)
C(221)–P(2)	1.829 (4)	C(14)–O(15)	1.338 (6)
C(2)–O(1)	1.240 (4)	O(15)–C(17)	1.436 (6)
C(2)–O(21)	1.330 (6)	C(14)–O(16)	1.196 (5)
Bond Angles <sup>b</sup>			
P(1)–Ru–P(2)	177.3 (1)	C(3)–Ru–C(12)	160.6 (2)
P(1)–Ru–O(1)	88.4 (1)	C(11)–Ru–C(12)	93.6 (2)
P(1)–Ru–C(3)	90.5 (1)	Ru–C(3)–C(4)	150.0 (4)
P(1)–Ru–C(11)	92.2 (1)	C(2)–C(3)–C(4)	119.7 (4)
P(1)–Ru–C(12)	90.3 (1)	C(3)–C(4)–C(5)	124.1 (4)
P(2)–Ru–O(1)	87.7 (1)	C(4)–C(5)–C(6)	122.9 (5)
P(2)–Ru–C(3)	90.5 (1)	C(5)–C(6)–C(7)	121.8 (5)
P(2)–Ru–C(11)	90.0 (1)	Ru–C(12)–C(13)	179.6 (3)
P(2)–Ru–C(12)	88.0 (1)	C(12)–C(13)–C(14)	168.2 (5)
O(1)–Ru–C(3)	63.5 (1)	Ru–C(11)–O(11)	179.6 (3)
O(1)–Ru–C(11)	169.2 (1)	Ru–O(1)–C(2)	90.8 (3)
O(1)–Ru–C(12)	97.2 (1)	O(1)–C(2)–C(3)	115.5 (4)
C(3)–Ru–C(11)	105.8 (2)	O(16)–C(14)–C(13)	126.2 (5)

<sup>a</sup> Mean C–C distances in benzene rings:  $1.383$  (7) Å. <sup>b</sup> Mean C–P–C:  $103.1$  (5)°. <sup>c</sup> Mean Ru–P–C:  $90.2$  (5)°. <sup>d</sup> Mean C–C–C in benzene rings:  $120.0$  (5)°.

only slightly shorter than C(6)–C(7) [ $1.467$  (6) Å], which corresponds to a C–C single bond. This could explain the weak coupling observed between the  $\text{H}_a$  and  $\text{H}_b$  protons in the  $^1\text{H}$  NMR spectrum of this complex, which can be attributed to a free rotation around the C(4)–C(5) single bond. Except for the angle Ru–C(3)–C(4) [ $150.0$  (4)°], all the remaining angles of the butadienyl system are approximately equal to  $120^\circ$ . This deviation can be due to the coordination of O(1) to Ru atom. In relation to the alkynyl ligand, the bond length C(12)–C(13) corresponds clearly to a triple bond, but the angle C(12)–C(13)–C(14) [ $168.2$  (5)°] deviates from the linearity of an  $\text{RC}\equiv\text{C}$ -acetylenic system, while the angle Ru–C(12)–C(13) [ $179.6$  (3)°] corresponds to the linearity expected and is equal to the angle Ru–C(11)–O(11) [ $179.6$  (3)°].

## Conclusions

On the basis of these results we can conclude that all complexes derived from a simple cis insertion of alkyne (1–4) into the Ru–H bond of  $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$  are five-coordinate species with an approximately bipyramidal configuration and a molecular structure similar to that of  $(\text{CO})\text{Cl}(\text{PPh}_3)_2\text{Ru}(\text{PhC}\equiv\text{CHPh})$ ,<sup>1</sup> in which both  $\text{PPh}_3$  molecules occupy the axial positions, the CO, Cl, and alkenyl ligands occupying the remaining coordination sites in the equatorial plane. The same bipyramidal configuration is probable for the type II bis-insertion complexes **5** and **6**, but containing a butadienyl instead of an alkenyl ligand.

