Activation of 2-Propyn-1-ol Derivatives by (Arene)ruthenium(II) Complexes: New Route to (Alkenylcarbene)- and (Polyenylcarbene)metal Complexes

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Reactions of the (arene)ruthenium(II) complexes (η^6-arene)(PMe_3)$RuCl_2$ (arene = C_6Me_6 (1), $C_6Me_4H_2$ (1′)) with disubstituted HC≡CC(R)(R′)OH (R, R′ = Me, Me (**a**), cyclohexyl (**b**), Ph, Ph (**c**)) or monosubstituted 2-propyn-1-ols HC≡CC(R)(H)OH (R = Me (**d**), Ph (**e**), 2-thienyl (**f**)), in methanol containing $NaPF_6$, lead to the cationic methoxyalkenylcarbene complexes [(η^6-arene)(PMe_3)(Cl)Ru=C(OMe)(CH=CRR′)]PF_6 (**2**, **2′**, R′ ≠ H; **3**, **3′**, R′ = H) in ca. 70% yield. Difference ^1H NOE experiments establish an s-cis conformation for ((monosubstituted alkenyl)carbene)ruthenium moieties (**3**, **3′**) and an s-trans conformation in (disubstituted alkenyl)carbene complexes **2** and **2′**. A crystal structure of [(η^6-C_6Me_6)(PMe_3)(Cl)Ru=C(OMe)(CH=CPh_2)]PF_6 (**2c**) has been determined by X-ray diffraction. It shows an s-trans conformation for the methoxy(diphenylalkenyl)carbene moiety. Crystal data are as follows: monoclinic, $P2_1/n$, with a = 9.826 (2) Å, b = 15.659 (1) Å, c = 21.552 (2) Å, β = 92.89 (1)°, V = 3312.0 (6) Å^3, Z = 4, R = 6.9%, R_w = 7.2%. Treatments of **1** and **1′** with HC≡CC(CH=CHR)(H)OH (R = Ph (**g**), Me (**h**)) and HC≡CC(CH=CHCH=CHMe)(H)OH (**i**) produce dienylcarbene (**4g**, **4′h**) and trienylcarbene (**5i**, **5′i**) ruthenium complexes in 70–90% yield. Reaction of **1** with HC≡CCH_2OH in methanol gives a double addition of MeOH and generates [(η^6-C_6Me_6)(PMe_3)(Cl)Ru=C(OMe)(CH_2CH_2OMe)]PF_6 (**7**). Methoxyalkenylcarbene complexes **2–5** and **2′–5′** are formed via allenylidene intermediates [(η^6-C_6Me_6)(L)(Cl)Ru=C=C=CPh_2]PF_6 that have been trapped during the reaction of (η^6-C_6Me_6)(L)$RuCl_2$ (L = PMe_3 (**1**), PPh_3 (**8**)) with HC≡$CCPh_2OH$ (**c**) in methanol (**9c**, **10c**). The (allenylidene)ruthenium intermediate can be stabilized by the introduction of a ferrocenyl group at C^3: reaction between HC≡CC(Ph)(Fc)OH (**j**) and **1** in methanol only leads to the stable complex [(η^6-C_6Me_6)(PMe_3)(Cl)Ru=C=C=C(Ph)(Fc)]PF_6 (**11j**).

Introduction

During the last decade, (alkenylcarbene)metal complexes have been shown to be of interest for both organic and organometallic syntheses. They undergo useful transformations such as Diels–Alder reactions,[1] cyclohexadienone annulations,[2] cyclopropanations,[3] and formation of bimetallic complexes.[4] They are also key intermediates in the polymerization of alkynes[5] and formation of living polyenes.[6] The polymerization of a (vinylcarbene)tungsten complex to organometallic polymers has also been recently described.[7] Most of this chemistry concerns the Fischer-type alkenylcarbene complexes of group 6 transition-metal carbonyls. They are typically prepared by the Fischer method via addition of an alkenyllithium species to $M(CO)_6$ followed by alkylation[1a,8] or by an aldol condensation with deprotonated methoxyalkylcarbenes of the type [$(CO)_5M$=C(OMe)(CH_2R)].[9] Another method deals with the reaction between $M(CO)_5^{2-}$ and acyl chloride followed by alkylation.[10] On the other hand, to our knowledge, no general route to alkenylcarbene complexes that do not contain any CO ligands has been reported. This paper presents a new strategy to build alkenylcarbene complexes, in one step, by activation of 2-propyn-1-ol derivatives with (arene)ruthenium(II) complexes which do not contain carbonyl ligands. Moreover, the propyn-1-ol derivatives, which are readily available from unsaturated aldehydes,[11] offer a unique access to (polyenylcarbene)-metal complexes.

We have recently reported that [(η^6-C_6Me_6)$RuCl_2$(PR_3)] compounds very efficiently produce (alkoxyalkylcarbene)ruthenium complexes by activation of 1-alkynes in alcohols, via highly reactive vinylidene intermediates.[12] On the other hand, (arene)ruthenium(II) complexes have been shown to be remarkable catalyst precursors for the addition of ammonium carbamates or carboxylic acids to 2-propyn-1-ols.[13] These results led us to investigate the stoichiometric activation of 2-propyn-1-ol derivatives with [(η^6-arene)$RuCl_2$(PMe_3)] (arene = hexamethylbenzene, tetramethylbenzene). Here we describe the full details of this work and we show (i) that (arene)ruthenium(II) complexes readily promote the dehydration of 2-propyn-1-ols

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Table I. Selected NMR Data for Methoxyalkenylcarbene Compounds[a]

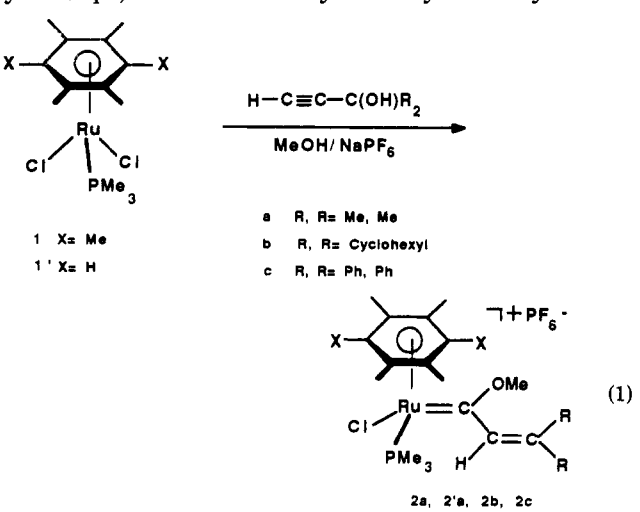
compd no.	$\delta(^{31}P)$, ppm PMe_3	$\delta(^{13}C$ and $^1H)$, ppm Ru=C ($^2J_{PC}$, Hz)	C^2 H^2	C^3 H^3	C^4 H^4	C^5 H^5	C^6 H^6	C^7 H^7
2a	7.71	306.89 (18.8)	138.73	149.37				
			6.68					
2'a	7.65	–	–					
			6.54					
2b	7.35	310.15 (22.4)	134.74	155.93				
			6.54					
2c	5.23	304.24 (18.7)	136.43	147.70				
			7.50					
3d	12.00	305.77 (20.6)	134.36	171.34				
			6.78	7.80				
3'd	13.33	303.74 (19.7)	136.17	173.17				
			6.82	7.91				
3e	12.18	302.56 (20.3)	126.56	168.23				
			7.32	8.46				
3'f	13.71	298.40 (20.6)	128.85	161.81				
			7.26	8.59				
4g	12.16	299.00 (21.2)	128.54	168.80	129.87	150.10		
			6.88	8.28	7.24	7.40		
4'h	13.43	298.31 (18.8)	130.82	170.65	132.86	152.67		
			6.76	8.20	6.60	6.84		
5i	11.89	297.34 (21.0)	128.41	170.60	130.25	151.66	132.34	143.71
			6.69	8.13	6.55	7.05	6.35	
5'i	13.37	295.02 (19.7)	130.18	170.82	130.98	151.81	132.32	143.86
			6.81	8.28	6.58	7.11	6.35	

[a] All spectra in CD_2Cl_2 at 297 K.

to give (alkenylcarbene)ruthenium derivatives and (ii) that these reactions occur via allenylidene intermediates, which have been isolated and characterized in several cases. Preliminary accounts of part of this work have been published.[14,15]

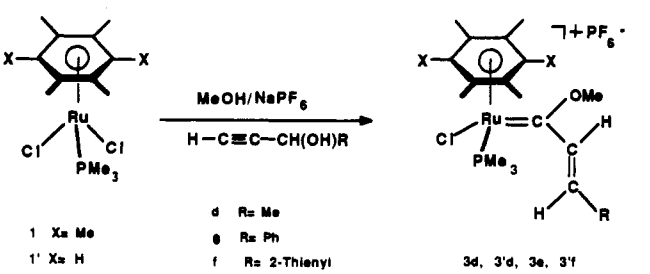
Results and Discussion

1. Synthesis of (Methoxyalkenylcarbene)ruthenium Complexes. (Hexamethylbenzene)- and (tetramethylbenzene)ruthenium dichloride trimethylphosphine complexes **1** and **1'** readily reacted (10 min to 2 h) with *disubstituted* propyn-1-ols **a** and **b** in methanol at room temperature, in the presence of 1 equiv of $NaPF_6$, to give (methoxyalkenylcarbene)ruthenium complexes **2a,b** and **2'a** in 70–75% yield. The synthesis of **2c** (R = Ph) from diphenylpropargyl alcohol (**c**) took more time: a deep purple solution rapidly appeared (15 min) and then slowly turned red (24 h), from which **2c** was obtained in 74% yield (eq 1). In a similar way a variety of alkenylcarbene



(1)

complexes **3d,e** and **3'd-f**, containing a hydrogen atom at C^3, was rapidly formed and isolated in good yield (70%) from *monosubstituted* propargyl alcohols **d–f** (eq 2).



