Alternative Mechanisms of the Alkyne to Vinylidene Isomerization Promoted by Half-Sandwich Ruthenium Complexes. X-ray Crystal Structures of [Cp*Ru═C═CHCOOMe(dippe)][BPh_4] and [Cp*RuH(C≡CCOOMe)(dippe)][BPh_4] (dippe = 1,2-bis(diisopropylphosphino)ethane; Cp* = C_5Me_5)

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Abstract: The complex [Cp*RuCl(dippe)] reacts with 1-alkynes in MeOH in the presence of $NaBPh_4$, yielding the metastable hydrido−alkynyl derivatives [Cp*Ru(H)(C≡CR)(dippe)][BPh_4] (R = COOMe, Ph or $SiMe_3$), intermediates in the formation of the corresponding vinylidene complexes, to which these compounds rearrange both in solution and in the solid state. The X-ray crystal structures of the isomers [Cp*Ru═C═CHCOOMe(dippe)][BPh_4] and [Cp*RuH(C≡CCOOMe)(dippe)][BPh_4] have been determined. Kinetic studies show that the mechanism for this isomerization process seems to be dissociative and that it is inhibited in solution by strong acids. In contrast with this, no hydrido−alkynyl complex has been observed in the course of the reaction of 1-alkynes with [CpRuCl(dippe)]. Instead, the alkyne adducts have been detected, and isolated in some cases. Such species have only been observed in the Cp*Ru system for acetylene, and [Cp*Ru(η^2-HC≡CH)(dippe)]$^+$ seems to be in equilibrium with the corresponding hydrido−alkynyl complex [Cp*RuH(C≡CH)(dippe)]$^+$, which isomerizes to [Cp*Ru═C═CH_2(dippe)]$^+$ *via* the formation of the π-alkyne complex. The effects on these tautomerization processes of the phosphine, Cp*, and Cp ligands, as well as the R group of the alkyne, are discussed.

Introduction

The rearrangement of acetylene to its vinylidene isomer is a thermodynamically disfavored process, given the fact that free vinylidene :C═CH_2 is *ca.* 44−47 kcal mol^{-1} less stable than acetylene HC≡CH.[1] However, this process becomes thermodynamically favorable on complexation to a metal center.[2] Upon coordination, the relative stability of acetylene and vinylidene is reversed, the vinylidene complex being *ca.* 35 kcal mol^{-1} more stable than the corresponding acetylene adduct, as shown by extended Hückel MO calculations.[3] Several possible mechanisms have been proposed for this conversion. It was initially suggested that oxidative addition of the alkyne to give an hydrido−alkynyl metal complex could be a feasible pathway for the formation of the corresponding vinylidene complex, *via* a concerted 1,3-hydrogen shift of the hydride from the metal to the β-carbon atom of the alkynyl ligand.[4] However, extended Hückel calculations made on the d^6 metal complex [CpMn(η^2-HC≡CH)$(CO)_2$] have shown that the concerted 1,3-hydrogen shift in the intermediate hydrido−alkynyl complex [CpMn(H)(C≡CH)$(CO)_2$] would have a very high activation energy, and a direct 1,2-hydrogen shift in the former complex seems more plausible.[3] A similar result was obtained from *ab initio* MO calculations for the tautomerization of the ruthenium complex [$RuCl_2$(η^2-HC≡CH)$(PH_3)_2$] to [Ru═C═$CH_2$$(Cl)_2$$(PH_3)_2$], in which the intermediate [$RuCl_2$(H)(C≡CH)$(PH_3)_2$] was shown to be of very high energy and, therefore, highly unstable.[5] It appears that the mechanism involving oxidative addition is difficult if the metal changes from d^6 to d^4, as in the case of Ru^{II} to Ru^{IV} (or Mn^{I} to Mn^{III}), but this process may take place when the metal changes from d^8 to d^6, i.e. M^{I} to M^{III} (M = Co, Rh, Ir).[3] Thus, there are several examples in the chemistry of these metals in which this sort of mechanism operates, i.e. in the reaction of [RhCl(P^iPr_3)$_2$] and [IrCl(P^iPr_3)$_2$] with 1-alkynes.[6] The π-adducts [MCl(HC≡CR)(P^iPr_3)$_2$] are formed first. Then, these rearrange to the Rh^{III} or Ir^{III} hydrido−alkynyl intermediates [M(H)(C≡CR)Cl(P^iPr_3)$_2$], and finally to the corresponding vinylidene complexes [M═C═CHR(Cl)(P^iPr_3)$_2$].[6] In a similar fashion, Bianchini and co-workers have shown[7] that the 16-electron fragment [Co(PP_3)]$^+$ (PP_3 = P$(CH_2CH_2PPh_2)_3$) reacts with 1-alkynes, yielding π-alkyne adducts of the type [Co(η^2-HC≡CR)(PP_3)]$^+$ which isomerize to the vinylidene complexes [Co═C═CHR(PP_3)]$^+$ passing through Co^{III} hydrido−alkynyl intermediates [Co(H)(C≡CR)(PP_3)]$^+$. At variance with this, the

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(1) (a) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F. *J. Am Chem. Soc.* **1990**, *112*, 8714. (b) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6133. Jensen, J. H.; Morokuma, K.; Gordon, M. S. *J. Chem. Phys.* **1994**, *100*, 1981.

(2) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59 and references therein.

(3) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(4) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55.

(5) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105.

(6) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414; Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, *272*, 105. García-Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406. Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.

(7) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.

