Regioselective Synthesis of Indenylruthenium(II) Vinylalkylidene Complexes via Proton Additions to Vinylalkenyl Derivatives

M. Pilar Gamasa, José Gimeno,*,† and Blanca M. Martín-Vaca‡

Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

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Vinylalkenyl complexes [Ru{(*E*)-CH=CHCR=CH_2}(η^5-C_9H_7)(dppm)] (dppm = bis(diphenylphosphino)methane; R = H (**1a**), CH_3 (**1b**)) and [Ru{(*E*)-CH=CHC=$CHCH_2(CH_2)_nCH_2$}(η^5-C_9H_7)(dppm)], (*n* = 1 (**2a**), 2 (**2b**), 3 (**2c**)) have been prepared by the regio- and stereoselective reaction of the hydride complex [RuH(η^5-C_9H_7)(dppm)] with propargylic alcohols HC≡CC(OH)RCH_3 (R = H, CH_3) and cyclic alcohols. The reactions proceed through the regio- and stereoselective insertion of the alcohols in the ruthenium-hydride bonds leading to the transient hydroxyvinyl complexes [Ru{(*E*)-CH=CHC(OH)RCH_3}(η^5-C_9H_7)(dppm)] and [Ru{(*E*)-CH=CHC(OH)$CH_2CH_2(CH_2)_nCH_2$}(η^5-C_9H_7)(dppm)], which undergo a rapid dehydration process to give the final products. The hydroxyalkenyl complex [Ru{(*E*)-CH=$CHCH_2$-OH}(η^5-C_9H_7)(dppm)] (**3a**) is sufficiently stable toward the dehydration and can be isolated from the insertion reaction of [RuH(η^5-C_9H_7)(dppm)] with HC≡CCH_2OH. Protonation at C_δ of the vinylalkenyl moiety of complexes **1a**,**b** and **2a**,**c** with HBF_4·Et_2O in diethyl ether affords the cationic vinylalkylidene complexes [Ru(=CHCH=CRCH_3)(η^5-C_9H_7)(dppm)][BF_4] (R = H (**4a**), CH_3 (**4b**)) and [Ru{=CHCH=C=$CH_2CH_2(CH_2)_nCH_2$}(η^5-C_9H_7)(dppm)][BF_4] (*n* = 1 (**4c**), 3 (**4e**)) in good yields. The analogous vinylalkylidene complexes [Ru(=CHCH=CRPh)(η^5-C_9H_7)(dppm)][BF_4] (R = H (**4f**), Ph (**4g**)) are obtained via one-pot synthesis by the reaction of [RuH(η^5-C_9H_7)(dppm)] with HC≡CCR(OH)Ph (R = H, Ph) in refluxing toluene followed by the addition of an stoichiometric amount of HBF_4·Et_2O. However, the protonation of complex **2b** is not regioselective, giving instead a mixture of the vinylalkylidene complex [Ru{=CHCH=C=$CH_2CH_2(CH_2)_2CH_2$}(η^5-C_9H_7)(dppm)][BF_4] (**4d**) and the π-olefin complex [Ru{η^2-H_2C=CHC=$CHCH_2(CH_2)_2CH_2$}(η^5-C_9H_7)(dppm)][BF_4] (**5**) in a 4/1 molar ratio. The mechanism of this process has been established by analyzing the ^{1}H NMR spectrum of the reaction of complex **2b** with DBF_4. It is shown that the π-olefin complex **5** is generated from the electrophilic addition at the C_β atom of the vinylalkenyl complex **2b**, which undergoes a favorable [1,2]-H shift to give **5**. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopic data are discussed for all the novel vinylalkenyl and vinylalkylidene complexes.

Introduction

Ring-opening metathesis polymerization (ROMP)[1] and ring-closing metathesis (RCM)[2a,b] of olefins and related processes have disclosed new synthetic methodologies for the generation of polymeric materials and five-, six-, seven-, and eight-membered carbocycles or heterocycles.[2c] Recent developments have established that ruthenium(II) vinylcarbene complexes (Chart 1, **A** and **B**; Grubbs metathesis catalysts) are highly efficient for ROMP of cyclic and acyclic olefins[3a−c] as well as for the RCM of functionalized dienes and dienynes.[3d−h,4] The wide applications of these active ruthenium(II) metathesis catalysts mainly stem from the remarkable stability toward protic species such as water and HCl and other polar functional groups. Although these unsaturated carbene complexes can be obtained in moderate to high yields from the reactions of [$RuCl_2$(PR_3)$_3$] and diphenylcyclopropene[5a] or alkyl- and aryldi-

† E-mail: jgh@sauron.quimica.uniovi.es.
‡ Present address: Laboratoire de Synthèse Organique et Organométallique, Tour 44−45 1er étage, 5, Place Jussieu, 75252 Paris Cédex 05, France.

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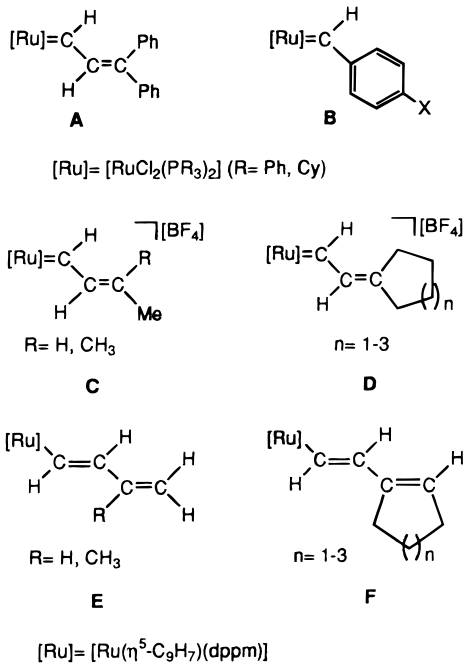
Chart 1



azoalkanes,[5b,c] the relatively difficult access to these reagents limits the general utility of this synthetic approach.[5d]

We have recently reported the synthesis and characterization of series of indenylruthenium(II) complexes containing unsaturated carbene groups of the following types: (i) the alkenylvinylidene complexes[6a] [Ru{=C=CHCR=CR′$_2$}(η^5-C_9H_7)(PPh_3)$_2$]$^+$ and (ii) the Fischer type alkenylcarbene complexes[6b] [Ru{=C(OMe)CH=CHR}(η^5-C_9H_7)L_2]$^+$ (L_2 = dppm, dppe; R = Ph; L_2 = dppm, R = H; dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane) which can be easily prepared from the reaction of [RuCl(η^5-C_9H_7)L_2] with 1-phenyl-2-propyn-1-ol and 2-propyn-1-ol in the presence of $NaPF_6$/MeOH.[6c] As part of our continuing interest in the synthesis of unsaturated carbene species and in view of the potential utility of the unsaturated ruthenium(II) alkylidene complexes, we have explored the synthesis of novel alkylidene complexes related to those described by Grubbs and co-workers.