(2)

These new carbene complexes were characterized on the basis of their elemental analyses and ^1H, ^{31}P, and ^{13}C NMR spectroscopy (Table I). The $^{31}P\{^1H\}$ NMR spectra show a single line between 5 and 8 ppm for disubstituted alkenylidene complexes **2** and **2'** and between 12 and 14 ppm for monosubstituted complexes **3** and **3'**. For complexes **3** and **3'** only the *E* isomers were produced, as determined by observing the strong vicinal coupling constants ($^3J_{HH} \approx 15$ Hz). The ^{13}C NMR spectra of **2** and **3** were diagnostic of the presence of the carbene ligands with low-field doublets found at 302–310 ppm, corresponding to the resonance of the metal-bonded (carbene) carbon nucleus coupled with the ^{31}P nucleus of the phosphorus ligand ($^2J_{PC} \approx 20$ Hz). Only the complex **3'f** showed a higher field ^{13}C NMR resonance for the carbene carbon atom (δ 298 ppm). A conjugation between the alkenylcarbene moiety and the thienyl substituent explains this shielding.

The conformation of the ruthenium alkenylidene moiety in **2**, **2'**, **3**, and **3'** was established by difference NOE experiments (Chart I). The methoxy ^1H NMR resonance

Chart I

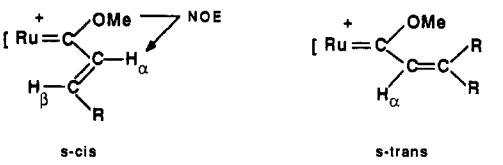


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Table II. Experimental Crystallographic Data for 2c

formula	$C_{31}H_{41}ClF_6OP_2Ru$
fw	742.13
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.826 (2)
b, Å	15.659 (1)
c, Å	21.552 (2)
β, deg	92.89 (1)
V, Å^3	3312.0 (6)
Z	4
d_{calc}, Mg m^{-3}	1.488
cryst size, mm	0.25 × 0.20 × 0.20
$2\theta_{max}$, deg	50
diffractometer	CAD-4
λ(Mo Kα radiation), Å	0.71069
T, K	291
F(000)	1520
abs coeff μ, cm^{-1}	7.0
scan type	$\omega/2\theta$
no. of rflns read	4679
no. of unique rflns	2527 ($I > 3\sigma(I)$)
R; R_w	0.069; 0.072

Table III. Selected Bond Distances (Å) for 2c

Ru–C(1)	1.98 (1)	C(1)–C(2)	1.47 (2)
Ru–Cl	2.418 (4)	C(1)–O	1.30 (2)
Ru–P	2.339 (4)	C(2)–C(3)	1.34 (2)
Ru–C(31)	2.25 (1)	O–C(5)	1.44 (2)
Ru–C(32)	2.25 (1)	C(3)–C(11)	1.49 (2)
Ru–C(33)	2.29 (1)	C(3)–C(21)	1.53 (2)
Ru–C(34)	2.29 (1)	P–C(6)	1.83 (6)
Ru–C(35)	2.32 (1)	P–C(7)	1.85 (2)
Ru–C(36)	2.33 (1)	P–C(8)	1.83 (1)

Table IV. Selected Bond Angles (deg) for 2c

C(1)–Ru–Cl	88.8 (4)	C(1)–Ru–P	92.6 (4)
Cl–Ru–P	81.8 (2)	Ru–C(1)–O	129.0 (1)
Ru–C(1)–C(2)	119.0 (1)	O–C(1)–C(2)	111.0 (1)
C(1)–O–C(5)	125.0 (1)	C(1)–C(2)–C(3)	126.0 (1)
C(2)–C(3)–C(11)	121.0 (1)	C(2)–C(3)–C(21)	123.0 (1)
C(11)–C(3)–C(21)	116.0 (2)	Ru–P–C(6)	110.5 (6)
Ru–P–C(7)	114.5 (6)	Ru–P–C(8)	122.7 (6)

of **3d** and **3e** was irradiated. A strong enhancement was observed in the HC^2 resonance (**3d**, 17%; **3e**, 14%) but none in the HC^3 resonance. Thus, an s-cis conformation was found for monosubstituted alkenylcarbene compounds **3** and **3′**, where the HC^2 protons are much closer to the methoxy group than those of HC^3. On the other hand, an analogous NOE experiment was conducted with (disubstituted alkenyl)carbene complexes **2a** and **2c**. No enhancement in the HC^2 proton resonance was observed, which is suggestive of an s-trans conformation. The alternative s-cis conformation may be disfavored in this case because of steric interaction of the R groups with the phosphine ligand.

2. X-ray Crystal Structure of [(C_6Me_6)(PMe_3)(Cl)Ru=C(OMe)CH=CPh_2]PF_6 (2c). Crystals of **2c** were grown by slow diffusion of hexane into a dichloromethane solution, and X-ray data were collected as summarized in Table II. The geometry about the ruthenium(II) center is nearly octahedral, with the arene ring occupying one face of the octahedron and the alkenylidene, the PMe_3, and the chloride ligands occupying the opposite face (Figure 1). Selected bond lengths and angles are listed in Tables III and IV.

The most interesting features of this structure are in the ruthenium alkenylidene moiety. It is noteworthy that **2c** also exhibits the s-trans conformation in the crystalline form, as it does in solution. The C(1)–C(2)–C(3) (126 (1)°), C(2)–C(3)–C(11) (121 (1)°), and C(2)–C(3)–C(21) (123 (1)°) angles are typical of C(sp^2) atoms. The Ru–C(1) distance

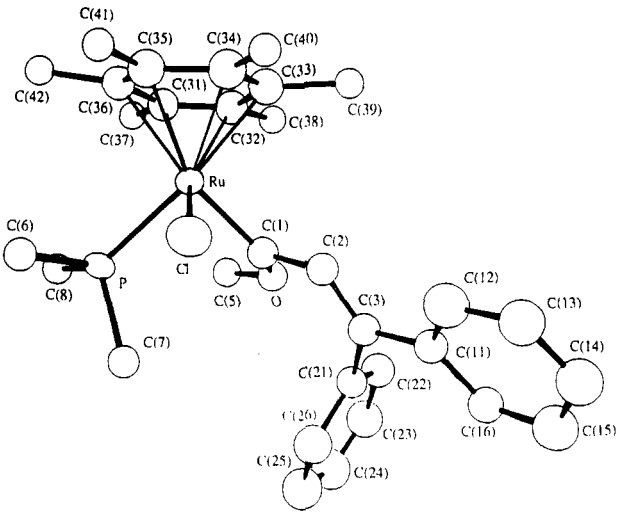
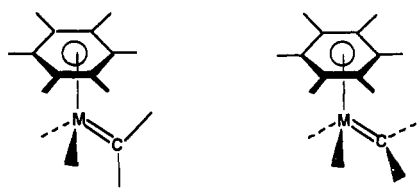


Figure 1. ORTEP diagram for [(C_6Me_6)(PMe_3)(Cl)Ru=C(OMe)CH=CPh_2]PF_6 (**2c**).

(1.98 (1) Å) is slightly longer than the ruthenium–carbon bond distance found in [Cp($Ph_2PCH(CH_3)CH_2PPh_2$)Ru=C(OMe)CH_2Ph]PF_6[16] (1.93 (2) Å). The C(1)–O distance (1.30 (2) Å) is within the range for other methoxyalkylcarbene complexes.[17] The C(1)–C(2) and C(2)–C(3) bond lengths, respectively 1.47 (2) and 1.34 (2) Å, are characteristic of a C(sp^2)–C(sp^2) single-bond (1.48 Å) and C(sp^2)–C(sp^2) double-bond (1.34 Å) distances. It can also be pointed out that in contrast to most of the structurally resolved (η^5-cyclopentadienyl)metal carbene complexes that adopt an "upright" orientation (I), the (η^6-hexamethylbenzene)ruthenium carbene **2c** adopts the alternative lateral orientation (II).