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related rhodium fragment $[Rh(PP_3)]^+$ reacts with 1-alkynes, yielding Rh^{III} hydrido−alkynyl derivatives, but these do not rearrange to yield the corresponding vinylidenes.[8] These examples of hydrido−alkynyl to vinylidene rearrangements are rather slow and presumably occur in a nonconcerted fashion.[9] Very recently, an *ab initio* MO study on the transformation of $[RhCl(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]$ to $[Rh{=}C{=}CH_2(Cl)(PH_3)_2]$ has shown that this process may occur through either an intramolecular or intermolecular proton transfer mechanism *via* the Rh^{III} oxidative addition product $[RhH(C{\equiv}CH)(Cl)(PH_3)_2]$.[10] In the case of ruthenium, it has been possible to isolate the π-adducts such as $[CpRu(\eta^2\text{-}HC{\equiv}CR)(PR_3)_2]^+$ as intermediates in the formation of the vinylidene complexes $[CpRu{=}C{=}CHR(PR_3)_2]^+$.[11,12] The isomerization in these species is expected to occur through a direct 1,2-hydrogen shift, and no hydrido−alkynyl intermediates have been detected, this being consistent with the affirmation that such species are of very high energy in the case of d^4 metal complexes.[3,5] In contrast with the cyclopentadienylruthenium vinylidene complexes, the data on the related pentamethylcyclopentadienyl derivatives are much more scarce. In fact, the first example of the activation of terminal alkynes with a Cp*Ru complex, $[Cp^*RuCl(PMe_2Ph)_2]$, was reported only recently.[13] On the other hand, the reports on the interaction of substituted alkynes with transition metal complexes are relatively abundant, but less so on similar processes involving acetylene, despite the fact that most theoretical papers dealing with the problem of alkyne−vinylidene tautomerization promoted by transition metal complexes use unsubstituted acetylene for calculations.[3,5,10] We now report that the hydrido−alkynyl Ru^{IV} complexes $[Cp^*Ru(H)(C{\equiv}CR)(dippe)][BPh_4]$ (dippe = 1,2-bis(diisopropylphosphino)ethane; R = COOMe, Ph, $SiMe_3$) are formed upon reaction of $[Cp^*RuCl(dippe)]$[14] with $Na[BPh_4]$ and HC≡CR in MeOH. These compounds rearrange both in the solid state and in solution to the vinylidene complexes $[Cp^*Ru{=}C{=}CHR(dippe)][BPh_4]$, being therefore feasible intermediates in the isomerization of 1-alkynes to vinylidene complexes, as well as rare examples of an alkyne to vinylidene rearrangement taking place at a d^4 metal center.[15] When the reaction is carried out with acetylene HC≡CH, both the η^2-alkyne and the hydrido−alkynyl isomers are formed, and these rearrange to give finally the primary vinylidene complex. No hydrido−alkynyl complexes have been isolated or detected in the reaction of the cyclopentadienyl complex [CpRuCl(dippe)] with 1-alkynes, suggesting that the role of the C_5Me_5 ligand in these processes seems to be very important.[13] In this work, we compare the reactivity of the C_5Me_5 and C_5H_5 systems and also describe the X-ray crystal structures of the two isomeric compounds $[Cp^*Ru{=}C{=}CHCOOMe(dippe)][BPh_4]$ and $[Cp^*Ru(H)(C{\equiv}CCOOMe)(dippe)][BPh_4]$. A preliminary account of this research has already been published.[16]

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane,[17] [CpRuCl(dippe)],[14] [Cp*RuCl(dippe)],[14] and $[CpRu(Me_2CO)(dippe)][BPh_4]$[18] were prepared according to reported procedures. IR spectra were recorded in Nujol mulls on Perkin Elmer 881 or Perkin Elmer FTIR Spectrum 1000 spectrophotometers. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). The phosphine protons for all the compounds appeared in the corresponding ^1H NMR spectra as a series of overlapping multiplets in the range δ 0.5−3.0 ppm and were not assigned. Microanalysis were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

Preparation of Vinylidene Complexes $[Cp^*Ru{=}C{=}CHR(dippe)][BPh_4]$ (R = COOMe, 1a; Ph, 1b; $SiMe_3$, 1c; Bu^t, 1d). In a typical preparation, a solution of [Cp*RuCl(dippe)] (0.25 g, *ca.* 0.5 mmol) in MeOH (15 mL) was treated with an excess of the corresponding 1-alkyne. To this mixture was added an excess of solid $NaBPh_4$ (0.3 g), and a microcrystalline precipitate was formed almost immediately. The mixture was stirred for several minutes at room temperature. Then the precipitate was filtered off, washed with EtOH and petroleum ether, and dried *in vacuo*. These compounds can be recrystallized from acetone/EtOH. Yield: 75−80% in all cases.

1a: Anal. Calcd for $C_{52}H_{71}BO_2P_2Ru$: C, 69.3; H, 7.88. Found: C, 69.9; H, 7.95. IR (Nujol): ν(C=C) 1588 cm^{-1}, ν(C=O) 1689 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.82 (t, J(H,P), 1.2 Hz, $C_5(CH_3)_5$), 3.64 (s, $COOCH_3$), 4.50 (t br, J(H,P) ∼ 8 Hz, Ru=C=C*H*COOMe). $^{31}P\{^1H\}$: δ 75.3 s. $^{13}C\{^1H\}$: 10.89 (s, $C_5(CH_3)_5$), 18.33, 19.50, 19.90 (s, $P(CH(CH_3)_2)_2$), 21.88 (t, J(C,P) = 18.2 Hz, PCH_2), 25.22 (q, J(C,P) = 9.0 Hz, $P(CH(CH_3)_2)_2$), 32.29 (m, $P(CH(CH_3)_2)_2$), 51.52 (s, $COOCH_3$), 104.40 (s, $C_5(CH_3)_5$), 109.23 (s, Ru=C=*C*HCOOMe), 164.37 (s, *C*$OOCH_3$), 338.10 (t, Ru=*C*=CHCOOMe, J(C,P) = 14.2 Hz).

1b: Anal. Calcd for $C_{56}H_{73}BP_2Ru$: C, 73.1; H, 7.95. Found: C, 72.7; H, 8.12. IR (Nujol): ν(C=C) 1595 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.88 (s, $C_5(CH_3)_5$), 4.86 (s br, Ru=C=C*H*Ph), 7.12, 7.25 (m, C_6H_5). $^{31}P\{^1H\}$ δ 83.5 s. $^{13}C\{^1H\}$: 11.19 (s, $C_5(CH_3)_5$), 17.51, 18.31, 18.45, 18.74, 19.99 (s, $P(CH(CH_3)_2)_2$), 21.39 (m, PCH_2), 25.06 (m, $P(CH(CH_3)_2)_2$), 32.51 (t, J(C,P) = 16.4 Hz, $P(CH(CH_3)_2)_2$), 103.33 (s, C_5Me_5), 115.97 (s, Ru=C=*C*HPh), 126.54, 128.70, 130.11 (s, C_6H_5), 345.30 (t, J(C,P) = 13.7 Hz, Ru=*C*=CHPh).

1c: Anal. Calcd for $C_{53}H_{77}BP_2RuSi$: C, 69.5; H, 8.42. Found: C, 69.8; H, 8.45. IR (Nujol): ν(C=C) 1604 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.14 (s, $Si(CH_3)_3$), 1.81 (t, J(H,P) = 2 Hz, $C_5(CH_3)_5$), 3.16 (t, J(H,P) = 12 Hz, Ru=C=C*H*$SiMe_3$), $^{31}P\{^1H\}$: δ 81.8 s. $^{13}C\{^1H\}$: 4.091 (s, Ru=C=CHSi(*C*$H_3)_3$), 13.36 (s, $C_5(CH_3)_5$), 20.25, 20.94, 21.50, 21.81 (s, $P(CH(CH_3)_2)_2$), 23.40 (t, J(C,P) = 19 Hz, PCH_2), 27.72 (t, J(C,P) = 9.8 Hz, $P(CH(CH_3)_2)_2$), 31.74 (m, $P(CH(CH_3)_2)_2$), 95.30 (s, Ru=C=*C*H$SiMe_3$), 331.16 (t, J(C,P) = 14 Hz, Ru=*C*=CH$SiMe_3$)).