The additional substitution of Cl by an alkynyl ligand seems to be related to the coordination of the C=O group of the substituent present at the carbon atom of the butadienyl chain directly bonded to Ru. The  $\pi$ -acceptor character of the alkynyl ligand could explain this effect. This C=O–Ru coordination gives rise to a six-coordinate species in which the Ru–C≡C bond is trans to the Ru–

C=C bond and the Ru—C≡O bond is trans to the Ru—O=C bond. In this case the chemical shifts of the alkylic protons vary in the order  $\delta(H_a) > \delta(H_b) > \delta(H_c)$  and are higher than those of the corresponding complexes of the type II. This effect can be due to the formation of a metallacycle. The IR band at 1576  $\text{cm}^{-1}$  seems to be characteristic of the C=O bonded to Ru in the carboxylate derivatives. A four-membered metallacycle is formed in the type III bis-insertion derivatives 7–9. To date only five-membered metallacycles containing a Ru—O=C bond have been described,<sup>3,9</sup> but there are examples in the literature of four-membered rings formed by additional coordination of a carboxylate oxygen atom for other metals.

### Experimental Section

Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub> was prepared according to a published procedure.<sup>12</sup> IR spectra were recorded with a Perkin-Elmer 325 instrument using KBr disks. The <sup>1</sup>H NMR spectra were recorded on a Bruker WM 360 spectrometer at 360 MHz; shifts are relative to Me<sub>4</sub>Si (0.00 ppm), and the samples were dissolved in CDCl<sub>3</sub>.

**Mono-Insertion Derivatives (CO)Cl(PPh<sub>3</sub>)<sub>2</sub>Ru(R'C=CHR) (1–4).** To a solution of 0.3 g (0.315 mmol) of Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added an excess of the alkyne, and the solution was stirred for 10–15 min. From the green or violet solution, after concentration, a greenish gray or brown-violet solid was precipitated by addition of Et<sub>2</sub>O. For purification, the precipitates of the RO<sub>2</sub>CC≡CH and MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me derivatives were dissolved in CH<sub>2</sub>Cl<sub>2</sub>, chromatographed in a short column packed with Florisil, and eluted with acetone. After evaporation of solvent, the solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, precipitated with Et<sub>2</sub>O, washed with Et<sub>2</sub>O, and dried under vacuum. This purification is unnecessary in the case of the brown-violet MeCOC≡CH derivative.

**1 (R = CO<sub>2</sub>Me, R' = H<sub>a</sub>) (Greenish Gray).** IR:  $\nu(\text{C}=\text{O})$  1924 vs,  $\nu(\text{C}=\text{O})$  1652 s,  $\nu(\text{C}=\text{C})$  1542 s,  $\nu(\text{COC})$  1168  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  3.50 (s, 3 H, Me), 5.38 (d,  $J = 16$  Hz, 1 H, H<sub>b</sub>), 7.00–7.66 (m, 30 H, 6Ph), 9.99 (d,  $J = 16$  Hz, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>41</sub>H<sub>35</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 63.65; H, 4.56. Found: C, 63.55; H, 4.63.

**2 (R = CO<sub>2</sub>Et, R' = H<sub>a</sub>) (Greenish Gray).** IR:  $\nu(\text{C}=\text{O})$  1915 vs,  $\nu(\text{C}=\text{O})$  1640 vs,  $\nu(\text{C}=\text{C})$  1545 vs,  $\nu(\text{COC})$  1165  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  1.17 (t, 3 H, Me), 3.82 (q, 2 H, CH<sub>2</sub>), 5.38 (d,  $J = 22$  Hz, 1 H, H<sub>b</sub>), 6.73–7.13 (m, 10 H, 2Ph), 7.13–7.60 (m, 10 H, 2Ph), 7.60–7.90 (m, 10 H, 2Ph), 10.38 (d,  $J = 22$  Hz, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>42</sub>H<sub>37</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 64.04; H, 4.73. Found: C, 63.54; H, 4.74.

**3 (R = COMe, R' = H<sub>a</sub>) (Brown-Violet).** IR:  $\nu(\text{C}=\text{O})$  1925 vs,  $\nu(\text{C}=\text{O})$  1718 m,  $\nu(\text{C}=\text{C})$  1510  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  1.77 (s, 3 H, Me), 5.95 (d,  $J = 16$  Hz, H<sub>b</sub>), 7.28–7.74 (m, 30 H, 6Ph), 10.16 (d,  $J = 16$  Hz, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>41</sub>H<sub>35</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 64.99; H, 4.65. Found: C, 64.15; H, 4.77.