I II

On the other hand, a lateral conformation (II) was also found in crystalline (η^6-C_6H_6)$(CO)_2$Cr=C(OEt)Ph.[18] MO calculations have indicated that the upright orientation is favored in cyclopentadienylmetal carbene complexes (Mn(I), Fe(II))[19] whereas the other conformation is preferred for the (benzene)(carbene)chromium(0) complex.[20] In complex **2c**, however, it seems that the steric interaction of the bulky diphenylalkenyl substituent determines the horizontal conformation found in the solid state.

3. Synthesis of (Methoxydienylcarbene)- and (Methoxytrienylcarbene)ruthenium Complexes. The simple and general formation of alkenylcarbenes **3** and **3′** from the alcohols HC≡CC(R)(H)OH actually offers a straightforward transformation of an aldehyde (III) into an alkenylcarbene (IV), via the addition of LiC≡CH to

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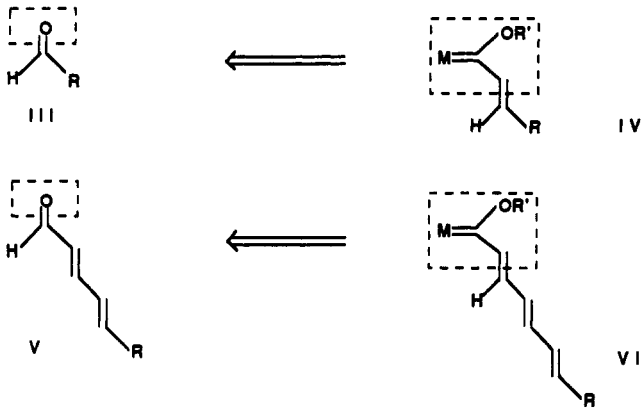
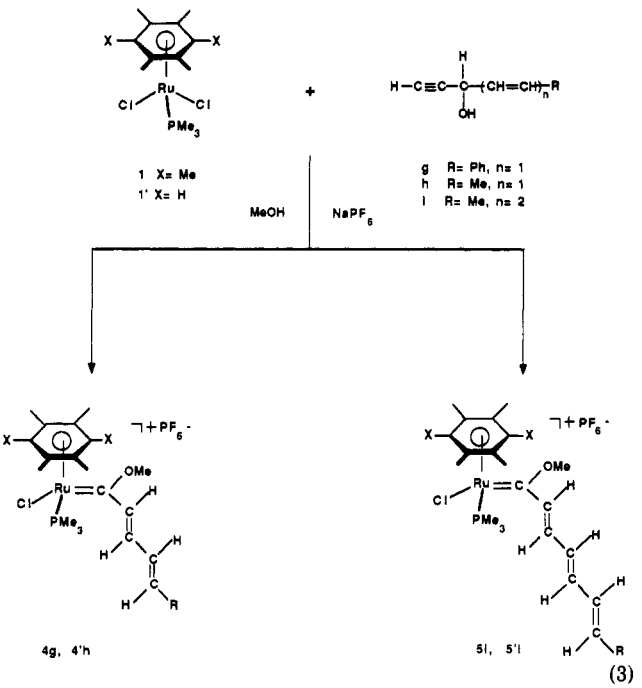
III. The absence of a direct route to polyenylcarbene derivatives of type VI motivated our attempts to demonstrate that unsaturated aldehydes such as V could be the key substrates to VI.



The 1-(styryl)propyn-1-ol (**g**), 1-(propenyl)propyn-1-ol (**h**), and 1-(penta-1,3-dienyl)propyn-1-ol (**i**) derivatives were prepared by addition of LiC≡CH to the corresponding unsaturated aldehydes.[11] Treatment of complexes **1** and **1′** with **g** and **h** in methanol gave more slowly the dienylcarbene complexes **4g** and **4′h** in ca. 70% yield (eq 3). **4g** and **4′h** are air-stable greenish black crystalline



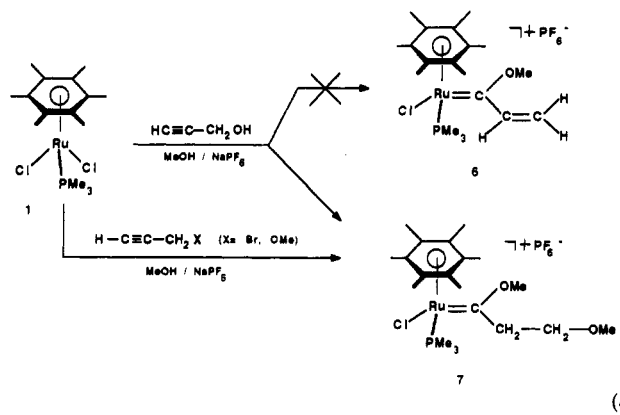
(3)

solids. The reaction of **1** and **1′** with **i** was also very slow: after 18 h at room temperature, the black octatrienylcarbene complexes **5i** and **5′i** were obtained in excellent yield (90%; eq 3). The IR spectra of these new unsaturated carbene complexes contained in the 1600-cm^{-1} region respectively two medium-intensity absorptions (for **4** and **4′**) and three medium-intensity absorptions (for **5** and **5′**), assigned to $\nu_{C=C}$ of the dienyl and trienyl substituents. The $^{31}P\{^1H\}$ NMR spectra showed, as for the monosubstituted alkenylidene complexes **3** and **3′**, a single line between 12 and 14 ppm. The ^1H spectra of **4**, **4′**, **5**, and **5′** revealed between 8.3 and 6.3 ppm several multiplets attributed to the olefinic hydrogens. These were easily assigned according to their coupling constants and ^1H–^1H decoupling experiments (Table I). As an example, the ^1H NMR spectrum of the trienylidene ligand in **5i** consisted of five multiplets at δ 8.13 (dd, H^3), 7.05 (dd, H^5), 6.69 (d, H^2), 6.55 (dd, H^4), and 6.35 (m, H^6 and H^7). $^3J_{HH}$ values across double bonds were found to be 14–15 Hz and those across single bonds 9–11 Hz. These coupling constants are typical of an all-trans geometry for the butadienyl and pentatrienyl ligands in **4**, **4′**, **5**, and **5′**.

Difference NOE experiments were conducted with complexes **4g** and **5i**. Irradiation of the methoxy protons led to a strong enhancement of the vinyl HC^2 signal (**4i**, 16%; **5g**, 21%) and no enhancement of the HC^3 signal, consistent with the s-cis conformation of the ruthenium vinylcarbene moiety in **4**, **4′**, **5**, and **5′** (Chart I).

The $^{13}C\{^1H\}$ NMR spectra showed characteristic doublet resonances in the region δ 295–299 ppm, due to the carbenic carbons of the di- and trienylidene ligands (Table I). As expected, these shifts were found at higher field than those observed for the alkenylidene complexes **2**, **2′**, **3**, and **3′** (δ 303–310 ppm), consistent with increased electron density at the carbene carbon atoms. The $^{13}C\{^1H\}$ spectra also exhibited singlets in the spectral region 125–170 ppm, corresponding to the olefinic carbon resonances of the di- and trienyl substituents. Their correct attributions were made possible by using a heteronuclear ^{13}C–^1H correlation (HETCOR) experiment on trienylcarbene **5i** as shown in Figure 2. By analogy the assignments of the olefinic carbon atoms for the other complexes were easily deduced (Table I).

4. Synthesis of a (Methoxy(methoxyethyl)carbene)ruthenium Complex. The reaction of **1** with 2-propyn-1-ol, $HC{\equiv}CCH_2OH$, in methanol was investigated in order to prepare the vinylcarbene **6**. Surprisingly, under the same conditions employed for the synthesis of the alkenylcarbene complexes **2** and **3**, the red methoxy(methoxyethyl)carbene complex **7** was obtained in 74% yield (eq 4). This new compound formally resulted from

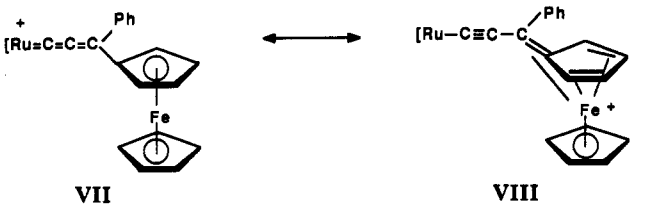


(4)

the dehydration of the coordinated propargyl alcohol and the double addition of methanol. **7** was also produced in ca. 70% yield by reacting **1** in *methanol* with either methyl propargyl ether or propargyl bromide (eq 4). Complex **7** exhibited in its ^{13}C NMR spectrum a doublet at δ 326 ppm characteristic of the carbene carbon resonance. This shift was 25–30 ppm downfield from those of the previous alkenylcarbene ligands but was similar to those found in (alkoxyalkylcarbene)ruthenium complexes (δ ~320–330 ppm).[12]