In this work we report the synthesis of the vinylcarbene derivatives [Ru(=CHCH=CRCH$_3$)(η^5-C_9H_7)(dppm)][BF_4] (**C**) and [Ru{=CHCH=CCH$_2$CH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(dppm)][BF_4] (**D**), which are obtained in high yield *via* protonation of the vinylalkenyl complexes [Ru{(*E*)-CH=CHCR=CH$_2$}(η^5-C_9H_7)(dppm)] (**E**) and [Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(dppm)] (**F**), respectively (Chart 1). The insertions of propargylic alcohols HC≡CC(OH)R^{1}R^2 into the Ru−H bond of the parent complex [RuH(η^5-C_9H_7)(dppm)] which lead to the synthesis of the precursor complexes **E** and **F** are also described.

Results and Discussion

Synthesis of Vinylalkenyl Complexes [Ru{(*E*)-CH=CHCR=CH$_2$}(η^5-C_9H_7)(dppm)] (R = H (1a), Me (1b)) and [Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(dppm)] (*n* = 1 (2a), 2 (2b), 3 (2c)). The reactions of [RuH(η^5-C_9H_7)(dppm)] with HC≡CC(OH)RCH$_3$ (R = H, CH$_3$) and HC≡CC(OH)CH$_2$CH$_2$(CH$_2$)$_n$CH$_2$ (*n* = 1, 2, 3) in toluene at 80 °C lead to red solutions from which the vinylalkenyl complexes [Ru{(*E*)-CH=CHCR=CH$_2$}(η^5-C_9H_7)(dppm)] (R = H (**1a**), CH$_3$ (**1b**)) and [Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C_9H_7)(dppm)] (*n* = 1 (**2a**), 2 (**2b**), 3 (**2c**)) are obtained (70−85% yield) after the dehydration of the corresponding hydroxyalkenyl complexes (Scheme 1). In contrast, [RuH(η^5-C_9H_7)(dppm)] reacts with HC≡CCH$_2$OH to give the hydroxyalkenyl complex [Ru{(*E*)-CH=CHCH$_2$OH}(η^5-C_9H_7)(dppm)] (**3a**), which is stable toward dehydration under these reaction conditions.

All the alkenyl complexes are isolated as orange solids and have been characterized by elemental analysis (see Experimental Section) and NMR ($^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$) spectroscopy. The spectra exhibit resonances of the indenyl and dppm ligands[7] in accordance with the proposed structures (see Tables 1 and 2 and Experimental Section). $^{31}P\{^1H\}$ NMR spectra (Table 1) show a single signal (**1a**,**b** and **2a**−**c**, δ 22.26−22.44; **3a**, δ 23.11 ppm), indicating the chemical equivalence of both phosphorus atoms. The *trans* stereochemistry of the vinylalkenyl ligand is assessed on the basis of the NMR data, which are in agreement with the data reported for similar α,β-unsaturated ruthenium(II) alkenyl

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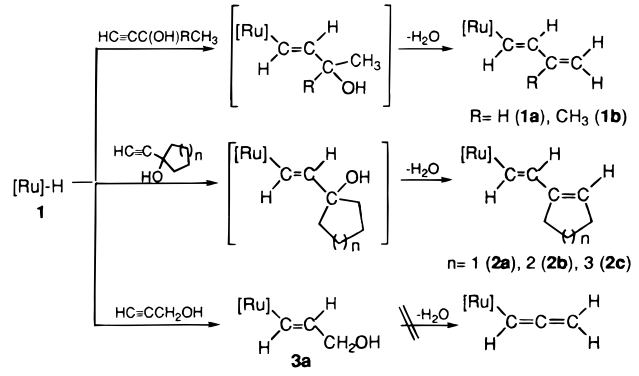
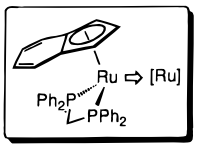
Scheme 1





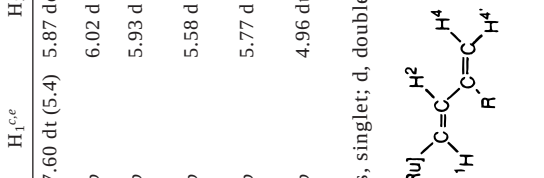
complexes.[8a,b] In particular, the ^{1}H NMR spectra in C_6D_6 (Table 1) show doublet signals in the range δ 5.58−6.02 ppm (**1b**, **2a**−**c**) and δ 5.87 dd (J_{HH} = 15.6, 9.9 Hz) (**1a**) due to the =C$_\beta$*H* vinylic proton, while signals corresponding to the proton of Ru*C*H= are overlapped by aromatic signals, except for complex **1a** (δ 7.60 dt; J_{HH} = 15.6, $^3J_{HP}$ = 5.4 Hz). The $^3J_{H-H}$ coupling constants (16.4−15.8 Hz) support the *trans* stereochemistry proposed for the RuCH=CHR double bond. ^{13}C{^{1}H} NMR spectra (Table 2) exhibit all the resonances corresponding to the α,*β*-unsaturated alkenyl ligands. Significantly, the Ru*C*H=*C*HR resonances of the alkenyl ligand, which appear as triplets at δ 140.93−157.68 and 138.47−143.99 ppm, have been assigned on the basis of the phosphorus−carbon coupling constants ($^2J_{C-P}$ = 15.3−15.7 and $^3J_{C-P}$ = 4.3−4.9 Hz). ^{1}H NMR spectrum of complex **3a** reveals the presence of the CH_2OH moiety, showing a triplet signal at δ −0.25 ppm (J_{HH} = 5.6 Hz) assigned to the O*H* proton (it disappears upon addition of D_2O) and a signal at δ 4.96 dt (J_{HH} = 15.8 and 6.6 Hz) due to the =C$_\beta$*H* proton. The ^{13}C{^{1}H} NMR spectrum exhibits the expected resonances of the *trans* Ru*C*H=*C*HR group (R = CH_2OH), which appear as triplets at δ 139.80 and 151.76 ppm (J_{CP} = 4.5 and 15.4 Hz, respectively).

The formation of complexes **1a**,**b** and **2a**−**c** is the result of the regio- and stereoselective insertion of the alkynols into the Ru−H bond followed by the spontaneous dehydration of the hydroxyalkenyl intermediate complexes (Scheme 1). The reactions proceed in a *cis* (*syn*) and *anti* Markovnikov fashion, as has been also found for the insertion of activated terminal alkynes in the precursor hydride complex [RuH(η^5-C_9H_7)(dppm)].[7] The formation of the transient hydroxyalkenyl species can be monitored by ^{31}P{^{1}H} NMR, revealing the rapid

Table 1. ^{31}P{^{1}H} and ^{1}H NMR Data for the Vinylalkenyl Complexes[a]