**4 (R = R' = CO<sub>2</sub>Me) (Greenish Gray).** IR:  $\nu(\text{C}=\text{O})$  1940 vs,  $\nu(\text{C}=\text{O})$  1705 sh, 1690 s, 1680 sh,  $\nu(\text{C}=\text{C})$  1565 s,  $\nu(\text{COC})$  1222 s, 1170  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  3.31 (s, 3 H, Me), 3.47 (s, 3 H, Me), 4.48 (t,  $J_{\text{HP}} = 2.56$  Hz, 1 H, H<sub>b</sub>), 7.28–7.41 (m, 20 H, 4 Ph), 7.56–7.66 (m, 10 H, 2Ph). Anal. Calcd for C<sub>43</sub>H<sub>37</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 62.10; H, 4.48. Found: C, 62.64; H, 4.72.

**Bis-Insertion Derivatives (CO)Cl(PPh<sub>3</sub>)<sub>2</sub>Ru[HC=C(CO<sub>2</sub>R)CH=CHCO<sub>2</sub>R] (Type IIb Complexes 5 and 6).**  
**Methyl Propiolate Derivative (R = Me, 5).** To a solution of 0.3 g (0.315 mmol) of Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (30 mL) was added an excess of MeO<sub>2</sub>CC≡CH, and the solution was stirred for 1 h. By concentration to 15 mL and crystallization, red crystals are formed after some days (yield 10–15%). IR:  $\nu(\text{C}=\text{O})$  1910 vs,  $\nu(\text{C}=\text{O})$  1695 s, 1655 sh,  $\nu(\text{C}=\text{C})$  1550 s,  $\nu(\text{COC})$  1250 s, 1180  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  3.28 (s, 3 H, Me), 3.55 (s, 3 H, Me), 4.87 (d,  $J = 17$  Hz, 1 H, H<sub>c</sub>), 5.75 (q,  $J_{\text{HP}} = 1.2$  Hz, H<sub>a</sub>), 6.30 (dd,  $J = 17$  Hz, 0.5 Hz, H<sub>b</sub>), 6.80–7.55 (m, 20 H, 4Ph), 7.65–7.95 (m, 10 H, 2Ph). Anal. Calcd for C<sub>45</sub>H<sub>39</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 63.01; H, 4.58. Found: C, 62.54; H, 4.60.

**Ethyl Propiolate Derivative (R = Et, 6).** From the red solution resulting after filtration of the mono-insertion product

**Table II. Final Atomic Coordinates for All Non-Hydrogen Atoms of 7 ( $\times 10^5$  for Ru, P(1), and P(2) and  $\times 10^4$  for the Remaining Atoms)<sup>a</sup>**