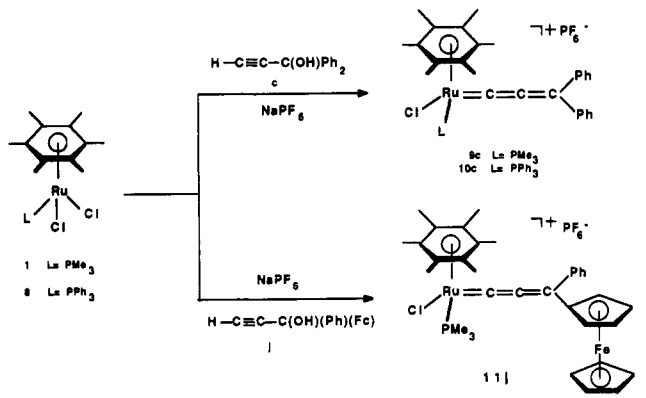
5. Synthesis of (Allenylidene)ruthenium Complexes. As mentioned before, the reaction of **1** with 1,1-diphenyl-2-propyn-1-ol (**c**) in methanol was slow and revealed the formation of a violet intermediate. When the reaction was quenched by addition of ether and the mixture was stirred for 20 min at room temperature, a violet precipitate was isolated in 69% yield and identified by IR

Scheme I



VII VIII

and ^1H NMR spectroscopy to be the (diphenylallenylidene)ruthenium complex **9c** (eq 5). **9c** was rather



(5)

unstable in solution, preventing its full spectroscopic characterization. The use of $Ru(\eta^6\text{-}C_6Me_6)(PPh_3)Cl_2$ (**8**), which contains the more bulky triphenylphosphine ligand, led to the isolation of the more stable (diphenylallenylidene)ruthenium species **10c** in 81% yield (eq 5). An analogous ruthenium diphenylallenylidene moiety was previously obtained by Selegue from the reaction of the isoelectronic derivative $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl$ and **c** in ethanol without any addition of alcohol and formation of the (alkenylcarbene)ruthenium complexes.[21] The allenylidene ligand in **9c** and **10c** was characterized by a strong $\nu_{C=C=C}$ band at ca. 1950 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum of **10c** contained three resonances at δ 288.3 (d), 191.0 (s), and 167.0 (s) corresponding respectively to the C^1 (carbene), C^2, and C^3 chemical shifts of the diphenylallenylidene ligand. These data were comparable to those of the same ligand in the isoelectronic cyclopentadienyl complex (C^1, δ 295.8; C^2, δ 216.0; C^3, δ 153.8).[21]

In order to study the influence of an electron-donor substituent at C^3, such as the ferrocenyl (Fc) group, on the stability of the ruthenium allenylidene moiety, the reaction between **1** and the alkyne $HC{\equiv}CC(C_5H_4FeC_5H_5)(Ph)OH$ (**j**) in methanol was carried out. The violet ferrocenylphenylallenylidene complex **11j** was isolated in 45% yield after 2 h at room temperature (eq 5). No formation of the corresponding (alkenylcarbene)ruthenium complex was observed, even after the reaction mixture was stirred at room temperature for several days. For **11j** the IR $\nu_{C=C=C}$ frequency was found at 1965 cm^{-1} and the ^{13}C NMR C^1, C^2, and C^3 resonances were observed at δ 243, 170, and 155 ppm, respectively. Comparison with those resonances found in **10c** showed a substantial shielding of C^1 (45 ppm) and of C^2 (21 ppm) and, to a lesser extent, of C^3 (12 ppm). Undoubtedly, these data suggest an important contribution of the mesomeric acetylide structure VIII (Scheme I), which might account for the stabilization of the ruthenium allenylidene moiety in **11j**. This acetylide structure explains the nonaddition of methanol to the C^1 center by replacement of a phenyl substituent (of **9c**) by the electron-releasing ferrocenyl substituent at C^3.

6. Mechanism. For the formation of (alkenylcarbene)ruthenium complexes from 2-propyn-1-ols, taking into account the isolation of (diphenylallenylidene)ruthenium intermediates **9c** and **10c**, we can propose the mechanism illustrated in Scheme II: initial displacement of a chloride ligand in methanol, in the presence of $NaPF_6$, coordination of the alkyne, and tautomerization to give the η^1-hydroxyvinylidene intermediate A, which readily dehydrates to allenylidene B. This mechanism has already been proposed by Selegue to explain the formation of $[(C_5H_5)(PMe_3)Ru{=}C{=}C{=}CPh_2]PF_6$.[21,22]

We have also recently shown that 1-alkynes can be activated by (hexamethylbenzene)ruthenium(II) derivatives, such as **1**, in alcohols to give alkoxyalkylcarbene complexes via highly reactive vinylidene intermediates.[12] By analogy the last step leading to the alkenylcarbene complexes is likely to be the nucleophilic attack of methanol on the electrophilic C^1 carbon of the allenylidene ligand. This addition can be inhibited when R and R′ are phenyl and ferrocenyl substituents, which contribute to delocalize the positive charge between the ruthenium center and R (or R′) and thus to stabilize the allenylidene ligand. If diphenylallenylidene complexes **9c** and **10c** slowly add methanol, the isoelectronic cyclopentadienyl complex seems to be indefinitely stable in ethanol:[21] we have already observed a similar variation of reactivity between the cyclopentadienyl- and the (arene)ruthenium series for the nucleophilic addition of methanol to vinylideneruthenium species.[12] This variation can be explained by the highest electron deficiency of the $[(arene)Ru(PR_3)(Cl)]^+$ vs the $[(C_5H_5)Ru(PR_3)_2]^+$ fragments. A decreasing of the electron density at the ruthenium center in (arene)ruthenium allenylidene species must increase the electrophilicity of the allenylidene ligand and especially that of the C^1 carbon.

The formation of the methoxy(methoxyethyl)carbene complex **7**, from $HC{\equiv}CCH_2OH$ and **1** in methanol, is likely to occur via a double addition of methanol to allenylidene B. MO calculations on a manganese allenylidene complex revealed that not only C^1 but also C^3 is an electrophilic center, whereas C^2 is a nucleophilic site.[23] Moreover, several examples of nucleophilic addition of phosphines or amines to the C^3 carbon have been published.[23,24] Methanol addition to the C^3 carbon of $[Ru^+{=}C{=}C{=}CH_2]$ (B), which does not contain any bulky and/or donor R substituent, may occur to afford the methoxyvinylidene intermediate D. D could also be formed during the reaction between **1** and methyl propargyl ether. The last step is expected[12] to be the rapid nucleophilic addition of methanol at the electrophilic C^1 carbon of the methoxyvinylidene ligand.

Summary

The present results offer an easy synthetic route to new (alkenylcarbene), (dienylcarbene), and (trienylcarbene)-

(21) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(22) Another type of dehydration of hydroxyvinylidenes of type A to give vinylvinylidene complexes have been recently reported. It only occurs from reaction of $CpRu(PMe_3)_2Cl$ with 2-propyn-1-ol derivatives, when hydrogen atoms are adjacent to the hydroxy group such as in 1-ethynylcyclohexanol (**b**); see: Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

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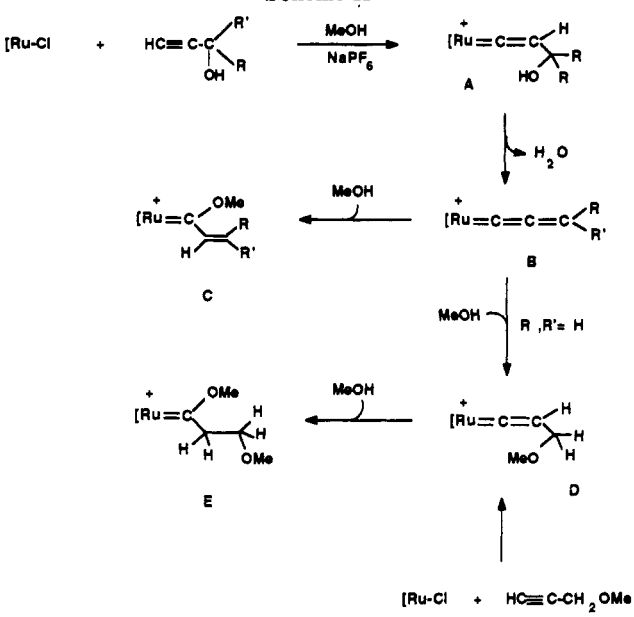
Scheme II



ruthenium complexes, by direct activation of readily available 2-propyn-1-ol derivatives with (arene)ruthenium(II) complexes. With the exception of 2-propyn-1-ol, $HC{\equiv}CCH_2OH$, which leads to a methoxy(methoxyethyl)carbene complex, the reaction appears to be quite general. It occurs via the intermediacy of allenylideneruthenium complexes which can be stabilized by introduction of bulky and donor substituents at C^3, such as a ferrocenyl (Fc) group. Attempts to apply this method to other transition-metal complexes are currently under investigation and have recently led to the formation of (alkenylcarbene)chromium carbonyl and (alkenylcarbene)tungsten carbonyl complexes.[25]

Experimental Section

General Data. All reactions were performed under an argon or nitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^1H (300.13 MHz), ^{13}C (75.47 MHz), and ^{31}P (121.49 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer at 297 K and referenced to TMS for ^1H and ^{13}C and to 85% H_3PO_4 for ^{31}P. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon, France.