1d: Anal. Calcd for $C_{54}H_{77}BP_2Ru$: C, 72.1; H, 8.57. Found: C, 72.4; H, 8.32. IR (Nujol): ν(C=C) 1634 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.08 (s, $C(CH_3)_3$), 1.81 (s, $C_5(CH_3)_5$), 3.28 (s br, Ru=C=C*H*CMe_3). $^{31}P\{^1H\}$: δ 83.4 s. $^{13}C\{^1H\}$: 11.11 (s, $C_5(CH_3)_5$), 18.61, 18.74, 19.73 20.18 (s, $P(CH(CH_3)_2)_2$), 21.73 (t, J(C,P) = 20 Hz, PCH_2), 25.70 (t, J(C,P) = 9.2 Hz, $P(CH(CH_3)_2)_2$), 32.72 (s, Ru=C=CHC(*C*$H_3)_3$), 32.93 (m, $P(CH(CH_3)_2)_2$), 102.21 (s, C_5Me_5), 121.89 (s, Ru=C=*C*HCMe_3), 330.6 (t, J(C,P) = 13 Hz, Ru=*C*=CHCMe_3).

Preparation of Hydrido−Alkynyl Derivatives $[Cp^*RuH(C{\equiv}CR)(dippe)][BPh_4]$ (R = COOMe, 2a; Ph, 2b; $SiMe_3$, 2c). These compounds were obtained following a method analogous to that for the corresponding vinylidene complexes, but reversing the order in which the reagents are added: $NaBPh_4$ is added first and then the 1-alkyne. The hydrido−alkynyl complexes precipitate from the reaction mixture as white microcrystalline materials, in *ca*. 75−80% yield. All these compounds rearrange to their vinylidene isomers both in solution and in the solid state, except **2a**, which only rearranges in solution. For this reason, all compounds except **2a** were not recrystallized or

(8) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramírez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179.
(9) Bruce, M. I. *Chem. Rev.* **1991**, *19*, 197.
(10) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360.
(11) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc*. **1992**, *114*, 5518.
(12) Bullock, R. M. *J. Chem. Soc., Chem. Commun*. **1989**, 165.
(13) Le Lagadec, R.; Román, E.; Toupet, L.; Müller, U.; Dixneuf, P. *Organometallics* **1994**, *13*, 5030.
(14) de los Ríos, I.; Jiménez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans*. **1996**, 377.
(15) Nickias, P. N.; Selegue, J. P.; Young, B. A. *Organometallics* **1988**, *7*, 2248.
(16) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun*. **1995**, 1757.
(17) Fryzuk, M. D.; Jones, M. D.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. Burt, T. A.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.
(18) de los Ríos, I.; Jiménez-Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565.

analyzed. Crystals of **2a** suitable for X-ray structure analysis were obtained by layering with ethanol an acidic acetone solution of this compound, made up using as solvent acetone containing a few drops of HBF_4.

2a: IR (Nujol): ν(C≡C) 2108 cm^{-1}, ν(C═O) 1680 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 223 K): ^{1}H δ −8.55 (t, J(H,P) = 27.6 Hz, Ru*H*), 2.00 (s, $C_5(CH_3)_5$), 3.60 (s, COOCH_3), ^{31}P{^{1}H} (223 K): δ 75.5 s.

2b: IR (Nujol): ν(C≡C) 2106 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 223 K): δ −8.79 (t, J(H,P) = 29 Hz, Ru*H*), 1.86 (s, $C_5(CH_3)_5$), 7.11, 7.50 (m, C_6H_5), ^{31}P{^{1}H} (223 K) δ 73.5 s.

2c: IR (Nujol): ν(C≡C) 2030 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 223 K): δ −9.13 (t, J(H,P) = 30.4 Hz, Ru*H*), 0.06 (s, $Si(CH_3)_3$), 1.85 (s, $C_5(CH_3)_5$), ^{31}P{^{1}H} (223 K): δ 72.4 s.

Preparation of Vinylidene Complexes [CpRu═C═CHR(dippe)][BPh$_4$] (R = COOMe, 3a; Ph, 3b; Bu^t, 3d). These compounds were obtained and recrystallized in a fashion analogous to that for the pentamethylcyclopentadienyl derivatives **1a**−**d** by starting from the appropriate amounts of [CpRuCl(dippe)]. Yield: 75−80%.

3a: Anal. Calcd for $C_{47}H_{61}BP_2O_2Ru$: C, 67.9; H, 7.34. Found: C, 67.6; H, 7.51. IR (Nujol): ν(C═C) 1641 cm^{-1}, ν(C═O) 1701 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 3.62 (s, COOCH_3), 4.91 (s, Ru═C═C*H*COOCH$_3$), 5.88 (s, C_5H_5). ^{31}P{^{1}H}: δ 97.18 s. ^{13}C{^{1}H}: δ 18.66, 18.90, 19.06, 19.25 (s, P(CH(CH_3)$_2$)$_2$), 22.85 (t, J(C,P) = 19.9 Hz, PCH_2), 30.08 (t, J(C,P) = 17.3 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 30.48 (t, J(C,P) = 12.0 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 51.17 (s, COOCH_3), 90.53 (s, C_5H_5), 112.77 (s, Ru═C═*C*HCOOMe), 337.89 (t, J(C,P) = 14.1 Hz, Ru═*C*═CHCOOMe).

3b: Anal. Calcd for $C_{51}H_{63}BP_2Ru$: C, 72.1; H, 7.42. Found: C, 72.2; H, 7.68. IR (Nujol): ν(C═C) 1624 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.22 (s, Ru═C═C*H*Ph), 5.44 (s, C_5H_5), 6.90 (t, J(H,H) = 7.4 Hz, C_6H_5), 7.14 (t, J(H,H) = 7.4 Hz, C_6H_5), 7.27 (t, J(H,H) = 7.4 Hz, C_6H_5). ^{31}P{^{1}H}: δ 97.45 s. ^{13}C{^{1}H}: δ 18.74, 18.84, 19.01, 19.27 (s, P(CH(*C*H$_3$)$_2$)$_2$), 22.72 (t, J(C,P) = 19.7 Hz, P*C*H$_2$), 30.22 (t, J(C,P) = 4.3 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 30.85 (t, J(C,P) = 4.9 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 89.60 (s, C_5H_5), 118.80 (s, Ru═C═*C*HPh), 126.57, 127.03, 128.88 (s, Ru═C═CH*C*$_6$H$_5$), 345.51 (t, J(C,P) = 15 Hz, Ru═*C*═CHPh).