		^{1}H									
		η^5-C_9H_7[e]									
complex	^{31}P{^{1}H}	H-1,3	H-2	J_{HH}	Ind-6	H$_1$[c,e]	H$_2$[d]	J_{HH}	PCH_aH$_b$P[c]	PCH$_a$H$_b$P[c]	J_{HH}	other
[Ru{(*E*)-CH=CHCH=CH$_2$}(η^5-C_9H_7)(dppm)] (**1a**)	22.44 s	5.50 d	5.26 t	2.6	*b*	7.60 dt (5.4)	5.87 dd (9.9)	15.6	3.92 dt (11.1)	4.39 dt (9.9)	13.9	4.48 (dd, J_{HH} = 9.9, 2.2, H$_4$), 4.75 (dd, J_{HH} = 16.9, 2.2, H$_4$), 6.38 (ddd, H$_3$), 6.50−7.40 (PPh$_2$)
[Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}(η^5-C_9H_7)(dppm)] (**1b**)	22.34 s	5.66 d	5.34 t	2.6	*b*	*b*	6.02 d	16.3	4.10 dt (11.2)	4.49 dt (9.6)	13.9	1.82 (CH$_3$), 4.52, 4.70 (s, br, H$_4$, H$_4'$), 7.18−7.61 (PPh$_2$, Ind, H$_1$)
[Ru{(*E*)-CH=CHC=CHCH$_2$CH$_2$CH$_2$}-(η^5-C_9H_7)(dppm)] (**2a**)	22.26 s	5.42 d	5.12 t	2.5	*b*	*b*	5.93 d	16.3	3.97 dt (11.1)	4.25 dt (9.7)	14.7	1.72, 2.12, 2.35 (m, CH$_2$), 4.80 (s, H$_4$), 6.06−8.00 (PPh$_2$, Ind, H$_1$)
[Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_2$CH$_2$}-(η^5-C_9H_7)(dppm)] (**2b**)	22.33 s	5.44 d	5.12 t	2.4	*b*	*b*	5.58 d	16.4	3.90 dt (11.3)	4.25 dt (9.6)	13.6	1.35, 1.46, 1.84, 2.00 (m, CH$_2$), 4.92 (s, H$_4$), 6.76−7.86 (PPh$_2$, Ind, H$_1$)
[Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_3$CH$_2$}-(η^5-C_9H_7)(dppm)] (**2c**)	22.39 s	5.70 br	5.34 br		*b*	*b*	5.77 d	16.2	4.11 m	4.50 m		1.13, 1.50, 1.66, 1.90, 2.20 (m, CH$_2$), 5.30 (t, J_{HH} = 7.3, H$_4$), 7.20−7.60 (PPh$_2$, Ind, H$_1$)
[Ru{(*E*)-CH=CHCH$_2$OH}(η^5-C_9H_7)(dppm)] (**3a**)	23.11 s	5.34 d	5.00 t	2.7	*b*	*b*	4.96 dt (6.6)	15.8	3.85 m	4.35 dt (9.9)	14.3	−0.28 (t, J_{HH} = 5.6, OH), 3.85 (m, CH$_2$), 7.00−8.00 (PPh$_2$, Ind, H$_1$)

[a] Spectra were recorded in CD_6Cl_6; δ in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] Overlapped by Ph signals. [c] J_{HP} in parentheses. [d] J_{HH} in parentheses. [e] Legend for vinylalkenyl and indenyl skeletons:



(8) (a) [Ru{(*E*)-CH=CHC=CH(CH$_2$)$_3$CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$]: Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258. (b) [Ru{(*E*)-CH=CHCMe=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$] and [Ru{(*E*)-CH=CHCMe=CH$_2$}Cl(CO)$_2$(P^{i}Pr$_3$)$_2$]: Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. (c) Other ruthenium(II) hydroxyalkenyl complexes, [Ru]−CH=CHC(OH)-R^{1}R^2 (R^1 = R^2 = H.; R^1 = H, R^2 = Ph; R^1 = R^2 = Ph) and [Ru]−CH=CHC(OH)(CH$_2$)$_4$CH$_2$. ([Ru] = RuCl(CO)(P^{i}Pr$_3$)$_2$), have been reported.[8a]

Table 2. $^{13}C\{^1H\}$ NMR Data for the Vinylalkenyl Complexes[a]

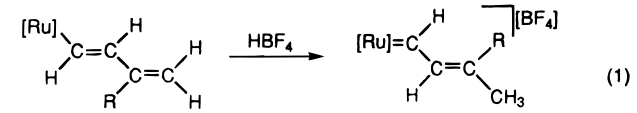
	η^5-C_9H_7										
complex	C-1,3	C-2	C-3a,7a	Δδ(C-3a,7a)[b]	C-4,7; C-5,6	C_α	C_β[c]	C_γ[c]	C_δ	PCH_2P	other
1a	68.64	91.27	108.49	−22.21	122.93, 124.32	157.68 t (15.5)	143.85 t (4.8)	143.27	102.31	49.34 t (21.3)	125.35−140.00 (m, PPh_2)
1b	68.62	90.88	108.54	−22.16	122.87, 124.24	150.28 t (15.7)	142.96 t (4.3)	145.01	104.17	49.20 t (21.0)	19.19 (s, CH_3), 129.14−140.00 (m, PPh_2)
2a	68.94 t (3.3)	91.37	108.82 t (1.8)	−21.88	124.59, 128.15	150.94 t (15.5)	138.47 t (4.5)	147.18	116.04	49.53 t (21.3)	23.76, 31.99, 32.93 (s, CH_2), 128.21−140.72 (m, PPh_2)
2b	67.10 t (3.3)	89.32	107.24 t (1.8)	−23.46	121.39, 122.90	140.93 t (15.3)	142.27 t (4.9)	137.74	115.81	47.62 t (21.4)	22.28, 22.44, 23.64, 24.59 (m, CH_2), 126.45−138.90 (m, PPh_2)
2c	69.18	91.49	109.32	−21.38	123.44, 124.96	143.16 t (15.6)	143.99 t (4.5)	147.34	121.86	49.82 t (21.5)	27.75, 27.95, 28.80, 29.28, 33.98 (m, CH_2), 128.24−133.31 (m, PPh_2)
3a	68.82 t (3.0)	91.33	108.72	−21.98	123.05, 124.27	151.76 t (15.4)	139.80 t (4.5)			49.76 t (20.6)	70.05 (s, CH_2OH), 125.18−140.00 (m, PPh_2)

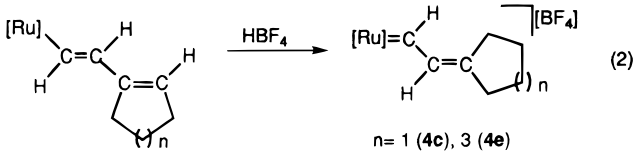
[a] Spectra were recorded in CD_6Cl_6; δ in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. J_{CP} in parentheses. [b] Δδ(C-3a,7a) = δ[C-3a,7a(η^5-indenyl complex)] − δ[C-3a,7a(sodium indenyl)]. δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] Assigned using DEPT 135 data.

appearance of a new phosphorus resonance at *ca.* δ 23.5 ppm, which can be compared to that of the complex **3a** (δ 23.11 ppm).[8c] As the reaction proceeds, the intensity of this signal gradually diminishes, giving rise to a new singlet resonance assigned to the vinylalkenyl complexes **1a**,**b** and **2a**−**c** (δ 22.26−22.44 ppm). However, all attempts to isolate the corresponding dehydrated species of **3a**, namely the allenyl complex [Ru]−CH=C=CH_2, by using dehydration agents were unsuccessful, leading instead to decomposition processes.