atom	x/a	y/b	z/c	B <sub>eq</sub> , Å <sup>2</sup>
Ru	22049 (2)	11374 (3)	27642 (3)	2.47 (2)
P(1)	13413 (5)	23401 (9)	28723 (10)	2.67 (4)
P(2)	30449 (5)	-01184 (9)	25383 (11)	2.87 (5)
C(101)	1286 (2)	2714 (3)	1221 (4)	2.93 (18)
C(102)	1553 (2)	3830 (4)	1228 (5)	4.34 (23)
C(103)	1552 (3)	4061 (5)	-0073 (6)	5.46 (29)
C(104)	1280 (3)	3181 (5)	-1379 (5)	5.33 (29)
C(105)	1021 (2)	2063 (5)	-1401 (5)	4.57 (24)
C(106)	1029 (2)	1817 (4)	-0112 (4)	3.62 (21)
C(111)	0466 (2)	1740 (3)	3033 (4)	2.88 (18)
C(112)	-0093 (2)	1693 (4)	2086 (5)	3.60 (21)
C(113)	-0750 (2)	1320 (4)	2332 (5)	4.26 (23)
C(114)	-0852 (2)	1034 (4)	3557 (6)	4.59 (25)
C(115)	-0308 (3)	1103 (4)	4536 (5)	4.71 (25)
C(116)	0349 (2)	1431 (4)	4259 (5)	4.03 (22)
C(121)	1443 (2)	3768 (3)	4411 (4)	3.10 (19)
C(122)	0949 (2)	4490 (4)	4533 (5)	4.27 (22)
C(123)	0989 (3)	5519 (4)	5758 (6)	5.45 (28)
C(124)	1520 (3)	5836 (4)	6855 (5)	5.26 (27)
C(125)	2019 (3)	5147 (4)	6732 (5)	5.10 (26)
C(126)	1980 (2)	4102 (4)	5497 (4)	3.93 (21)
C(201)	3821 (2)	0597 (4)	3813 (4)	3.33 (19)
C(202)	4308 (2)	1424 (4)	3547 (5)	4.34 (23)
C(203)	4865 (3)	2029 (4)	4598 (7)	5.74 (29)
C(204)	4915 (3)	1837 (5)	5911 (7)	6.52 (32)
C(205)	4439 (3)	1058 (6)	6182 (6)	6.27 (31)
C(206)	3888 (2)	0428 (4)	5145 (5)	4.60 (24)
C(211)	3314 (2)	-0643 (4)	0697 (4)	3.39 (20)
C(212)	3978 (2)	-0680 (5)	0371 (5)	4.88 (25)
C(213)	3605 (3)	-1540 (5)	-2211 (6)	6.26 (31)
C(214)	4114 (3)	-1133 (6)	-1087 (6)	6.76 (32)
C(215)	2941 (3)	-1541 (5)	-1901 (5)	5.82 (28)
C(216)	2790 (2)	-1083 (4)	-0467 (5)	4.24 (22)
C(221)	2843 (2)	-1507 (4)	2893 (5)	3.49 (20)
C(222)	3236 (3)	-2399 (4)	2390 (6)	5.56 (28)
C(223)	3143 (3)	-3406 (5)	2800 (7)	6.96 (35)
C(224)	2645 (3)	-3503 (5)	3707 (7)	6.33 (32)
C(225)	2228 (3)	-2676 (5)	4158 (5)	5.21 (27)
C(226)	2330 (2)	-1674 (4)	3756 (5)	4.34 (23)
O(1)	2406 (1)	1285 (2)	586 (3)	3.30 (13)
O(2)	2839 (2)	2189 (4)	1203 (4)	3.44 (21)
O(21)	3192 (2)	2773 (3)	0477 (3)	5.08 (17)
O(22)	3028 (3)	2329 (5)	-1116 (5)	6.90 (32)
C(3)	2956 (2)	2562 (4)	2811 (4)	3.06 (19)
C(4)	3443 (2)	3498 (4)	3569 (5)	3.64 (20)
C(5)	3640 (2)	3873 (4)	5132 (5)	3.82 (21)
C(6)	4108 (2)	4838 (4)	5871 (5)	4.77 (24)
C(7)	-4309 (3)	-5185 (5)	2547 (6)	5.48 (28)
O(7)	4059 (2)	-4711 (4)	1752 (4)	8.95 (27)
O(8)	-4805 (2)	-6130 (3)	2072 (4)	6.62 (20)
C(9)	-5042 (3)	-6546 (6)	0511 (7)	8.81 (39)
C(11)	2169 (2)	1259 (4)	4668 (4)	3.29 (19)
O(11)	2146 (2)	1328 (3)	5869 (3)	5.25 (17)
C(12)	1477 (2)	-0381 (4)	1966 (4)	2.96 (18)
C(13)	1100 (2)	-1324 (4)	1518 (4)	3.54 (21)
C(14)	0762 (2)	-2542 (4)	1095 (5)	3.65 (21)
O(15)	0585 (2)	-2786 (3)	2277 (3)	4.82 (16)
O(16)	0658 (2)	-3262 (3)	-0125 (4)	6.53 (20)
C(17)	0274 (3)	-3987 (5)	2029 (6)	6.31 (31)