3d: Anal. Calcd for $C_{49}H_{67}BP_2Ru$: C, 71.0; H, 8.08. Found: C, 70.8; H, 8.13. IR (Nujol): ν(C═C) 1648 cm^{-1}. ^{1}H NMR ($CDCl_3$): ^{1}H δ 1.08 (s, Ru═C═CHC(C*H*$_3$)), 3.84 (s br, Ru═C═C*H*CMe$_3$), 5.32 (s, C_5H_5). ^{31}P{^{1}H}: δ 96.6 s. ^{13}C{^{1}H}: δ 19.03, 19.46, 19.61 (s, P(CH(*C*H$_3$)$_2$)$_2$), 22.79 (m, P*C*H$_2$), 30.72 (m, P(*C*H(CH$_3$)$_2$)$_2$), 31.52 (m, P(*C*H(CH$_3$)$_2$)$_2$), 32.46 (s, Ru═C═CHC(*C*H$_3$)), 85.25 (s, Ru═C═*C*HCMe$_3$), 89.01 (s, *C*$_5$H$_5$), 342.05 (t, J(C,P) = 14 Hz, Ru═*C*═CHCMe$_3$).

Preparation of [CpRu═C═CH$_2$(dippe)][BPh$_4$] (3e). This compound can be prepared by the same procedure described for the vinylidene complexes **3a**−**3d**, using HC≡CSiMe$_3$. Methanolysis of the trimethylsilylvinylidene complex yields compound **3e**. Yield: *ca.* 80%. Anal. Calcd for $C_{45}H_{59}BP_2Ru$: C, 69.9; H, 7.63. Found: C, 69.6; H, 7.76. IR (Nujol): ν(C═C) 1628 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.71 (s br, Ru═C═C*H*$_2$), 5.37 (s, C_5H_5). ^{31}P{^{1}H}: δ 98.6 s. ^{13}C{^{1}H}: δ 18.80, 19.03, 19.43, 19.60 (s, P(CH(*C*H$_3$)$_2$)$_2$), 23.12 (m, P*C*H$_2$), 28.60 (m, P(*C*H(CH$_3$)$_2$)$_2$), 30.21 (m, P(*C*H(CH$_3$)$_2$)$_2$), 89.44 (s, *C*$_5$H$_5$), 99.34 (s, Ru═C═*C*H$_2$), 337.29 (t, J(C,P) = 15.1 Hz, Ru═*C*═CHCMe$_3$).

Identification in Solution of η^2-Alkyne Complexes [CpRu(η^2-HC≡CR)(dippe)][BPh$_4$] (R = COOMe, 4a; Ph, 4b). Solutions of the complex [CpRu(Me$_2$CO)(dippe)][BPh$_4$] in CD_3COCD_3, prepared under inert atmosphere in NMR tubes, were frozen by inmersion into liquid N_2. One drop of the corresponding alkyne was added. The solvent was allowed to melt. Then, the tubes were shaken, to mix the reagents, and stored in an ethanol/liquid N_2 bath. The samples prepared in this way were studied by NMR at low temperatures, as indicated.

4a: ^{1}H NMR (CD_3COCD_3) (193 K): 5.60 (s, C_5H_5), 4.47 (s br, Ru(*H*C≡CCOOMe)). ^{31}P{^{1}H} (303 K): 90.1 s. ^{31}P{^{1}H} (193 K): 89.2, 93.5 (s br).

4b: ^{1}H NMR (CD_3COCD_3) (183 K): 5.56 (s, C_5H_5), 4.49 (s br, Ru(*H*C≡CPh)). ^{31}P{^{1}H} (243 K): 88.7 s. ^{31}P{^{1}H} (183 K): 84.6, 93.5 (d, J(P,P) = 21.5 Hz).

Preparation of [CpRu(η^2-MeOOCC≡CCOOMe)(dippe)][BPh$_4$] (5). To a solution of [CpRuCl(dippe)] (0.23 g, *ca.* 0.5 mmol) in THF were added MeOOCC≡CCOOMe (0.2 g, *ca.* 0.5 mmol) and $AgBF_4$ (0.1 g). A precipitate of AgCl was formed. The mixture was stirred at room temperature for 15 min. Then, it was centrifuged, to remove AgCl. To the resulting solution was added an excess of $NaBPh_4$ (0.3 g) in ethanol (15 mL). Concentration and cooling to −20 °C afforded yellow-orange crystals. Yield: 0.27 g, 63%. Anal. Calcd for $C_{49}H_{63}P_2BO_2Ru$: C, 68.6, H 7.40. Found: C, 68.9; H, 7.28. IR (Nujol): ν(C≡C) 1857 cm^{-1}, ν(C═O) 1705 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.85 (s, Ru(C*H*$_3$OOCC≡CCOOC*H*$_3$), 5.22 (s, C_5H_5). ^{31}P{^{1}H}: δ 87.9 s. ^{13}C{^{1}H}: δ 18.66, 18.81, 18.95, 19.03 (s, P(CH(*C*H$_3$)$_2$)$_2$), 22.28 (t, J(C,P) = 19.7 Hz, P*C*H$_2$), 28.81 (t, J(C,P) = 12.4 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 31.29 (t, J(C,P) = 12 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 53.35 (s, Ru(H$_3$-*C*OOCC≡CCOOCH$_3$)), 84.87 (s br, Ru(H$_3$COOC*C*≡*C*COOCH$_3$)), 87.66 (s, C_5H_5), 163.48 (s, Ru(H$_3$COO*C*C≡C*C*OOCH$_3$)).

Preparation of [CpRu(η^2-HC≡CH)(dippe)][BPh$_4$] (4e). To a solution of [CpRuCl(dippe)] (0.23 g, 0.5 mmol) in MeOH (20 mL) was added an excess of $NaBPh_4$. Acetylene was bubbled through the mixture. A yellow microcrystalline solid precipitates almost immediately. It was filtered, washed with ethanol and petroleum ether, and dried *in vacuo*. Yield: 86%. This material appears always mixed with small amounts of the primary vinylidene complex **3e**, to which **4e** isomerizes both in the solid state (slow) and in solution (faster). For this reason, it was not analyzed, being characterized by IR and NMR spectroscopy. IR (Nujol): ν(C≡C) 1747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 243 K): δ 4.29 (t, J(H,P) = 4.6 Hz, Ru(*H*C≡C*H*), 4.80 (s, C_5H_5). ^{31}P{^{1}H}: δ 88.0 s.

Reaction of [Cp*RuCl(dippe)] with HC≡CH: [Cp*RuH(C≡CH)(dippe)][BPh$_4$] (2e), [Cp*Ru(η^2-HC≡CH)(dippe)][BPh$_4$] (6e), and [Cp*Ru═C═CH$_2$(dippe)][BPh$_4$] (1e). To a solution of [Cp*RuCl(dippe)] (0.25 g, *ca.* 0.5 mmol) in MeOH was added an excess of solid $NaBPh_4$. Acetylene was bubbled through the mixture, yielding an off-white microcrystalline precipitate, which was filtered off, washed with ethanol and petroleum ether, and dried *in vacuo*. This material showed to be a mixture of the hydrido−alkynyl complex **2e** and the η^2-alkyne adduct **6e**. Both compounds isomerize to the primary vinylidene **1e**, both in the solid state an in solution. Anal. Calcd for $C_{50}H_{69}BP_2Ru$: C, 71.2; H, 8.19. Found: C, 71.4; H, 8.08.