Synthesis of the Vinylalkylidene Complexes [Ru(=CHCH=CRCH$_3$)(η^5-C$_9$H$_7$)(dppm)][BF$_4$] (R = H (4a), CH$_3$ (4b)), Ru{=CHCH=CCH$_2$CH$_2$-(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)(dppm)][BF$_4$] (*n* = 1 (4c), 3 (4e)), and [Ru(=CHCH=CRPh)(η^5-C$_9$H$_7$)(dppm)][BF$_4$] (R = H (4f), Ph (4g)). Theoretical studies[9] on transition-metal vinyl complexes have shown that the nucleophilic site is located at the C_β atom of the vinyl group. In accordance with these expectations, vinylmetal derivatives may undergo typical electrophilic additions to give carbene complexes.[10,11] Following this synthetic methodology, we have investigated the ability of the vinylalkenyl complexes **1a**,**b** and **2a**−**c** to behave as precursors of the corresponding alkylidene derivatives *via* protonation reactions.

The treatment of a solution of **1a**,**b** or **2a**,**c** in diethyl ether with HBF_4·Et_2O, at −40 °C, leads to the instantaneous formation of the alkylidene complexes [Ru(=CHCH=CRCH$_3$)(η^5-C$_9$H$_7$)(dppm)][BF$_4$] (R = H (**4a**), CH_3 (**4b**)) and [Ru{=CHCH=CCH$_2$CH$_2$(CH$_2$)$_n$CH$_2$}(η^5-C$_9$H$_7$)-(dppm)][BF$_4$] (*n* = 1 (**4c**), 3 (**4e**)), which have been isolated from the reaction mixture as insoluble tetrafluoroborate salts in good yield (80−90%; eqs 1 and 2). Complexes **4a**,**b**,**c**,**e** are air-sensitive solids soluble in chlorinated solvents and tetrahydrofuran.





In contrast, the protonation of the hydroxyalkenyl complex **3a** under similar reaction conditions leads to

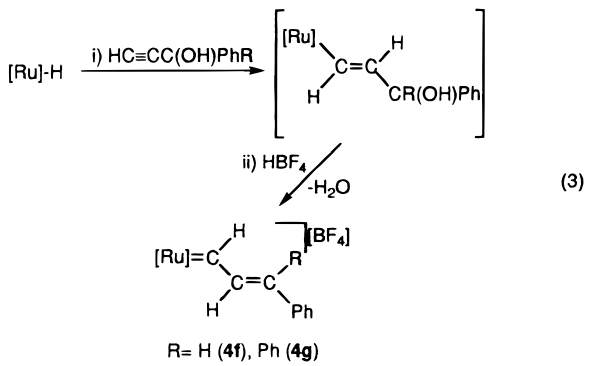
(9) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(10) For leading references see the following. [Re]: (a) Brodner, G. S.; Smith, D. E.; Halton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. [Fe]: (b) Kremer, K. A. M.; Kuo, G. H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (c) Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (d) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (e) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. [W]: (f) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometalics* **1993**, *12*, 2131.

(11) [Ru]: References 8a,b. [Os]: Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

a mixture of the corresponding alkylidene complex (identified by ^{1}H NMR) along with other unidentified species, from which the carbene complex could not be isolated.

Analogous alkenylcarbene complexes **4f**,**g** have also been prepared *via* one-pot synthesis by heating a toluene solution of the hydride precursor complex and HC≡CCR(OH)Ph (R = H, Ph) at 80 °C for 3 h followed by the addition of a stoichiometric amount of HBF_4·OEt_2 to the resulting reaction mixture (eq 3).



(3)

Complexes **4f**,**g**, which precipitate from the reaction mixture, have been isolated (95% yield) as air-stable red tetrafluoroborate salts. The reaction proceeds through the formation of the hydroxyalkenyl derivative (as ascertained by ^{1}H and ^{31}P{^{1}H} NMR), but attempts to isolate this intermediate were unsuccessful.

Elemental analyses and mass spectra (FAB) of all the carbene complexes support these formulations (see Experimental Section). IR spectra (KBr) show the typical ν(B−F) strong absorption of the tetrafluoroborate anion at *ca.* 1060 cm^{-1}. Conductance measurements (Me_2CO solutions) show that they behave as 1:1 electrolytes, confirming the cationic nature of the complexes (see Experimental Section). The formulations as alkenylcarbene derivatives, arising from a formal proton addition at C_δ of the alkenylvinyl chain (**4a**−**c**,**e**) and at C_γ of the hydroxyalkenyl intermediate complex (**4f**,**g**), are consistent with the NMR data (Tables 3 and 4). The presence of the carbene moiety Ru=CH is confirmed by the ^{13}C{^{1}H} NMR spectra ($CDCl_3$), which show the typical low-field resonance of the carbenic carbon nuclei at δ 292.10−302.88 ppm as a triplet ($^2J_{CP}$ = 9.5 Hz; **4a**,**g**) or a multiplet (**4b**,**c** and **4e**,**g**). The spectra also show resonances assignable to the C_β and C_γ signals at 143.04−148.21 (Ru=CH*C*H=) and 141.43−163.94 ppm (Ru=CHCH=*C*R_2). In the ^{1}H NMR spectra the most remarkable features (Table 3) are the downfield resonances (δ 13.33−14.60 ppm) of the Ru=C*H* proton (coupled with the phosphorus atoms of dppm) and the signals of the Ru=CHC*H*= proton at δ 6.05−6.75 ppm ($^3J_{HH}$ = *ca.* 13 Hz)). The ^{31}P{^{1}H} NMR spectra display a single resonance which appears, as expected, at a higher field than that of the precursor vinyl derivatives (δ 11.91−13.64 ppm), indicating the chemical equivalence of both phosphorus nuclei. This is consistent with a free rotation of the carbene moiety around the ruthenium−carbon bond at room temperature. All these spectroscopic data agree well with those reported for analogous vinylalkylidene complexes.[12]

Protonation Reaction of the Vinylalkenyl Com-

Table 3. ^{31}P{^{1}H} and ^{1}H NMR Data for the Alkylidene Complexes[a]