$$^a B_{\text{eq}} = 8\pi^2/3 \sum (U_{ij} a_i^* a_j^* a_i a_j) \cos(a_i a_j).$$

2, 6 can be isolated by addition of MeOH, concentration, and precipitation with petroleum ether. The red powder can be crystallized in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (yield 10%). IR:  $\nu(\text{C}=\text{O})$  1935 vs,  $\nu(\text{C}=\text{O})$  1670 vs, 1620 sh,  $\nu(\text{C}=\text{C})$  1530 m,  $\nu(\text{COC})$  1255 m, 1200  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  0.92 (t, 3 H, Me), 1.19 (t, 3 H, Me), 3.74 (q, 2 H, CH<sub>2</sub>), 4.01 (q, 2 H, CH<sub>2</sub>), 4.80 (d,  $J = 16$  Hz, 1 H, H<sub>c</sub>), 5.74 (q,  $J = 1.2$  Hz, H<sub>a</sub>), 6.20 (dd,  $J = 16$  Hz, 0.5 Hz, 1 H, H<sub>b</sub>). Anal. Calcd for C<sub>47</sub>H<sub>43</sub>ClO<sub>5</sub>P<sub>2</sub>Ru: C, 63.73; H, 4.89. Found: C, 63.20; H, 4.91.

**[(CO)(PPh<sub>3</sub>)<sub>2</sub>(RCOC≡C)Ru[RC(O)C=CHCH=CHCOR]] (Type III Complexes 7–9).** **Methyl Propiolate Derivative (R = Me, 7).** To a solution of 0.3 g (0.315 mmol) of Ru(CO)ClH-

(12) Ahmed, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F.; *Inorg. Synth.* 1974, 15, 48.

(PPh<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added an excess of MeO<sub>2</sub>C≡CH. After 5–10 min of stirring, the green solution was concentrated, chromatographed in a short column packed with silica gel, and eluted with 1:1 ethyl acetate/hexane. The green compound 1 remains retained in the silica column. The yellow eluate was concentrated to dryness and the solid dissolved in CH<sub>2</sub>Cl<sub>2</sub> and precipitated with petroleum ether. The yellow precipitate was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH (yield 50–60%). IR:  $\nu(\text{C}\equiv\text{C})$  2100 s,  $\nu(\text{C}\equiv\text{O})$  1932 vs,  $\nu(\text{C}=\text{O})$  1720 s, 1685 s, 1576 vs,  $\nu(\text{C}=\text{C})$  1618 m, 1565 sh;  $\nu(\text{COC})$  1260 m, 1210 s, 1195 sh cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.93 (s, 3 H, Me), 3.43 (s, 3 H, Me), 3.78 (s, 3 H, Me), 5.68 (d,  $J = 16$  Hz, 1 H, H<sub>c</sub>), 6.89 (d,  $J = 16$  Hz, 1 H, H<sub>b</sub>), 7.00 (s, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>49</sub>H<sub>42</sub>O<sub>7</sub>P<sub>2</sub>Ru: C, 64.97; H, 4.67. Found: C, 64.02; H, 4.28.

An alternative preparation, with a slightly lower yield (ca. 50%), uses the yellow solution resulting after filtration of 1, previously precipitated with Et<sub>2</sub>O, in the synthesis of the compounds 1–5 described above.

**Ethyl Propiolate Derivative (R = EtO, 8).** To a solution of 0.3 g (0.315 mmol) of Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>/MeOH 1:1 (30 mL) was added an excess of EtO<sub>2</sub>C≡CH, and the solution was stirred for 1 h and then concentrated to dryness. By extraction with petroleum ether a yellow solution was obtained from which a yellow crystalline solid was formed by concentration (yield 10%). IR:  $\nu(\text{C}\equiv\text{C})$  2100 s,  $\nu(\text{C}\equiv\text{O})$  1935 vs,  $\nu(\text{C}=\text{O})$  1710 s, 1686 s, 1575 s,  $\nu(\text{C}=\text{C})$  1620 m, 1560 s;  $\nu(\text{COC})$  1250 m, 1200 s cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.89, 1.08, 1.25 (t, 3 H, Me), 3.40, 3.78, 4.21 (q, 2 H, CH<sub>2</sub>), 5.66 (d,  $J = 16$  Hz, 1 H, H<sub>c</sub>), 6.88 (d,  $J = 16$  Hz, 1 H, H<sub>b</sub>), 6.95 (s, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>52</sub>H<sub>48</sub>O<sub>7</sub>P<sub>2</sub>Ru: C, 65.89; H, 5.10. Found: C, 65.51; H, 4.89.