The complexes $(\eta^6\text{-}C_6Me_6)RuCl_2(PMe_3)$, $(\eta^6\text{-}C_6Me_6)RuCl_2(PPh_3)$, and $(\eta^6\text{-}C_6H_2Me_4)RuCl_2(PMe_3)$[26] and the different propargyl alcohols[11] were prepared by literature methods.

General Procedure. In a Schlenk tube, 1 mmol of the complex (arene)$RuCl_2(PMe_3)$ (1 or 1′) was dissolved in 30 mL of methanol (arene = hexamethylbenzene (HMB)) or in 40 mL of a methanol/dichloromethane (1:1) mixture (arene = tetramethylbenzene (TMB)). To the red solution was added 167 mg (1 mmol) of $NaPF_6$ and an excess of propargyl alcohol (from 2 to 6 equiv). After 10 min to 18 h of stirring at room temperature, the solvent was removed under vacuum. The precipitate was washed with 30 mL of diethyl ether and then dissolved in 20 mL of dichloromethane. The solution was filtered through a filter-paper-tipped cannula. The slow addition of 60 mL of diethyl ether allowed the formation of a biphasic system affording crystals in 70% yield.

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CMe_2]PF_6$ (2a). From 410 mg of the crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 0.5 mL of $HC{\equiv}CC(OH)Me_2$ (5.2 mmol), 450 mg of red crystals of **2a** (73%) was isolated after 10 min of reaction. Anal. Calcd for $C_{21}H_{37}ClF_6OP_2Ru$: C, 40.84; H, 5.99; P, 10.04. Found: C, 41.04; H, 6.01; P, 10.21. IR (cm^{-1}; KBr): 1595 (m, $\nu_{C=C}$), 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 6.68 (s, 1 H, C*H*=), 4.73 (s, 3 H, OMe), 2.10 (s, 18 H, C_6Me_6), 1.94 (s, 3 H, Me_2C=), 1.90 (s, 3 H, Me_2C=), 1.42 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.3 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 306.89 (d, Ru=C, $^2J_{PC}$ = 18.86 Hz), 149.37 (s, =*C*Me_2), 138.73 (s, H*C*=), 106.29 (s, C_6Me_6), 68.68 (s, OMe), 28.31 (s, =CMe_2), 23.49 (s, =CMe_2), 16.18 (s, C_6Me_6), 15.95 (d, PMe_3, $^1J_{PC}$ = 35.5 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.71 (s, PMe_3), −143.79 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

$[C_6H_2Me_4(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CMe_2]PF_6$ (2′a). From 382 mg of crystalline 1′ (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 0.5 mL of $HC{\equiv}CC(OH)Me_2$ (5.2 mmol), 440 mg of an orange powder of **2′a** (75%) was isolated after 10 min of reaction. IR (cm^{-1}; KBr): 1600 (m, $\nu_{C=C}$), 1275 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 6.54 (s, 1 H, C*H*=), 5.83 (s, 2 H, $C_6H_2Me_4$), 4.88 (s, 3 H, OMe), 2.01 (s, 6 H, $C_6H_2Me_4$), 1.95 (s, 3 H, Me_2C=), 1.91 (s, 6 H, $C_6H_2Me_4$), 1.90 (s, 3 H, Me_2C=), 1.49 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.6 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.65 (s, PMe_3), −143.88 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}C(CH_2)_5]PF_6$ (2b). From 410 mg of crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 620 mg of $HC{\equiv}CC(OH)(CH_2)_5$ (5.0 mmol), 425 mg of red crystals of **2b** (65%) were isolated after 10 min of reaction. Anal. Calcd for $C_{24}H_{36}ClF_6OP_2Ru$: C, 44.14; H, 5.52; P, 9.50. Found: C, 44.21; H, 5.60; P, 9.54. IR (cm^{-1}; KBr): 1590 (m, $\nu_{C=C}$), 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 6.54 (s, 1 H, C*H*=), 4.65 (s, 3 H, OMe), 2.08 (s, 18 H, C_6Me_6), 1.71–1.62–1.51–1.46 (m, 10 H, −(CH_2)$_5$−), 1.40 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.4 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 310.15 (d, Ru=C, $^2J_{PC}$ = 22.5 Hz), 155.93 (s, =C(CH_2)$_5$), 134.74 (s, HC=), 106.64 (s, C_6Me_6), 68.84 (s, OMe), 38.77, 33.36, 29.30, 28.16, 26.16 (s, (CH_2)$_5$), 16.54 (s, C_6Me_6), 16.00 (d, PMe_3, $^1J_{PC}$ = 34.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.35 (s, PMe_3), −143.50 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CPh_2]PF_6$ (2c). From 410 mg of crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 1040 mg of $HC{\equiv}CC(OH)Ph_2$ (5.0 mmol), 512 mg of red crystals of **2c** (69%) was isolated after 24 h of reaction. Anal. Calcd for $C_{31}H_{41}ClF_6OP_2Ru$: C, 50.17; H, 5.53; P, 8.36. Found: C, 49.98; H, 5.60; P, 8.32. IR (cm^{-1}; KBr): 1590 (m, $\nu_{C=C}$), 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.50 (s, 1 H, C*H*=), 7.43–7.11 (m, 10 H, Ph_2), 4.11 (s, 3 H, OMe), 2.13 (s, 18 H, C_6Me_6), 1.46 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.3 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 304.24 (d, Ru=C, $^2J_{PC}$ = 18.7 Hz), 147.70 (s, =CPh_2), 140.25, 139.75 (s, Ph), 136.43 (s, CH=), 131.30, 129.69, 129.48, 129.04, 128.67 (s, Ph), 107.14 (s, C_6Me_6), 67.87 (s, OMe), 16.68 (s, C_6Me_6), 16.66 (d, PMe_3, $^1J_{PC}$ = 34.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 5.23 (s, PMe_3), −143.47 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHMe]PF_6$ (3d). From 410 mg of crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 0.4 mL of HC≡CCH(OH)Me (5.1 mmol), 420 mg of red crystals of **3d** (70%) was isolated after 2 h of reaction. Anal. Calcd for $C_{20}H_{35}ClF_6OP_2Ru$: C, 39.80; H, 5.81; P, 10.21. Found: C, 39.30; H, 5.76; P, 9.81. IR (cm^{-1}; KBr): 1630 (m, $\nu_{C=C}$), 1300 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.80 (dq, 1 H, =C*H*Me, $^3J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 6.9 Hz), 6.78 (d, 1 H, C*H*=, $^3J_{HH}$ = 14.7 Hz), 4.37 (s, 3 H, OMe), 2.17 (dd, 3 H, *Me*CH=, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz), 2.05 (s, 18 H, C_6Me_6), 1.37 (d, 9 H, PMe_3, $^2J_{PH}$ = 12.0 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 305.77 (d, Ru=C, $^2J_{PC}$ = 20.6 Hz), 171.34 (s, =CHMe), 134.36 (s, *C*H=), 106.55 (s, C_6Me_6), 65.50 (s, OMe), 21.80 (s, *Me*CH=), 16.60 (s, C_6Me_6), 16.25 (d, PMe_3, $^1J_{PC}$ = 35.0 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 12.00 (s, PMe_3), −149.30 (sept, PF_6^-, $^1J_{PF}$ = 710.4 Hz).