complex	^{31}P{^{1}H}	η^5-C_9H_7 H-1,3	H-2	J_{HH}	Ind-6	H$_1$[c]	H$_2$[d,e]	J_{HH}	PCH_aH_bP[c]	PCH_aH_bP[c]	J_{HH}	other
[Ru{=CHCH=C(CH$_3$)H}(η^5-C_9H_7)(dppm)][BF$_4$] (**4a**)	11.91 s	5.98 d	5.13 t	2.7	*b*	13.73 dt (2.6)	6.35 dd (13.5)	13.1	4.94 dt (11.3)	5.48 dt (11.1)	16.3	0.92 (dd, J_{HH} = 7.0, 1.3, CH$_3$), 5.70 (dq, J = 13.5, 7.0, H$_3$), 7.08−7.46 (m, PPh$_2$, Ind)
[Ru{=CHCH=C(CH$_3$)$_2$}(η^5-C_9H_7)(dppm)][BF$_4$] (**4b**)	13.17 s	5.99 d	5.02 t	2.8	*b*	14.60 dt (2.0)	6.06 d	13.1	5.22 dt (11.6)	5.73 dt 911.3)	16.5	0.92, 0.98 (s, CH$_3$), 7.17−7.44 (m, PPh$_2$, Ind)
[Ru(=CHCH=CCH$_2$CH$_2$CH$_2$)(η^5-C_9H_7)(dppm)][BF$_4$] (**4c**)	13.11 s	5.96 d	5.10 t	2.7	*b*	13.93 d	6.24 d	13.5	5.04 dt (11.3)	5.60 dt (11.3)	16.4	1.16, 1.30 (m, CH$_2$), 7.08−7.36 (m, PPh$_2$, Ind)
[Ru{=CHCH=CCH$_2$CH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C_9H_7)(dppm)][BF$_4$] (**4d**)	13.26 s	5.97 d	5.05 t	2.7	*b*	14.24 d	6.05 d	13.1	4.90 m	5.46 dt (10.9)	16.4	0.80−1.60 (m, CH$_2$), 7.00−7.80 (m, PPh$_2$, Ind)
[Ru{=CHCH=CCH$_2$CH$_2$(CH$_2$)$_3$CH$_2$}(η^5-C_9H_7)(dppm)][BF$_4$] (**4e**)	13.64 s	6.02 d	5.01 br	1.6	*b*	14.13 d	6.05 d	12.4	5.13 dt (11.4)	5.70 dt (10.9)	16.6	1.13−1.75 (m, CH$_2$), 7.18−7.41 (m, PPh$_2$, Ind)
[Ru{=CHCH=C(Ph)H}(η^5-C_9H_7)(dppm)][BF$_4$] (**4f**)	12.38 s	6.01 br	5.00 br		*b*	13.69 d	6.75 dd (14.1)	12.6	5.27 dt (11.6)	5.84 dt (11.3)	16.4	6.28 (d, J = 14.1, H$_3$), 7.05−7.43 (m, PPh$_2$, Ind)
[Ru{=CHCH=C(Ph)$_2$}{η^5-C_9H_7)(dppm)][BF$_4$] (**4g**)	13.43 s	5.98 d	4.83 t	2.7	*b*	13.33 d	6.57 d	12.9	5.00 dt (11.3)	5.69 dt (11.6)	16.3	6.27, 6.42 (m, Ph), 6.81−7.34 (m, PPh$_2$, Ind)

[a] Spectra were recorded in $CDCl_3$; δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] Overlapped by Ph signals. [c] J_{HP} in parentheses. [d] J_{HH} in parentheses. [e] Legend for vinylalkylidene skeleton:

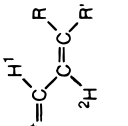
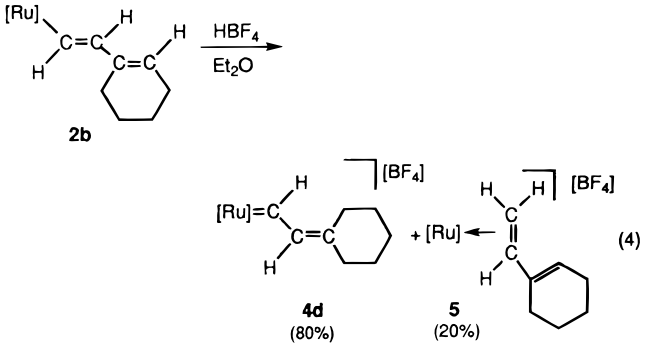


Table 4. $^{13}C\{^1H\}$ NMR Data for the Vinylalkylidene Complexes[a]

	η^5-C_9H_7									
complex	C-1,3	C-2	C-3a,7a	Δδ(C-3a,7a)[b]	C-4,7; C-5,6	C_α	C_β[c]	C_γ[c]	PCH_2P	other
4a	83.63 t (2.4)	96.79	112.87	−17.83	123.62, 127.96	302.88 t (9.5)	144.95	151.22	48.60 t (26.8)	26.19 (CH_3), 129.27−135.31 (PPh_2)
4b	83.83 t (2.9)	96.41	112.95	−17.75	123.88, 128.17	294.26 m	147.18 t (1.9)	150.20	49.85 t (25.1)	20.74, 27.30 (CH_3), 129.30−135.40 (PPh_2)
4c	83.12	96.74	112.64	−18.06	127.70, 129.17	294.15 m	143.04	163.94	49.31 t (25.6)	25.48, 25.96, 32.44, 35.92 (CH_2), 129.67−135.34 (PPh_2)
4d	83.59	96.39	112.73	−17.97	123.82, 127.72		143.90	157.46	49.43 t (26.5)	22.53−39.66 (s, CH_2), 128.09−131.32 (m, PPh_2)
4e	83.98	95.97	112.71	−17.99	123.82, 127.59	292.10 m	146.98	159.16	49.40 t (27.7)	26.33, 26.79, 28.60, 29.45, 32.24, 39.34 (CH_2), 129.18−135.34 (PPh_2)
4f	84.46	96.05	112.99	−17.71	124.01, 128.25	297.10 t (9.5)	145.08	141.43	49.30 t (25.8)	129.25−137.24 (PPh_2, Ph)
4g	85.27	94.82	112.75 t (1.8)	−17.95	123.60, 128.29	294.80 m	148.21 t (2.2)	144.69	49.20 t (24.4)	128.33−140.86 (PPh_2, Ph)

[a] Spectra were recorded in $CDCl_3$; δ in ppm and *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. J_{CP} in parentheses. [b] Δδ(C-3a,7a) = δ[C-3a,7a(η-indenyl complex)] − δ[C-3a,7a(sodium indenyl)]. δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] Assigned using DEPT 135 data.

plex [Ru{(*E*)-CH=CHC=CHCH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)] (2b). In contrast to the regioselective protonation of complexes **1a**,**b** and **2a,c**, yielding the vinylalkylidene derivatives **4a**−**c**,**e**, respectively, the addition of a stoichiometric amount of $HBF_4 \cdot Et_2O$ to a solution of the complex **2b** in Et_2O at −78 °C leads instead to a solution from which a 4:1 mixture of the carbene complex [Ru{=CHCH=CCH$_2$CH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)][BF_4] (**4d**) and the cationic π-olefin complex [Ru{(*E*)-η^2-H$_2$C=CHC=CHCH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)][BF_4] (**5**) is obtained in an overall yield of 85% (eq 4). If the protonation is performed at room temperature, a 1:4 mixture of complexes **4d** and **5** is obtained.