2e: IR (Nujol): ν(C≡C) 1965 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 223 K): δ −8.83 (t, J(H,P) = 30 Hz, Ru*H*), 2.00 (s, C(C*H*$_3$)$_5$), 2.62 (t, J(H,P) = 2.9 Hz, RuC≡C*H*), ^{31}P{^{1}H} (223 K): δ 73.2 s.

6e: IR (Nujol): ν(C≡C) 1743 cm^{-1}. ^{1}H NMR (CD_3COCD_3, 223 K): δ 1.70 (s, C(C*H*$_3$)$_5$), 4.83 (t, J(H,P) = 5.2 Hz, Ru(*H*C≡C*H*), ^{31}P-{^{1}H} (223 K): δ 74.9 s.

1e: IR (Nujol): ν(C═C) 1619 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (t, J(H,P) = 1.2 Hz, C(C*H*$_3$)$_5$), 3.49 (s br, Ru═C═C*H*$_2$). ^{31}P{^{1}H}: δ 87.0 s. ^{13}C{^{1}H}: δ 10.92 (s, C(*C*H$_3$)$_5$), 18.07, 18.79, 19.38, 19.70 (s, P(CH(*C*H$_3$)$_2$)$_2$), 21.35 (t, J(C,P) = 20 Hz, P*C*H$_2$), 25.84 (t, J(C,P) = 10.2 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 30.00 (t, J(C,P) = 16.2 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 95.99 (s, Ru═C═*C*H$_2$), 102.42 (s, *C*$_5$(CH$_3$)$_5$), 340.83 (t, J(C,P) = 14.6 Hz, Ru═*C*═CH$_2$).

Neutral Alkynyl Complexes [Cp*Ru(C≡CR)(dippe)] (R = COOMe, 7a; Ph, 7b; SiMe$_3$, 7c; Bu^t, 7d; H, 7e). A THF solution of the corresponding vinylidene complex was treated with an excess of solid KOBu^t. The mixture was stirred at room temperature for 1 h at room temperature. Then, the solvent was removed *in vacuo*. The residue was extracted with toluene and the solution filtered through Celite. Concentration, addition of petroleum ether, and cooling to −20 °C afforded crystals of these compounds.

7a: Yield: 65%. Anal. Calcd for $C_{28}H_{50}P_2O_2Ru$: C, 57.8; H, 8.66. Found: C, 57.5; H, 8.53. IR (Nujol): ν(C≡C) 2031 cm^{-1}, ν(CO) 1651 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.81 (t, J(H,P) = 1 Hz, C(C*H*$_3$)$_5$), 3.52 (s, RuC≡CCOOC*H*$_3$). ^{31}P{^{1}H}: δ 88.4 s. ^{13}C{^{1}H}: δ 11.28 (s, C(*C*H$_3$)$_5$), 18.73, 19.30, 19.63, 20.90 (s, P(CH(*C*H$_3$)$_2$)$_2$), 21.53 (t, J(C,P) = 19.9 Hz, P*C*H$_2$), 25.52 (t, J(C,P) = 8.5 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 28.87 (m, P(*C*H(CH$_3$)$_2$)$_2$), 50.54 (s, COO*C*H$_3$), 93.08 (s, *C*$_5$(CH$_3$)$_5$), 104.80 (s, RuC≡*C*COOMe), 147.12 (t, J(C,P) = 21.7 Hz, RuC≡CCOOMe).

7b: Yield: 62%. Anal. Calcd for $C_{32}H_{52}P_2Ru$: C, 64.1; H, 8.74. Found: C, 64.4; H, 8.66. IR (Nujol): ν(C≡C) 2063 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, C(C*H*$_3$)$_5$), 6.89, 7.06, 7.10 (m, RuC≡CC$_6$*H*$_5$). ^{31}P-{^{1}H}: δ 88.7 s. ^{13}C{^{1}H}: δ 11.19 (s, C(*C*H$_3$)$_5$), 18.89, 19.03, 19.51, 21.02 (s, P(CH(*C*H$_3$)$_2$)$_2$), 21.31 (t, J(C,P) = 19.5 Hz, P*C*H$_2$), 25.46 (t, J(C,P) = 7.5 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 28.31 (t, J(C,P) = 14.5 Hz, P(*C*H(CH$_3$)$_2$)$_2$), 91.91 (s, *C*$_5$(CH$_3$)$_5$), 121.85 (s, RuC≡*C*Ph), 125.04, 127.65, 129.95 (s, RuC≡C*C*$_6$H$_5$), RuC≡CC$_6$H$_5$ not observed.

7c: Yield: 60%. Anal. Calcd for $C_{29}H_{56}P_2RuSi$: C, 58.5; H, 9.47. Found: C, 58.7; H, 9.43. IR (Nujol): ν(C≡C) 1925 cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.35 (s, RuC≡CSi(C*H*$_3$)$_3$), 1.84 (t, J(H,P) = 1.2 Hz,

C(CH_3)$_5$). ^{31}P{^{1}H}: δ 88.8 s. ^{13}C{^{1}H}: δ 2.44 (s, RuC≡CSi(CH_3)$_3$), 11.32 (s, C(CH_3)$_5$), 18.97, 19.45, 19.73 (s, P(CH(CH_3)$_2$)$_2$), 21.42 (m, PCH_2), 25.42 (m, P(CH(CH$_3$)$_2$)$_2$), 28.27 (m, P(CH(CH$_3$)$_2$)$_2$), 92.01 (s, C$_5$(CH$_3$)$_5$), 110.94 (s, RuC≡C SiMe$_3$), 158.23 (t, J(C,P) = 21.3 Hz, RuC≡CSiMe$_3$).

7d: Yield: 61%. Anal. Calcd for $C_{30}H_{56}P_2Ru$ C, 62.2; H, 9.74. Found: C, 62.3; H, 9.71. IR (Nujol): ν(C≡C) 2077 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.39 (s, RuC≡CC(CH_3)$_3$), 1.87 (t, J(H,P) = 1.2 Hz, C(CH_3)$_5$). ^{31}P{^{1}H}: δ 89.2 s. ^{13}C{^{1}H}: δ 11.48 (s, C(CH_3)$_5$), 19.16, 19.34, 19.83 (s, P(CH(CH_3)$_2$)$_2$), 21.37 (t, J(C,P) = 19.5 Hz, PCH_2), 25.44 (t, J(C,P) = 7.6 Hz, P(CH(CH$_3$)$_2$)$_2$), 28.00 (t, J(C,P) = 14.5 Hz, P(CH(CH$_3$)$_2$)$_2$), 33.73 (s, RuC≡CC(CH_3)$_3$), 65.84 (s, RuC≡C C(CH$_3$)$_3$), 91.08 (s, C$_5$(CH$_3$)$_5$), 104.86 (t, J(C,P) = 22 Hz, RuC≡CCMe$_3$), 113.73 (s, RuC≡CCMe$_3$).