$[C_6H_2Me_4(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHMe]PF_6$ (3′d). From 382 mg of crystalline 1′ (1.0 mmol), 167 mg of $NaPF_6$ (1.0

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(26) (a) Bennett, M. A.; Robertson, G. B.; Smith, A. K. *J. Organomet. Chem.* **1972**, *43*, C41. (b) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

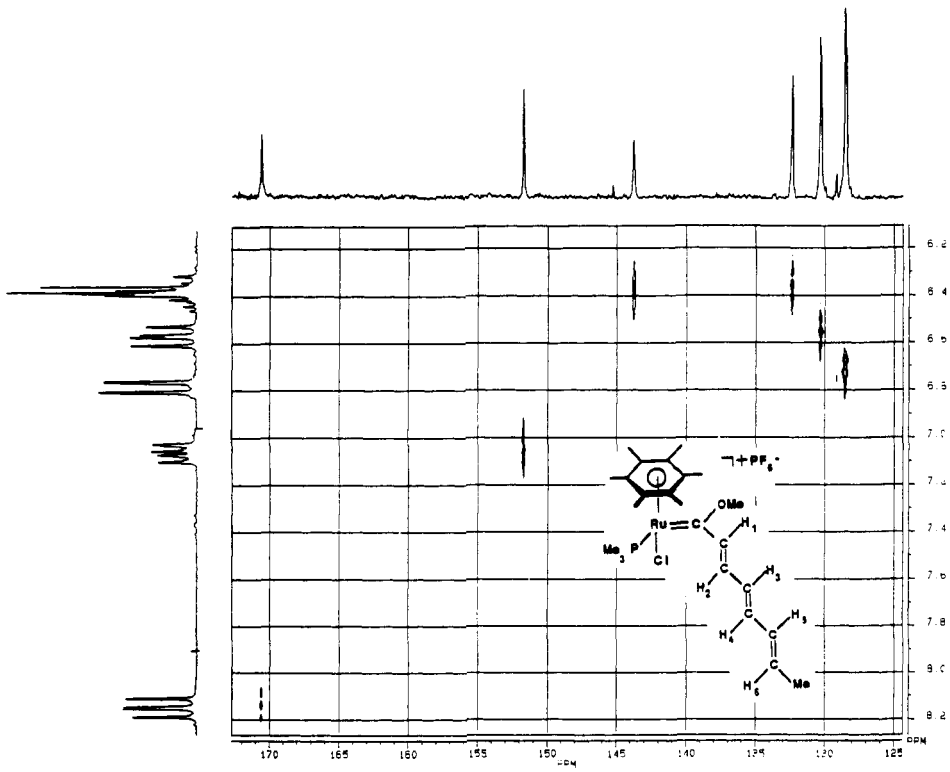

Figure 2. Heteronuclear ^{13}C–^{1}H correlation experiment on $[(C_6Me_6)(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHCH{=}CHCH{=}CHMe]PF_6$ (**5i**).

mmol), and 0.5 mL of HC≡CCH(OH)Me (5.7 mmol), 460 mg of red crystals of **3′d** (80%) was isolated after 2 h of reaction. Anal. Calcd for $C_{18}H_{31}ClF_6OP_2Ru$: C, 37.54; H, 5.43; Cl, 6.16; P, 10.76. Found: C, 37.73; H, 5.51; Cl, 6.49; P, 10.57. IR (cm^{-1}; KBr): 1612 (m, $\nu_{C=C}$), 1286 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.91 (dq, 1 H, =C*H*Me, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.9 Hz), 6.82 (dm, 1 H, C*H*=, $^3J_{HH}$ = 14.6 Hz, $^4J_{HH}$ = 1.2 Hz), 5.75 (s, 2 H, $C_6H_2Me_4$), 4.37 (s, 3 H, OMe), 2.21 (dd, 3 H, *Me*CH=, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.4 Hz), 1.98, 1.87 (s, 6 H, $C_6H_2Me_4$), 1.45 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 303.74 (d, Ru=C, $^2J_{PC}$ = 19.7 Hz), 173.17 (s, =*C*HMe), 136.17 (s, *C*H=), 108.75, 106.98, 98.71, 98.63 (s, $C_6H_2Me_4$), 65.22 (s, OMe), 22.11 (s, *Me*CH=), 17.40 (s, $C_6H_2Me_4$), 17.23 (d, PMe_3, $^1J_{PC}$ = 18.3 Hz), 16.94 (s, $C_6H_2Me_4$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 13.33 (s, PMe_3), −143.90 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHPh]PF_6$ (3e). Using the same procedure, 400 mg of black crystals of **3e** (60%) was obtained from 410 mg of crystalline **1** (1 mmol), 167 mg of $NaPF_6$ (1 mmol), and 264 mg of HC≡CCH(OH)Ph (2.0 mmol). Anal. Calcd for $C_{20}H_{35}ClF_6OP_2Ru$: C, 45.09; H, 5.55; P, 9.31. Found: C, 44.31; H, 5.50; P, 8.92. IR (cm^{-1}; KBr): 1610 (m, $\nu_{C=C}$), 1580 (m, $\nu_{C=C}$), 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.46 (dd, 1 H, =C*H*Ph, $^3J_{HH}$ = 15.1 Hz), 7.81–7.48 (m, 5 H, Ph), 7.32 (dd, 1 H, C*H*=, $^3J_{HH}$ = 15.1 Hz), 4.44 (s, 3 H, OMe), 2.07 (s, 18 H, C_6Me_6), 1.39 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 302.56 (d, Ru=C, $^2J_{PC}$ = 20.3 Hz), 168.23 (s, =*C*HPh), 135.04, 134.05, 130.67, 130.11 (s, Ph), 126.56 (s, *C*H=), 106.70 (s, C_6Me_6), 65.15 (s, OMe), 16.51 (s, C_6Me_6), 16.16 (d, PMe_3, $^1J_{PC}$ = 35.1 Hz). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K; δ, ppm): 12.18 (s, PMe_3), −143.44 (sept, PF_6, $^1J_{PF}$ = 710.3 Hz).

$[C_6H_2Me_4(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CH(2\text{-thienyl})]PF_6$ (3′f). From 382 mg of crystalline **1′** (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 277 mg of HC≡CCH(OH)(2-thienyl) (2.0 mmol), 460 mg of black crystals of **3′d** (72%) was isolated after 4 h of reaction. Anal. Calcd for $C_{21}H_{31}ClF_6OP_2SRu$: C, 39.17; H, 4.85. Found: C, 39.11; H, 4.85. IR (cm^{-1}; KBr): 1587 (m, $\nu_{C=C}$), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.59 (d, 1 H, =C*H*(2-thienyl), $^3J_{HH}$ = 14.7 Hz), 8.11 (dd, 1 H, 2-thienyl, $^4J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 1.2 Hz), 7.56 (dd, 1 H, 2-thienyl, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.3 Hz), 7.51 (ddd, 1 H, 2-thienyl, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 2.7 Hz, $^5J_{HH}$ = 0.5 Hz), 7.26 (d, 1 H, C*H*=, $^3J_{HH}$ = 14.7 Hz), 5.79 (s, 2 H, $C_6H_2Me_4$), 4.42 (s, 3 H, OMe), 2.04, 1.89 (s, 6 H, $C_6H_2Me_4$), 1.48 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 298.40 (d, Ru=C, $^2J_{PC}$ = 20.6 Hz), 161.81 (s, =*C*H(2-thienyl)), 139.28, 136.76, 128.94 (s, $C_{2\text{-thienyl}}$), 128.85 (s, *C*H=), 126.29 (s, $C_{2\text{-thienyl}}$), 107.77, 105.94, 98.86, 98.79 (s, $C_6H_2Me_4$), 64.99 (s, OMe), 17.43 (s, $C_6H_2Me_4$), 17.25 (d, PMe_3, $^1J_{PC}$ = 35.1 Hz), 17.02 (s, $C_6H_2Me_4$). $^{31}P\{^1H\}$ NMR (121.496 MHz, CD_2Cl_2, 297 K; δ, ppm): 13.71 (s, PMe_3), −143.87 (sept, PF_6^-, $^1J_{PF}$ = 711.3 Hz).

$[C_6Me_6(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHCH{=}CHPh]PF_6$ (4g). From 410 mg of crystalline **1** (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 320 mg of HC≡CCH(OH)CH=CHPh (2.0 mmol), 490 mg of black crystals of **4g** (71%) was isolated after 18 h of reaction. Anal. Calcd for $C_{27}H_{39}ClF_6OP_2Ru$: C, 46.90; H, 5.64; P, 8.96. Found: C, 44.99; H, 5.26; P, 8.38. IR (cm^{-1}; KBr): 1620 (m, $\nu_{C=C}$), 1590 (m, $\nu_{C=C}$), 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.28 (dd, 1 H, C*H*=CH=CHPh, $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 11.0 Hz), 7.67–7.42 (m, 5 H, Ph), 7.40 (d, 1 H, =C*H*Ph, $^3J_{HH}$ = 14.3 Hz), 7.24 (dd, 1 H, C*H*=CHPh, $^3J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 11.0 Hz), 6.88 (d, 1 H, C*H*=CHCH=CHPh, $^3J_{HH}$ = 14.1 Hz), 4.33 (s, 3 H, OMe), 2.06 (s, 18 H, C_6Me_6), 1.37 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 299.36 (d, Ru=C, $^2J_{PC}$ = 21.2 Hz), 168.80, 150.10 (s, *C*H=), 136.00, 131.57 (s, Ph), 129.87 (s, *C*H=), 129.68, 128.98 (s, Ph), 128.54 (s, CH=), 106.10 (s, C_6Me_6), 64.56 (s, OMe), 16.45 (s, C_6Me_6), 16.16 (d, PMe_3, $^1J_{PC}$ = 34.8 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 12.16 (s, PMe_3), −143.42 (sept, PF_6^-, $^1J_{PF}$ = 710.3 Hz).