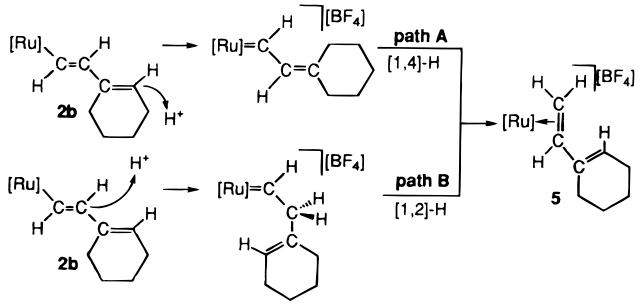
The formation of both species seems to be the result of independent proton additions, since the complex ratio in the reaction mixture remains unchanged after stirring the solution in dichloromethane at room temperature (monitored by ^1H NMR). Although we have not been able to separate the complexes, their formation has been assessed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectrum of the mixture exhibits a single resonance at δ 13.26 ppm, assigned to complex **4d**, and the typical set of signals of an AB system at δ −0.35 and 6.90 ppm ($^2J_{PP'}$ = 94.3 Hz) due to complex **5**.[13a] The nonequivalent phosphorus atoms of dppm arise from the hindered rotation of the olefin, as has been also reported for related complexes.[13b] The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra (in $CDCl_3$) show the expected resonances for the alkenylcarbene linkage in complex **4d** which appear at chemical shifts similar to those of the related complexes **4a**−**c**,**e** (Tables 3 and 4). The spectra also show resonances assignable to the presence of the coordinated diolefin in complex **5**, in accordance with the presence of the π-coordinated olefin H_2C=$CH(C_6H_9)$ (see Experimental Section).

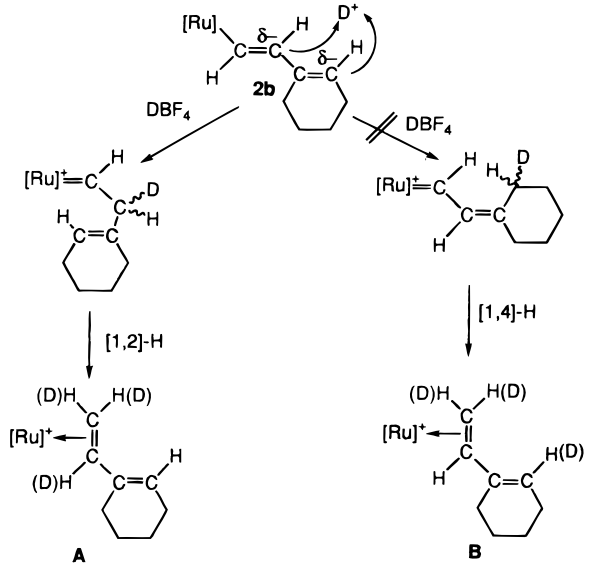
(12) For comparison see, for instance, the following. (a) Reference 8a: [Ru(=CHCH=CHPh)Cl$_2$(CO)(P^{i}Pr$_3$)$_2$][BF_4]. ^1H NMR: δ 16.67 ppm (*J*(HH) = 13.4 Hz), Ru=C*H*. ^{13}C NMR: δ 314.48 ppm, Ru=*C*H. (b): Reference 5c: [Ru(=CHCH=CMe$_2$)Cl$_2$(PCy$_3$)$_2$]. ^1H NMR: δ 19.26 ppm (*J*(HH) = 11.7 Hz), Ru=C*H*. ^{13}C NMR: δ 288.4 t ppm (*J*(CP) = 9.6 Hz), Ru=*C*H. (c) Reference 8b: [Ru(=CHCH=CMe$_2$)Cl(CO)(P^{i}Pr$_3$)$_2$][BF_4]. ^1H NMR: δ 15.92 d, br (*J*(HH) = 11.0 Hz) ppm, Ru=C*H*. ^{13}C NMR: δ 285.3 br ppm, Ru=*C*H.

(13) (a) The protonation of the alkenyl complex [Ru{(*E*)-CH=CHPh}(η^5-C$_9$H$_7$)(dppm)] with HBF_4 leads to the π-olefin complex [Ru(η^2-CH$_2$=CHPh)(η^5-C$_9$H$_7$)(dppm)]. The $^{31}P\{^1H\}$ NMR spectrum of this complex also shows that the phosphorus atoms of dppm are inequivalent (AB system; δ.1.60−5.90 ppm, $^2J_{PP'}$ = 94.0 Hz), indicating the hindered rotation of the alkene: Martín-Vaca, B. M. Doctoral Thesis, University of Oviedo, 1995. (b) Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta* **1980**, *42*, 277. (c) Lehmkuhl, H.; Grundke, J.; Mynott, R. *Chem. Ber.* **1983**, *116*, 159.

Scheme 2



Scheme 3



The formation of complex **5** can be understood as the result of proton addition at both the C_δ and the C_β atoms of the vinyl chain of complex **2b** (see Scheme 2). A subsequent isomerization *via* a [1,4]-H or [1,2]-H shift (paths A and B, respectively) would lead to the formation of the olefin complex **5**.

To probe the mechanism of the isomerization, the reaction of complex **2b** with DBF_4 (prepared *in situ* by mixing HBF_4 with D_2O (1:3)) in Et_2O at room temperature was studied by ^1H NMR. Scheme 3 shows the formation of the putative π-olefin complexes **A** and **B**, which may be formed through the isomerization of the deuterated carbene species generated by the addition at C_β and C_δ of the complex **2b**.

In particular, the spectrum shows that the resonance at δ 3.17 ppm assigned to the proton at the C-2 atom of the resulting deuterated π-olefin complex has decreased in intensity (ca. 50%) while that at δ 5.53 ppm due to the proton of C-4 remains unchanged, indicating that complex **A** has been formed. Accordingly, it may be concluded that the olefin complex **5** is generated through the partial protonation of the vinyl complex **2b** at the C_β atom followed by the thermodynamically favorable isomerization *via* a [1,2]-H migration. It is interesting to note that a similar [1,2]-H shift mechanism has been proposed for the isomerization of isoelectronic alkylidene rhenium[14a] ($[Re(=CHCH_2(R))(\eta^5\text{-}C_5H_5)(NO)(PPh_3)]^+$), iron[10e] ($[Fe(=CHCH_2CH_3)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$), and ruthenium[14c] ($[Ru(=CHCH_2Ph)(L_{OEt})(CO)(PPh_3)]^+$; L_{OEt} = $(\eta^5\text{-}C_5H_5)Co\{P(O)(OEt_2)\}_3$) complexes to the corresponding [M]−(η^2-olefin) derivatives. It is apparent that in this case the selectivity of the protonation reaction is dependent on the reaction temperature, which contrasts with the regioselective additions observed for the remaining vinylalkenyl cyclic derivatives (n = 1,3).

Concluding Remarks

We have recently reported[7] that the hydrido complex $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ undergoes insertion reactions with terminal and internal alkynes, leading to the regio- and stereoselective formation of alkenyl derivatives:

$$[RuH(\eta^5\text{-}C_9H_7)(dppm)] + R^1C{\equiv}CR^2 \rightarrow [Ru\{(E)\text{-}CR^1{=}CHR^2\}(\eta^5\text{-}C_9H_7)(dppm)]$$