7e: Yield: 67%. Anal. Calcd for $C_{26}H_{48}P_2Ru$: C, 59.6; H, 9.24. Found: C, 59.4; H, 9.18. IR (Nujol): ν(CH) in the alkynyl, 3240 cm^{-1}, ν(C≡C) 1925 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.85 (s, C(CH_3)$_5$), 1.98 (t, J(H,P) = 2 Hz, Ru(C≡CH)). ^{31}P{^{1}H}: δ 88.5 s. ^{13}C{^{1}H}: δ 11.45 (s, C(CH_3)$_5$), 19.08, 19.47, 19.83 (s, P(CH(CH_3)$_2$)$_2$), 21.31 (m, PCH_2), 25.49 (m, P(CH(CH$_3$)$_2$)$_2$), 28.26 (m, P(CH(CH$_3$)$_2$)$_2$), 91.55 (s, RuC≡CH), 92.23 (s, C$_5$(CH$_3$)$_5$; RuC≡CH not observed.

Neutral Alkynyl Complexes [CpRu(C≡CR)(dippe)] (R = COOMe, 8a; Ph, 8b; Bu^t, 8d; H, 8e). These compounds were obtained following an experimental procedure identical to that for **7a**−**7e**, starting from the corresponding cyclopentadienyl vinylidene complex **3a**−**3e**.

8a: Yield: 68%. Anal. Calcd for $C_{23}H_{40}P_2O_2Ru$: C, 54.0; H, 7.88. Found: C, 54.1; H, 7.82. IR (Nujol): ν(C≡C) 2028 cm^{-1}, ν(C═O) 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.55 (s, RuC≡CCOOCH_3), 4.96 (s, RuC$_5H_5$). ^{31}P{^{1}H}: δ 100.8 s. ^{13}C{^{1}H}: δ 18.93, 19.64, 19.75, 20.46 (s, P(CH(CH_3)$_2$)$_2$), 23.66 (t, J(C,P) = 19.8 Hz, PCH_2), 27.33 (t, J(C,P) = 14.5 Hz, P(CH(CH$_3$)$_2$)$_2$), 29.36 (t, J(C,P) = 10.7 Hz, P(CH(CH$_3$)$_2$)$_2$), 51.19 (s, COOCH_3), 80.79 (s, C$_5$H$_5$), 104.07 (s, RuC≡CCOOMe), 126.74 (m, RuC≡CCOOMe).

8b: Yield: 69%. Anal. Calcd for $C_{27}H_{42}P_2Ru$: C, 61.2; H, 7.99. Found: C, 61.1; H, 7.91. IR (Nujol): ν(C≡C) 2069 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.94 (s, RuC$_5H_5$), 6.89−7.10 (m, RuC≡CC$_6H_5$). ^{31}P{^{1}H}: δ 102.1 s. ^{13}C{^{1}H}: δ 18.85, 19.82, 19.89, 20.65 (s, P(CH(CH_3)$_2$)$_2$), 23.90 (t, J(C,P) = 19.7 Hz, PCH_2), 27.27 (m, P(CH(CH$_3$)$_2$)$_2$), 29.36 (m, P(CH(CH$_3$)$_2$)$_2$), 79.74 (s, C$_5$H$_5$), 109.53 (s, RuC≡C Ph), 118.42 (t, J(C,P) = 23.3 Hz, RuC≡CPh), 122.48, 127.62, 130.33,-151.00 (s, RuC≡CC$_6$H$_5$).

8d: Yield: 57%. Anal. Calcd for $C_{25}H_{46}P_2Ru$: C, 58.9; H, 9.10. Found: C, 58.7; H, 9.06. IR (Nujol): ν(C≡C) 2089 cm^{-1}. ^{1}H NMR-(C_6D_6): δ 1.34 (s, RuC≡CC(CH_3)$_3$), 4.87 (s, RuC$_5H_5$). ^{31}P{^{1}H}: δ 103.6 s. ^{13}C{^{1}H}: δ 18.26, 19.45, 19.62, 20.86 (s, P(CH(CH_3)$_2$)$_2$), 23.97 (m, PCH_2), 27.15 (m, P(CH(CH$_3$)$_2$)$_2$), 28.93 (m, P(CH(CH$_3$)$_2$)$_2$), 33.02 (s, RuC≡CC(CH_3)$_3$), 79.33 (s, C$_5$H$_5$), 114.28 (s, RuC≡CCMe$_3$), 125.21 (m, RuC≡CCMe$_3$).

8e: Yield: 70%. Anal. Calcd for $C_{21}H_{38}P_2Ru$: C, 55.6; H, 8.44. Found: C, 55.5; H, 8.52. IR (Nujol): ν(C≡C) 1930 cm^{-1}; ν(C−H) in the alkynyl, 3285 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.79 (t, J(H,P) = 1.96 Hz, RuC≡CH), 4.92 (s, RuC$_5H_5$). ^{31}P{^{1}H} 101.0 s. ^{13}C{^{1}H} 18.93, 19.87, 19.99, 21.18 (s, P(CH(CH_3)$_2$)$_2$), 23.95 (t, J(C,P) = 19.7 Hz, PCH_2), 27.38 (t, J(C,P) = 14.6 Hz, P(CH(CH$_3$)$_2$)$_2$), 29.44 (t, J(C,P) = 10.2 Hz, P(CH(CH$_3$)$_2$)$_2$), 80.05 (s, C$_5$H$_5$), 94.22 (s, RuC≡CH), 128.30 (m, RuC≡CH).

Kinetics Studies of the Hydrido-Alkynyl or η^2-Alkyne to Vinylidene Isomerization. Samples of the corresponding hydrido−alkynyl or η^2-alkyne complex, prepared as described above, were immersed into a liquid N_2/ethanol bath, to "freeze" the isomerization process during transport and handling. The sample was removed from the bath and inserted into the precooled probe of the Varian UNITY-400 spectrometer at 203 K. Once shims were adjusted, the probe was warmed to the desired temperature. The NMR temperature controller was previously calibrated against a methanol sample, the reproducibility being ±0.5 °C. ^{31}P{^{1}H} NMR spectra were recorded for at least 3 half-lives at regular intervals using the spectrometer software for accurate time control. Peak intensities were analyzed from stacked plots of the ^{31}P{^{1}H} NMR spectra. First-order rate constants were derived from the least-squares best-fit lines of the ln(intensity) *versus* time plots. The uncertainty in the isomerization rate constants represents one standard deviation (±σ) derived from the slope of the best fit line. Uncertainties in the activation enthalpies and entropies were calculated from the uncertainties in the slope and intercept of the best-fit lines of the Eyring plots.