$[C_6H_2Me_4(Cl)(PMe_3)Ru{=}C(OMe)CH{=}CHCH{=}CHMe]PF_6$ (4′h). From 382 mg of crystalline **1′** (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 490 mg of HC≡CCH(OH)CH=CHMe (5.1 mmol), 450 mg of dark red crystals of **4′h** (75%) was isolated after 18 h of reaction. Anal. Calcd for $C_{20}H_{33}ClF_6OP_2Ru$: C, 39.89; H, 5.48; Cl, 5.90; P, 10.30. Found: C, 39.69; H, 5.56; Cl, 6.89; P, 9.67. IR (cm^{-1}; KBr): 1637 (m, $\nu_{C=C}$), 1574 (m, $\nu_{C=C}$), 1282 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K); δ, ppm): 8.20 (dd, 1 H, CH=C*H*CH=CHMe, $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 11.1 Hz), 6.83 (sext, 1 H, =C*H*Me, $^3J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 7.0 Hz), 6.76 (d, 1 H, C*H*=CHCH=CHMe, $^3J_{HH}$ = 14.1 Hz), 6.60

(ddd, 1 H, C*H*=CHMe, $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 11.1 Hz, $^4J_{HH}$ = 1.4 Hz), 5.73 (s, 2 H, $C_6H_2Me_4$), 4.31 (s, 3 H, OMe), 1.98 (dd, 3 H, Me, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz), 1.99, 1.85 (s, 6 H, $C_6H_2Me_4$), 1.44 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 298.31 (d, Ru=C, $^2J_{PC}$ = 18.8 Hz), 170.65, 152.67, 132.86, 130.82 (s, *C*H=), 107.41, 105.68, 98.69, 98.56 (s, $C_6H_2Me_4$), 64.48 (s, OMe), 20.24 (s, *Me*CH=), 17.39 (s, $C_6H_2Me_4$), 17.20 (d, PMe_3, $^1J_{PC}$ = 28.5 Hz), 16.92 (s, $C_6H_2Me_4$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 13.43 (s, PMe_3), −143.87 (sept, PF_6^-, $^1J_{PF}$ = 711.3 Hz).

[C_6Me_6(Cl)(PMe_3)Ru=C(OMe)CH=CHCH=CHCH=CHMe]PF_6 (5i). From 410 mg of crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 500 mg of HC≡CCH(OH)CH=CHCH=CHMe (4.1 mmol), 580 mg of black crystals of **5i** (88%) was isolated after 18 h of reaction. Anal. Calcd for $C_{24}H_{39}ClF_6OP_2Ru$: C, 43.93; H, 5.95. Found: C, 44.36; H, 5.75. IR (cm^{-1}; KBr): 1610 (m, $\nu_{C=C}$), 1580 (m, $\nu_{C=C}$), 1250 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.13 (dd, 1 H, CH=C*H*(CH=CH)$_2$Me, $^3J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 11.8 Hz), 7.05 (dd, 1 H, =C*H*CH=CHMe, $^3J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 9.5 Hz), 6.69 (d, 1 H, C*H*=CH(CH=CH)$_2$Me, $^3J_{HH}$ = 13.9 Hz), 6.55 (dd, 1 H, C*H*=CHCH=CHMe, $^3J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 11.8 Hz), 6.45–6.28 (m, 2 H, C*H*=C*H*Me), 4.24 (s, 3 H, OMe), 2.17 (d, 3 H, *Me*CH=, $^3J_{HH}$ = 5.4 Hz), 2.02 (s, 18 H, C_6Me_6), 1.33 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 297.34 (d, Ru=C, $^2J_{PC}$ = 21.0 Hz), 170.6, 151.66, 143.71, 132.34, 130.25, 128.41 (s, CH=), 105.62 (s, C_6Me_6), 64.56 (s, OMe), 19.58 (s, *Me*CH=), 16.41 (s, C_6Me_6), 16.00 (d, PMe_3, $^1J_{PC}$ = 34.9 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 11.89 (s, PMe_3), −143.40 (sept, PF_6^-, $^1J_{PF}$ = 710.3 Hz).

[$C_6H_2Me_4$(Cl)(PMe_3)Ru=C(OMe)CH=CHCH=CHCH=CHMe]PF_6 (5'i). From 382 mg of crystalline 1' (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 500 mg of HC≡CCH(OH)CH=CHCH=CHMe (4.1 mmol), 380 mg of black crystals of **5'i** (60%) were isolated after 18 h of reaction. Anal. Calcd for $C_{22}H_{35}ClF_6OP_2Ru$: C, 42.07; H, 5.57. Found: C, 42.30; H, 5.51. IR (cm^{-1}; KBr): 1630 (w, $\nu_{C=C}$), 1600 (m, $\nu_{C=C}$), 1570 (m, $\nu_{C=C}$), 1286 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.28 (dd, 1 H, C*H*(CH=CH)$_2$Me, $^3J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 11.6 Hz), 7.11 (dd, 1 H, C*H*CH=CHMe, $^3J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 9.7 Hz), 6.81 (d, 1 H, C*H*=CH(CH=CH)$_2$Me, $^3J_{HH}$ = 14.0 Hz), 6.58 (dd, 1 H, C*H*=CHCH=CHMe, $^3J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 11.6 Hz), 6.44–6.30 (m, 2 H, C*H*=C*H*Me), 5.73 (s, 2 H, $C_6H_2Me_4$), 4.28 (s, 3 H, OMe), 1.99 (s, 6 H, $C_6H_2Me_4$), 1.88 (dd, 3 H, Me, $^3J_{HH}$ = 5.7 Hz), 1.86 (s, 6 H, $C_6H_2Me_4$), 1.44 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 295.02 (d, Ru=C, $^2J_{PC}$ = 19.7 Hz), 170.82, 151.81, 143.84, 132.32, 130.95, 130.18 (s, CH=), 107.40, 105.40, 98.40, 98.34 (s, $C_6H_2Me_4$), 64.36 (s, OMe), 19.60 (s, *Me*CH=), 17.37 (s, $C_6H_2Me_4$), 17.20 (d, PMe_3, $^1J_{PC}$ = 34.9 Hz), 16.90 (s, $C_6H_2Me_4$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 13.37 (s, PMe_3), −143.86 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

[C_6Me_6(Cl)(PMe_3)Ru=C(OMe)CH_2CH_2OMe]PF_6 (7). From 410 mg of crystalline 1 (1.0 mmol), 167 mg of $NaPF_6$ (1.0 mmol), and 0.5 mL of HC≡CCH_2OH (5.0 mmol), 460 mg of red crystals of **7** (74%) was isolated after 2 h of reaction. Anal. Calcd for $C_{20}H_{37}ClF_6O_2P_2Ru$: C, 38.58; H, 5.99; P, 9.95. Found: C, 38.32; H, 5.96; P, 9.89. IR (cm^{-1}; KBr): 1280 (w, ν_{C-O}), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 4.60 (s, 3 H, OMe), 3.86 (d, 1 H, −CH_2OMe, $^2J_{HH}$ = 24.0 Hz), 3.77 (d, 1 H, =C(OMe)CH_2, $^2J_{HH}$ = 13.0 Hz), 3.71 (d, 1 H, =C(OMe)CH_2, $^2J_{HH}$ = 13.0 Hz), 3.38 (d, 1 H, −CH_2OMe, $^2J_{HH}$ = 24.0 Hz), 3.29 (s, 3 H, CH_2OMe), 2.10 (s, 18 H, C_6Me_6), 1.37 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 325.84 (d, Ru=C, $^2J_{PC}$ = 21.2 Hz), 107.90 (s, C_6Me_6), 69.50 (s, −CH_2OMe), 67.66 (s, OMe), 58.97 (s, OMe), 51.14 (s, −CH_2−), 16.51 (s, C_6Me_6), 15.70 (d, PMe_3, $^1J_{PC}$ = 32.5 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 8.80 (s, PMe_3), −143.50 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

[C_6Me_6(Cl)(PMe_3)Ru=C=C=CPh_2]PF_6 (9c). To a red solution of 410 mg (1.0 mmol) of 1 in methanol (30 mL) was added 167 mg of $NaPF_6$ (1.0 mmol) and 1040 mg of HC≡CC(OH)Ph_2 (5.0 mmol). The solution rapidly turned violet. After 20 min of stirring at room temperature, half of the solvent was removed under vacuum and 20 mL of diethyl ether was added. The violet precipitate was dissolved in 10 mL of dichloromethane and the solution filtered through a filter-paper-tipped cannula. A total of 490 mg of a violet powder, **9c** (69%), was obtained by addition of 10 mL of diethyl ether. IR (cm^{-1}; KBr): 1940 (s, $\nu_{C=C=C}$), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.30 (m, 10 H, Ph), 2.00 (s, 18 H, C_6Me_6), 1.40 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 1.90 (s, PMe_3), −143.50 (sept, PF_6^-, $^1J_{PF}$ = 711.1 Hz).