R^1 = H, R^2 = Ph; R^1 = CO_2Me, R^2 = H; R^1 = R^2 = CO_2Me

This remarkable reactivity, likely due to the presence of the small-bite bidentate phosphine dppm, contrasts with the limited reactivity of the related hydridoruthenium(II) complexes $[RuH(\eta^5\text{-}C_9H_7)LL']$ (L = L′ or L ≠ L′ = monodentate phosphines), which are inert toward nonactivated alkynes under similar reaction conditions. Taking advantage of the versatile ability of the metal moiety $[Ru(\eta^5\text{-}C_9H_7)(dppm)]$ to activate the insertion of alkynes into the Ru−H bond, in this paper we report the insertion of terminal alkynols to give the stereoselective and high-yield formation of alkenylvinyl complexes $[Ru\{(E)\text{-}CH{=}CHCR{=}CH_2\}(\eta^5\text{-}C_9H_7)(dppm)]$ (R = H, CH_3) and $[Ru\{(E)\text{-}CH{=}CH\overline{C{=}CHCH_2(CH_2)_nCH_2}\}(\eta^5\text{-}C_9H_7)(dppm)]$. Recently, the reactions of alkynols with hydride 16-electron complexes $[MHCl(CO)(P^iPr_3)_2]$ (M = Ru, Os) leading to analogous α,β-unsaturated alkenyl ruthenium(II) and osmium(II) complexes have been also described.[8a,b]

The novel alkenylvinyl derivatives have been shown to be good precursors for the cationic alkylidene complexes $[Ru(=CHCH=CRCH_3)(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$ (R = H, CH_3) and $[Ru\{=CHCH=\overline{CCH_2CH_2(CH_2)_nCH_2}\}(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$, which are obtained by reaction with $HBF_4{\cdot}OEt_2$. The formation of these α,β-unsaturated alkylidene complexes proceeds through regioselective electrophilic addition at either the C_γ or the C_δ atom, revealing the high electron density on these positions of the vinylalkenyl moiety, in contrast to the more common electrophilic additions at the C_β atom of the vinyl group [M]−CH=CHR. Regarding this fact, it is surprising that the protonation of the vinylalkenyl complex $[Ru\{(E)\text{-}CH{=}CH\overline{C{=}CHCH_2(CH_2)_2CH_2}\}(\eta^5\text{-}C_9H_7)(dppm)]$ **(2b)** proceeds in a different way, leading instead to a mixture of the vinylalkylidene complex $[Ru\{=CHCH=\overline{CCH_2CH_2(CH_2)_2CH_2}\}(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$ **(4d)** (resulting from the protonation at the C_δ atom) and the π-alkene complex $[Ru\{\eta^2\text{-}H_2C{=}CH\overline{C{=}CHCH_2(CH_2)_2CH_2}\}(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$ **(5)**. In this study it is

(14) (a) Roger, C.; Bodner, G. S.; Hatton, W. G.; Gladysz, J. A. *Organometallics* **1991**, *10*, 3266. (b) For iron(II) complexes see ref 10e. (c) Leung, W. H.; Chan, E. Y. Y.; Williams, I. D.; Wong, W. T. *Organometallics* **1997**, *16*, 3234.

shown that the formation of **5** is the result of the simultaneous protonation at the C_β atom of the vinyl-alkenyl chain in **2b** to give the transient alkylidene complex $[Ru\{=CHCH_2C=CH(CH_2)_3CH_2\}(\eta^5\text{-}C_9H_7)(dppm)]^+$, which undergoes a thermodynamically favorable isomerization *via* [1,2]-H migration to afford the π-alkene complex. The prototropic rearrangement of alkylidene to alkene complexes is a well-known process, and the mechanism of isomerization has been probed for a large number of rhenium alkylidene complexes.[14] However, we are not aware of the reasons which govern the different nucleophilicities of the C_β and C_δ atoms of the alkenyl groups in the complexes bearing the cycloolefin moieties $[Ru\{(E)\text{-}CH=CHC=CHCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(dppm)]$ (**2a** ($n = 1$) and **2c** ($n = 3$) vs **2b** ($n = 2$)), which determine for the last compound the proton addition at both the C_β and C_δ atoms.

To summarize, in this work an efficient entry into the stereo- and regioselective synthesis of ruthenium(II) alkenylalkylidene complexes $[Ru]^+=CHCH=CR^1R^2$ is reported, *via* protonation of the readily available vinyl complexes $[Ru]-CHCH=CR^1R^2$. In addition, it is shown that this methodology, previously used in the synthesis of a limited number of other transition-metal alkylidene complexes $[M]^+=CHCHR^1R^2$,[10] can be also applied to the synthesis of α,β-unsaturated akylidene derivatives, of current interest as catalysts in the metathesis and polymerization of olefins. The general utility of this methodology has been also shown by Esteruelas *et al.*, who have recently reported[11] the synthesis of similar ruthenium(II) and osmium(II) alkenylalkylidene complexes.

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complex $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ was prepared by the literature method.[7] HBF_4 and the propargylic alcohols $HC\equiv CC(OH)CH_2CH_2(CH_2)_nCH_2$ ($n = 1, 2, 3$), $HC\equiv CC(OH)Ph_2$, and $HC\equiv CCH(OH)Ph$ (Lancaster Chemical Co.) and $HC\equiv CCH(OH)CH_3$, $HC\equiv CC(OH)(CH_3)_2$, and $HC\equiv CCH_2OH$ (Fluka AG Chemical Co.) were used as received.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 or AC200 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) or at 200 MHz (^1H), 50.32 MHz (^{13}C), or 81.01 MHz (^{31}P), using $SiMe_4$ or 85% H_3PO_4 as standard. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data for the complexes are collected in Tables 1−4.

Preparation of the Vinylalkenyl Complexes $[Ru\{(E)\text{-}CH=CHCR=CH_2\}(\eta^5\text{-}C_9H_7)(dppm)]$ (R = H (1a), CH_3 (1b)). A solution of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ (0.25 g, 0.41 mmol) and the corresponding propargylic alcohol (0.41 mmol) in toluene (30 mL) was heated at 80 °C (time of reaction is indicated below). The solution color progressively changed from yellow to red. After the mixture was cooled, the solvent was evaporated to dryness and the resulting orange solid washed with hexane (10 mL) and dried under vacuum. Reaction time, yield, and analytical data (NMR spectroscopic data are collected in Tables 1 and 2) are as follows. **1a**: 3h; 85%. Anal. Calcd for $C_{38}H_{34}P_2Ru$: C, 69.83; H, 5.20. Found: C, 69.14; H, 5.38. **1b**: 4.5 h; 80%. Anal. Calcd for $C_{39}H_{36}P_2Ru$: C, 70.16; H, 5.40. Found: C, 69.54; H, 5.54.

Preparation of the Vinylalkenyl Complexes $[Ru\{(E)\text{-}CH=CHC=CHCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(dppm)]$, ($n$ = 1 (2a), 2 (2b), 3 (2c)). A solution of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ (0.25 g, 0.41 mmol) and the corresponding propargylic alcohol (0.41 mmol) in toluene (30 mL) was heated under reflux (time of reaction is indicated below). The solution color progressively changed from yellow to red. The solvent was then evaporated to dryness and the resulting orange solid washed with hexane (10 mL) and dried under vacuum. Reaction time, yield, and analytical data (NMR spectroscopic data are collected in Tables 1 and 2) are as follows. **2a**: 4 h; 70%. Anal. Calcd for $C_{41}H_{38}P_2Ru$: C, 70.98; H, 5.52. Found: C, 71.40; H, 5.69. **2b**: 8 h; 80%. Anal. Calcd for $C_{42}H_{40}P_2Ru$: C, 71.38; H, 5.52. Found: C, 70.48; H, 5.16. **2c**: 9 h; 70%. Anal. Calcd for $C_{43}H_{42}P_2Ru$: C, 71.51; H, 5.86. Found: C, 70.92; H, 5.54.