Table 1. Summary of Data for the Crystal Structure Analysis of **1a** and **2a**

	1a	**2a**
formula	$C_{52}H_{71}BO_2P_2Ru$	$C_{52}H_{71}BO_2P_2Ru$
fw	901.96	901.96
crystal size (mm)	0.28 × 0.10 × 0.17	0.20 × 0.08 × 0.45
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
cell parameters	a = 13.275(2) Å	a = 16.167(6) Å
	b = 14.672(3) Å	b = 28.707(4) Å
	c = 12.172(2) Å	c = 10.257(6) Å
	α = 96.81(2)°	
	β = 91.09(1)°	
	γ = 94.36(1)°	
volume (Å^3)	2350.9(7)	4760(5)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.274	1.258
λ(Mo Kα) (Å)	0.71069	0.71069
μ(Mo Kα) (cm^{-1})	4.30	4.25
F(000)	956	1912
transmision factors	0.86−1.00	0.92−1.00
scan speed (ω) (deg min^{-1})	8	8
2θ interval	5° < 2θ < 50°	5° < 2θ < 50°
no. of measured reflections	7516	3880
no. of unique reflections	7201 (R_{int} = 0.052)	3733 (R_{int} = 0.150)
no. of obsd reflns ($I > 3\sigma_I$)	4322	2821
no. of parameters	495	383
refln/parameter ratio	8.73	7.37
R^a	0.058	0.064
R_w ($w = \sigma_F^{-2}$)^b	0.069	0.073
maximum Δ/σ in final cycle	5.70	0.02
GOF	1.69	1.53

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Experimental Data for the X-ray Crystal Structure Determinations. A summary of crystallographic data for compounds **1a** and **2a** is given in Table 1. X-ray measurements were made on crystals of the appropriate size, which were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo Kα graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the $\omega-2\theta$ scan method for compound **1a** and the ω scan method for **2a**. Lorentz, polarization, and absorption (ψ-scan method) corrections were applied. A small decay correction was also applied for each of the compounds. Reflections having $I > 3\sigma(I)$ were used for structure refinement. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[19] software system and ORTEP[20] for plotting. All the structures were solved by the Patterson method and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. The hydride atom in compound **2a** was located on a regular difference Fourier map, and it was not refined. Most of the other hydrogen atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.95 and −0.80 e Å^{-3} for **1a** and +0.60 and −0.94 e Å^{-3} for **2a**. Selected bond lengths and angles for each compound are listed in Tables 2 and 3.

Results

The complex [Cp*RuCl(dippe)] reacts readily with 1-alkynes in MeOH at room temperature yielding the corresponding vinylidene complexes [Cp*Ru═C═CHR(dippe)]$^+$ (R = COOMe, **1a**; Ph, **1b**; SiMe$_3$, **1c**; Bu^t, **1d**), isolable as tetraphenylborate salts. These are crystalline solids, soluble in polar organic solvents except alcohols, which display one strong ν(C═C) band

(19) *TEXSAN, Single-Crystal Structure Analysis Software*, version 5.0, Molecular Structure Corp., Texas, 1989.

(20) Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory; Oak Ridge, TN, 1965.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cp*Ru=C=CHCOOMe(dippe)][BPh_4]

Intramolecular Distances[a]

atom	atom	distance	atom	atom	distance
Ru(1)	P(1)	2.348(2)	Ru(1)	C(4B)	2.32(2)
Ru(1)	P(2)	2.380(2)	Ru(1)	C(5A)	2.42(2)
Ru(1)	C(1A)	2.26(2)	Ru(1)	C(5B)	2.36(2)
Ru(1)	C(1B)	2.26(2)	Ru(1)	C(11)	1.807(9)
Ru(1)	C(2A)	2.30(2)	O(1)	C(13)	1.19(1)
Ru(1)	C(2B)	2.23(2)	O(2)	C(13)	1.34(1)
Ru(1)	C(3A)	2.31(2)	O(2)	C(14)	1.46(1)
Ru(1)	C(3B)	2.24(2)	C(11)	C(12)	1.32(1)
Ru(1)	C(4A)	2.44(2)	C(12)	C(13)	1.46(1)

Intramolecular Bond Angles[b]

atom	atom	atom	angle
P(1)	Ru(1)	P(2)	82.50(8)
P(1)	Ru(1)	C(11)	90.1(3)
P(2)	Ru(1)	C(11)	93.7(3)
C(13)	O(2)	C(14)	115.1(8)
Ru(1)	C(11)	C(12)	170.5(8)
C(11)	C(12)	C(13)	129(1)
O(1)	C(13)	O(2)	124(1)
O(1)	C(13)	C(12)	125(1)
O(2)	C(13)	C(12)	111.7(8)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses. [b] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Cp*RuH(C≡CCOOMe)(dippe)][BPh_4]

Intramolecular Distances

atom	atom	distance	atom	atom	distance
Ru(1)	P(1)	2.340(4)	Ru(1)	C(5)	2.25(2)
Ru(1)	P(2)	2.342(5)	Ru(1)	C(11)	2.04(2)
Ru(1)	C(1)	2.30(2)	Ru(1)	H(1)	1.35
Ru(1)	C(2)	2.26(2)	C(11)	C(12)	1.18(2)
Ru(1)	C(3)	2.24(2)	C(12)	C(13)	1.43(3)
Ru(1)	C(4)	2.25(2)			

Intramolecular bond angles

atom	atom	atom	angle
P(1)	Ru(1)	P(2)	87.5(2)
P(1)	Ru(1)	C(1)	161.6(5)
P(1)	Ru(1)	C(2)	142.2(5)
P(1)	Ru(1)	C(3)	108.6(5)
P(1)	Ru(1)	C(4)	102.0(5)
P(1)	Ru(1)	C(5)	126.8(5)
P(1)	Ru(1)	C(11)	80.9(5)
P(1)	Ru(1)	H(1)	52.48
P(2)	Ru(1)	C(1)	106.6(5)
P(2)	Ru(1)	C(2)	124.2(5)
P(2)	Ru(1)	C(3)	160.7(5)
P(2)	Ru(1)	C(4)	151.9(5)
P(2)	Ru(1)	C(5)	117.1(6)
P(2)	Ru(1)	C(11)	82.3(5)
P(2)	Ru(1)	H(1)	67.78
C(11)	Ru(1)	H(1)	123.75
Ru(1)	C(11)	C(12)	175(2)
C(11)	C(12)	C(13)	173(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses. [b] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

near 1600 cm^{-1} in their IR spectra. The ^1H NMR spectra show the signal corresponding to the proton on the β-carbon of the vinylidene ligands as one triplet or broad singlet in the range 3−5 ppm, a pattern which has also been observed for other half-sandwich ruthenium phosphine vinylidene complexes of the type $[CpRu{=}C{=}CHR(P)_2]^+$ (Cp = C_5H_5 or C_5Me_5; P_2 = one bidentate or two monodentate phosphine ligands).[11−13,21,22] The carbon atom of the vinylidene ligand directly attached to