[C_6Me_6(Cl)(PPh_3)Ru=C=C=CPh_2]PF_6 (10c). To a red solution of 450 mg (0.8 mmol) of **8** in methanol (30 mL) was added 127 mg of $NaPF_6$ (0.8 mmol) and 512 mg of HC≡CC(OH)Ph_2 (2.0 mmol). The solution rapidly turned violet. After 24 h of stirring at room temperature, half of the solvent was removed under vacuum and 20 mL of diethyl ether was added. The violet precipitate was dissolved in 10 mL of dichloromethane and the solution filtered through a filter-paper-tipped cannula. A total of 545 mg of dark green crystals of **10c** (81%) was obtained by addition of 10 mL of diethyl ether. Anal. Calcd for $C_{45}H_{43}ClF_6P_2Ru$: C, 60.30; H, 4.80; P, 6.92. Found: C, 58.97; H, 4.31; P, 6.73. IR (cm^{-1}; KBr): 1965 (s, $\nu_{C=C=C}$), 1600 (m, $\nu_{C=C}$), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.83–7.26 (m, 25 H, Ph and PPh_3), 1.87 (s, 18 H, C_6Me_6). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 288.30 (d, Ru=C, $^2J_{PC}$ = 29.1 Hz), 191.04 (s, =*C*=), 167.38 (s, =*C*Ph_2), 144.50 (s, Ph), 135.06 (d, P*Ph*$_3$, $^1J_{PC}$ = 9.7 Hz), 134.30, 132.61, 130.30 (s, Ph), 129.44, 128.80, 126.85 (d, PPh_3, $^2J_{PC}$ = 10.7 Hz), 116.26 (s, C_6Me_6), 16.27 (s, C_6Me_6). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 47.04 (s, PPh_3), −143.47 (sept, PF_6^-, $^1J_{PF}$ = 707.0 Hz).

[C_6Me_6(Cl)(PMe_3)Ru=C=C=C(Ph)(Fc)]PF_6 (11j). To a red solution of 410 mg (1.0 mmol) of 1 in 30 mL of methanol was added 167 mg of $NaPF_6$ (1.0 mmol) and 1040 mg of HC≡CC(OH)(Fc)(Ph) (5.0 mmol). The solution rapidly turned violet. After 2 h of stirring at room temperature, half of the solvent was removed under vacuum and 20 mL of diethyl ether was added. The violet precipitate was dissolved in 10 mL of dichloromethane and the solution filtered through a filter-paper-tipped cannula. The compound was purified by chromatography on silica gel with a dichloromethane/diethyl ether mixture as eluent. A total of 370 mg of a violet powder, **11j** (45%), is obtained after evaporation of the solvent. Anal. Calcd for $C_{34}H_{41}ClF_6P_2FeRu$: C, 49.90; H, 5.01. Found: C, 50.14; H, 4.90. IR (cm^{-1}; KBr): 1965 (s, $\nu_{C=C=C}$), 1600 (m, $\nu_{C=C}$), 840 (s, ν_{P-F}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.77–7.40 (m, 5 H, Ph), 5.59–5.56 (m, 2 H, C_5H_4), 4.36 (s, 5 H, C_5H_5), 4.25–3.90 (m, 2 H, C_5H_4), 2.00 (s, 18 H, C_6Me_6), 1.40 (d, 9 H, PMe_3, $^2J_{PH}$ = 10.7 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 243.26 (d, Ru=C, $^2J_{PC}$ = 30.5 Hz), 169.40 (s, =C=), 154.70 (s, =*C*(Ph)(Fc)), 143.20, 132.52, 129.30, 126.40 (s, Ph), 109.00 (s, C_6Me_6), 91.90, 82.66, 76.42, 74.52, 71.25 (s, C_5H_4), 17.00 (d, PMe_3, $^2J_{PC}$ = 30.5 Hz), 16.80 (s, C_6Me_6). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 297 K; δ, ppm): 11.73 (s, PMe_3), −143.55 (sept, PF_6^-, $^1J_{PF}$ = 710.4 Hz).

Crystal Structure Analysis of 2c. A red crystal was obtained by diffusion of ethyl ether saturated nitrogen into a concentrated CH_2Cl_2 solution of **2c**. Data were collected at 291 K on a CAD-4 diffractometer from an irregular fragment of dimensions 0.25 × 0.20 × 0.20 mm. A total of 4679 reflections (2527 >3σ(*I*)) were collected by 2θ scans to a 2θ limit of 50°. The intensity of three reflections was monitored throughout data collection as a check on crystal movement or decomposition, no nonstatistical variations being observed. Lorentz and polarization corrections were applied, and absorption corrections were applied by the empirical azimuthal method.[27] The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares using the program SHELX-76.[28] The hexafluorophosphate group is disordered and has been modeled by the inclusion of two sets of fluorine atoms weighted 3:1. Least-squares weights were

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$w = 1.53/(\sigma^2(F) + 0.002F^2)$. Refinement converged to the residuals $R = 0.069$ and $R_w = 0.072$.

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Supplementary Material Available: For **2c**, lists of bond lengths and angles, least-squares planes, and atomic fractional coordinates and thermal parameters (4 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Study of the Reactivity of the Nitriles RCN (R = CH_3, C_6H_5) toward the Unsaturated $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ Complex: Reversible Hydrogen Elimination (R = Me) or Hydrometalation Reactions (R = C_6H_5)

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The complex $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (**1**) reacts with acetonitrile to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(MeCN)(PPh_3)_2$ (**2**). The reaction is reversible under hydrogen at atmospheric pressure. The complex **1** reacts with benzonitrile to afford $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (**3**), which results from a hydrometalation of the nitrile. Complex **3** has been both spectroscopically and crystallographically characterized. Crystallographic data for **3**: monoclinic, $P2_1/n$, $a = 14.775$ (2) Å, $b = 23.775$ (2) Å, $c = 21.695$ (3) Å, $\beta = 92.53$ (1)°, $V = 7613$ (2) Å^3, $Z = 4$, $R = 0.049$, $R_w = 0.060$ for 4489 observations ($F_o^2 > 3\sigma(F_o^2)$) and 299 variable parameters. Under CO at atmospheric pressure, the benzonitrile ligand in **3** is easily displaced to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2)$ (**4**). Under 10 atm of hydrogen, **3** reverts to **1** with liberation of benzonitrile and formation of traces of benzylamine.

Introduction

We have recently shown that $ReRuH_5(CO)(PPh_3)_4$ (**1**), an unsaturated heterodinuclear complex resulting from the reaction of $[ReH_6(PPh_3)_2]^-$ with $RuHCl(CO)(PPh_3)_3$, was readily protonated, leading to the first example of a heterodinuclear complex containing molecular hydrogen, $[ReRu(H_2)H_4(CO)(PPh_3)_4]^+$.[1]

Pursuing the study of the reactivity of complex **1**, we have investigated possible reactions with nitriles.

Indeed, homogeneous hydrogenation of heteroatomic triple bonds is not usually an easy process.[2] The literature gives examples of hydrometalation of nitriles either with an unsaturated dimetallic rhenium hydride complex[3] or with $Ru_3(CO)_{12}$ under a hydrogen atmosphere.[4] Therefore, it was tempting to test the reactivity of our mixed Re–Ru unsaturated complex **1** toward nitriles, RCN. In this paper, we report two types of reactions which have been actually observed: (i) a reversible substitution reaction of two hydride ligands by the incoming nitrile (R = CH_3); (ii) a substitution reaction *and* a hydrometalation of the nitrile leading to a complex containing a benzonitrile ligand and a benzylideneimido ligand (R = C_6H_5).

Results and Discussion

Reactivity of $ReRuH_4(CO)(PPh_3)_4$ (1) toward Acetonitrile. The complex **1** dissolves in acetonitrile at room temperature, and the brown precipitate **2** rapidly appears (Scheme I). The infrared spectrum (Table I) of **2** shows that the ν_{CO} stretching wavenumber is lowered by 65 cm^{-1} compared to that for **1** and an absorption is observed at 2255 cm^{-1}, which can be attributed to the ν_{CN} stretching vibration of a coordinated acetonitrile. The ^{1}H NMR spectrum confirms the presence of coordinated acetonitrile, as a resonance is observed at 1.21 ppm, which is integrated as three protons by comparison with the phenyl resonances. In the hydride region, at 298 K, three resonances in a 1/1/1 intensity ratio are observed: two broad ones centered at −4.42 and −5.64 ppm, and a third one, an unresolved multiplet, at −14.38 ppm. At 193 K, the last signal remains the same but the broad resonances become a doublet and a double pseudotriplet centered at −3.39 and −6.15 ppm, respectively. The room-temperature $^{31}P\{^1H\}$ NMR spectrum shows two broad signals of equal intensities centered at 60.2 and 42.5 ppm. At 193 K, these two signals split into four resonances of equal intensity: one doublet centered at 73.6 ppm, a doublet of doublets centered at 58.2 ppm, one doublet centered at 45.65 ppm, and a singlet at 42.5 ppm. By analogy with the $^{31}P\{^1H\}$ NMR data for **1**,[1] we attribute the two signals observed at low field to the phosphine ligands bonded to ruthenium. Se-

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