Preparation of the Hydroxyalkenyl Complex $[Ru\{(E)\text{-}CH=CHCH_2OH\}(\eta^5\text{-}C_9H_7)(dppm)]$ (3a). A solution of $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ (0.25 g, 0.41 mmol) and propargyl alcohol (0.41 mmol) in toluene (30 mL) was heated at 80 °C for 1.5 h. The solvent was then evaporated to dryness and the resulting orange solid washed with hexane (10 mL) and dried under vacuum. Yield and analytical data (NMR spectroscopic data are collected in Tables 1 and 2) are as follows. Yield: 85%. Anal. Calcd for $C_{37}H_{34}OP_2Ru$: C, 67.58; H, 5.17. Found: C, 66.96; H, 5.38.

Preparation of the Vinylalkylidene Complexes $[Ru(=CHCH=CRCH_3)(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$ (R = H (4a), CH_3 (4b)). A stirred solution of the corresponding alkenyl complex (**1a**,**b**; 0.14 mmol) in diethyl ether, cooled at −40 °C, was treated dropwise with a dilute solution of HBF_4 in diethyl ether (0.20 mL, 0.15 mmol). Immediately, an unsoluble orange solid precipitated. The solution was decanted and the solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield, IR (KBr, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m*/*e*), and analytical data (NMR spectroscopic data are collected in Tables 3 and 4) are as follows. **4a**: 90%; 1060, broad strong (BF_4^-); 135. Anal. Calcd for $C_{38}H_{35}BF_4P_2Ru$: C, 61.55; H, 4.58. Found: C, 62.12; H, 4.65. **4b**: 90%; 1060, strong (BF_4^-); 124; $[M^+] = 669$, $[M^+ - R] = 601$, $[M^+ - Ind] = 553$, $[M^+ - R - Ind] = 485$ (R = C_5H_8). Anal. Calcd for $C_{39}H_{37}BF_4P_2Ru$: C, 61.99; H, 4.93. Found: C, 61.77; H, 5.23.

Preparation of the Vinylalkylidene Complexes $[Ru\{=CHCH=CCH_2CH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$, ($n$ = 1 (4c), 3 (4e)). The procedure is analogous to that described for the complexes **4a**,**b**. Yield, IR (KBr, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m*/*e*), and analytical data (NMR spectroscopic data are collected in Tables 3 and 4) are as follows. **4c**: 80%; 1059, broad, strong (BF_4^-); 128. Anal. Calcd for $C_{41}H_{39}BF_4P_2Ru$: C, 63.00; H, 5.03. Found: C, 63.15; H, 5.23. **4e**: 85%; 1062, broad, strong (BF_4^-); 139; $[M^+] = 723$; $[M^+ - R] = 601$, $[M^+ - R - C_9H_7] = 485$ (R = C_9H_{12}). Anal. Calcd for $C_{43}H_{43}BF_4P_2Ru$: C, 63.79; H, 5.35. Found: C, 63.29; H, 5.05.

Preparation of the Vinylalkylidene Complexes $[Ru(=CHCH=CRPh)(\eta^5\text{-}C_9H_7)(dppm)][BF_4]$ (R = H (4f), Ph (4g)). A solution of the complex $[RuH(\eta^5\text{-}C_9H_7)(dppm)]$ (0.25 g, 0.41 mmol) and the propargylic alcohol $HC\equiv CCR(OH)Ph$ (R = H, Ph; 0.8 mmol) in toluene was heated at 80 °C for 3 h. The toluene was removed under vacuum, and the resulting residue was dissolved in diethyl ether. The solution was then cooled at −40 °C and treated with an ethereal solution of HBF_4 (0.42 mmol) to give a solid which was worked up as for the complexes **4a**,**b**. Yield, color, IR (KBr, cm^{-1}), conductivity

(acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m*/*e*), and analytical data (NMR spectroscopic data are collected in Tables 3 and 4) are as follows. **4f**: 95%; red; 1059, broad strong (BF_4^-); 132; [M^+] = 717, [M^+ − R] = 601, [M^+ − R − Ind] = 485. (R = C_9H_8). Anal. Calcd for $C_{43}H_{37}BF_4P_2Ru$: C, 64.27; H, 4.64. Found: C, 64.19; H, 4.58. **4g**: 90%; violet; 1060, broad strong (BF_4^-); 117; [M^+] = 793; [M^+ − Ind] = 677, [M^+ − R] = 601 (R = $C_{15}H_{12}$). Anal. Calcd for $C_{49}C_{41}BF_4P_2Ru$: C, 66.90; H, 4.70. Found: C, 66.95; H, 4.35.

Protonation Reaction of the Alkenyl Complex [Ru{(*E*)-CH═CHC═CHCH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)] (2b). A stirred solution of complex **2b** (0.14 mmol) in diethyl ether was treated dropwise with a dilute solution of HBF_4 in diethyl ether (0.20 mL, 0.15 mmol). Immediately, an insoluble orange solid precipitated. The solution was decanted and the solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. The solid was characterized as a mixture of the complexes [Ru{═CHCH═CCH$_2$CH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)][BF_4] (**4d**) and [Ru{η^2-H$_2$C═CHC═CHCH$_2$(CH$_2$)$_2$CH$_2$}(η^5-C$_9$H$_7$)(dppm)][BF_4] (**5**) in a proportion which depends on the reaction temperature (global yield: 85%). Although we have not been able to separate these two complexes, they have been characterized by NMR spectroscopy (data for complex **4d** are collected in Tables 3 and 4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.90, 0.35 (both d, $^2J_{PP'}$ = 94.3 Hz) ppm. ^1H NMR ($CDCl_3$): δ 0.80−1.60 (m, 11H, CH_2, ═CH_1H$_{1'}$), 2.36 (d, 1H, J_{HH} = 13.4 Hz, ═CH$_1$$H_{1'}$), 3.17 (ddd, J_{HH} = 13.4 Hz, J_{HH} = 8.0 Hz, J_{HP} = 7.7 Hz, 1H, H_2), 4.07 (dt, 1H, J_{HH} = 14.8 Hz, $^2J_{HP}$ = 11.4 Hz, PCH_aH$_b$P), 4.42 (s br, 1H, Ind), 4.95 (m, 1H, PCH$_a$$H_b$P), 5.53 (s br, 1H, H_4), 6.47 (s br, 1H, Ind), 7.00−7.80 (m, PPh_2, Ind) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.84, 23.18, 26.11, and 29.61 (s, 4 CH_2), 46.05 (t, J_{CP} = 25.0 Hz, PCH_2P), 45.85 (s, C_1), 70.43 and 76.08 (s, C-1 and C-3), 89.64 (d, $^2J_{CP}$ = 7.3 Hz, C_2), 90.10 (s, C-2), 107.27 and 107.33 (s, C-3a and C-7a), 122.65, 123.13, 124.54, and 128.16 (s, C-4−7), 129.37−132.98 (m, PPh_2, C_4), 138.68 (s, C_3) ppm. $\Delta\delta$(C-3a,7a) = −23.4.

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