**3-Butyn-2-one Derivative (R = Me, 9).** From the orange solution remaining after filtration of the mono-insertion product 3 an orange precipitate was obtained by concentration and precipitation with petroleum ether or hexane (yield 30%). IR:  $\nu(\text{C}\equiv\text{C})$  2080 m,  $\nu(\text{C}\equiv\text{O})$  1930 vs,  $\nu(\text{C}=\text{O})$  1665 s, 1640 s, 1590 s;  $\nu(\text{C}=\text{C})$  1533 s cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  1.54, 1.65, 1.73 (s, 3 H, Me), 5.03 (d,  $J = 16$  Hz, 1 H, H<sub>c</sub>), 6.23 (d,  $J = 16$  Hz, 1 H, H<sub>b</sub>), 6.31 (s, 1 H, H<sub>a</sub>). Anal. Calcd for C<sub>49</sub>H<sub>42</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 68.60; H, 4.93. Found: C, 68.08; H, 4.96.

**Crystal Data.** C<sub>49</sub>H<sub>42</sub>O<sub>7</sub>P<sub>2</sub>Ru: fw = 907.9, triclinic,  $a = 19.943$  (2) Å,  $b = 12.118$  (2) Å,  $c = 9.747$  (1) Å,  $\alpha = 110.05$  (1)°,  $\beta = 93.34$  (1)°,  $\gamma = 97.78$  (1)°,  $V = 2178.5$  (8) Å<sup>3</sup>,  $P\bar{1}$ ,  $d = 1.384$  g cm<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 936$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo K}\alpha) = 4.80$  cm<sup>-1</sup>,  $T = 288$  K.

**X-ray Data Collection and Structure Determination.** A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ( $4^\circ < \theta < 12^\circ$ ) and refined by least squares. Intensities were collected with graphite-monochromatized Mo K $\alpha$  radiation, by using the  $\omega$ -scan

technique (scan width 0.8°, scan speed 0.03° s<sup>-1</sup>). A total of 4968 independent reflections were measured in the range  $2^\circ < \theta < 25^\circ$ , 4907 of which were assumed to be observed by applying the condition  $I > 2.5\sigma(I)$ . Three intensities were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization, but no absorption, corrections were made.

The Ru atom was located from a Patterson synthesis, and the remaining non-hydrogen atoms were located by using the DIRDIF system of computer programs.<sup>13</sup> The structure was isotropically and anisotropically refined by the full-matrix least-squares method, using the SHELX76 computer program.<sup>14</sup> The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = (\sigma^2|F_o| + 0.00039|F_o|^2)^{-1}$ .  $f$ ,  $f'$ , and  $f''$  were taken from ref 15. A total of 41 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The remaining atoms were refined anisotropically. The final  $R = \sum||F_o| - |F_c|| / \sum|F_o| = 0.035$  for all observed reflections, the  $R_w = \sum w||F_o| - |F_c|| / \sum w|F_o|$  being 0.076. A final  $\Delta F$  synthesis showed a maximum peak of  $0.3 \text{ e \AA}^{-3}$  at  $1.27 \text{ \AA}$  from C(225) and a minimum value of  $\rho = -0.4 \text{ e \AA}^{-3}$ .

Final coordinates for all non-hydrogen atoms of 7 are given in Table II.

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**Registry No.** 1, 106904-72-7; 2, 106904-73-8; 3, 106904-74-9; 4, 106904-75-0; 5, 106904-76-1; 6, 106904-77-2; 7, 106904-78-3; 8, 106904-79-4; 9, 106904-80-7; Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>, 16971-33-8; HC≡CCO<sub>2</sub>Me, 922-67-8; HC≡CCO<sub>2</sub>Et, 623-47-2; HC≡CCOCH<sub>3</sub>, 1423-60-5; MeOC≡CCO<sub>2</sub>Me, 762-42-5.

**Supplementary Material Available:** Listing of anisotropic thermal parameters, fractional coordinates for hydrogen atoms, supplementary distances, and supplementary angles (6 pages); a listing of observed and calculated structure factors a listing of (19 pages). Ordering information is given on any current masthead page.

(13) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van den Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Hiltiwanger, R. C. Technical Report 1983/1, 1983; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands.

(14) Sheldrick, G. M. *SHELX76 Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(15) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974.