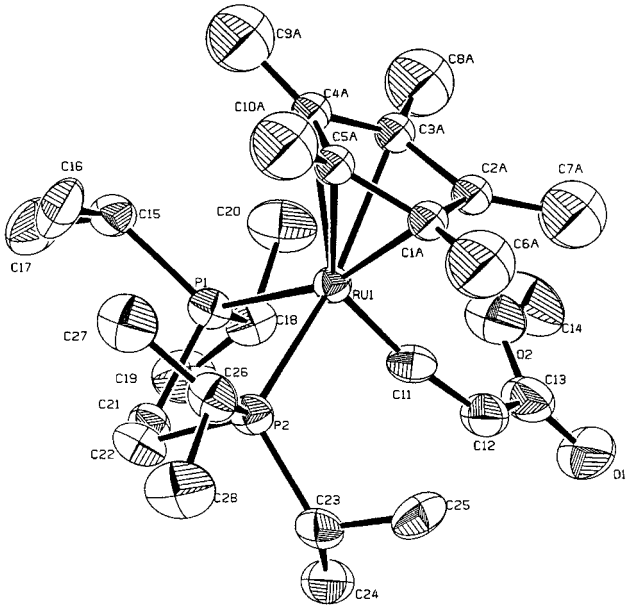


Figure 1. ORTEP drawing of the cation [Cp*Ru=C=CHCOOMe-(dippe)]$^+$ with 50% probability thermal ellipsoids.

ruthenium (C_α) appears as a very low resonance, near 350 ppm, in the $^{13}C\{^1H\}$ NMR spectra. This strongly deshielded resonance for C_α is a characteristic feature of vinylidene complexes, being due to the sign and magnitude of the paramagnetic contributions to nuclear shielding.[23] One singlet is observed in the $^{31}P\{^1H\}$ NMR spectra of these compounds, suggesting the equivalence of the phosphorus atoms. These spectral data are consistent with a three-legged piano-stool structure for these complexes, as has been observed for other related derivatives. The X-ray crystal structure of compound **1a** has been determined. An ORTEP view of the cation [Cp*Ru=C=CHCOOMe-(dippe)]$^+$ is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The ruthenium atom appears in a formally octahedral coordination, in which the Cp* ligand fills three coordination positions, the other three being occupied by the two phosphorus atoms of the chelating dippe, and by the C_α atom of the (methoxycarbonyl)vinylidene group. The Ru−C(11) bond distance of 1.807(9) Å corresponds to a double bond, and it is shorter than the reported Ru−C separations for cyclopentadienylruthenium vinylidene complexes, i.e. 1.845-(7) Å in $[CpRu{=}C{=}CHMe(PMe_3)_2][PF_6]$[22] or 1.843(1) Å in $[CpRu{=}C{=}CH_2(PMe_2Ph)_2][BF_4]$,[11] being slightly longer than that in one of the few structurally characterized Cp*Ru vinylidene complexes, 1.76(1) Å in $[Cp^*Ru{=}C{=}CH_2(PMe_2Ph)_2][PF_6]$.[13] These parameters are indicative of an increased electron-releasing capability of Cp^*RuP_2 moieties compared to that for their Cp counterparts. The C(11)−C(12) bond distance, 1.32(1) Å, corresponds to a double bond and compares well with previously reported data. The vinylidene group assembles almost linearly with the Ru atom, having a Ru−C(11)−C(12) angle of 170.5(8)°.

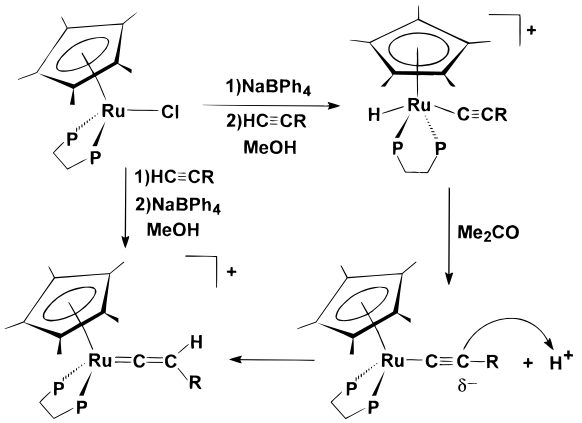
Whereas vinylidene complexes **1a**−**d** are obtained by reaction of [Cp*RuCl(dippe)] with the corresponding 1-alkyne in MeOH, followed by $NaBPh_4$, if the order in which the reagents are added is reversed, different products are isolated. Thus, if $NaBPh_4$ is added first, and then the 1-alkyne, a white microcrystalline precipitate is formed almost immediately. These materials

(21) Consiglio, G.; Morandini, F. *Inorg. Chim. Acta* **1987**, *127*, 79. Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976.

(22) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.

(23) Czech, P. T.; Xe, X.-Q.; Fenske, R. F. *Organometallics* **1990**, *9*, 2016.

Scheme 1. Suggested Reaction Sequence for the Alkyne to Vinylidene Isomerization through Hydrido−Alkynyl Complexes $[Cp^*RuH(C{\equiv}CR)(dippe)]^+$



display one strong band near 2100 cm^{-1} in their IR spectra attributable to $\nu(C{\equiv}C)$ and consistent with the formation of the hydrido−alkynyl complexes $[Cp^*RuH(C{\equiv}CR)(dippe)][BPh_4]$ (R = COOMe, **2a**; Ph, **2b**; $SiMe_3$, **2c**) (Scheme 1). In the case of R = ^{t}Bu, the only product isolated is always the vinylidene complex **1d**, irrespective of the order in which the reagents are added. The hydrido−alkynyl complexes **2a**−**c** are formally derived from the insertion of the metal atom into the C−H bond of the 1-alkyne and, therefore, must be considered Ru^{IV} (d^4) species. These compounds rearrange to their respective vinylidene isomers **1a**−**c** when they are dissolved in acetone, dichloromethane, or tetrahydrofuran at room temperature. Furthermore, this isomerization takes place also in the solid state for compounds **2b**,**c** at room temperature, but not for **2a**, which seems to be stable as a solid at this temperature. A solid state hydrido−alkynyl to vinylidene rearrangement has been recently observed for cobalt and rhodium complexes, i.e. the transformation of $[CoH(C{\equiv}CR)(pp_3)][BPh_4]$ to $[Co{=}C{=}CHR(pp_3][BPh_4]$[7] or $[RhCl(H)(C{\equiv}CSiMe_3)(P^iPr_3)_2]$ to $[Rh{=}C{=}CHSiMe_3(Cl)(P^iPr_3)_2]$,[24] but this is the first report of such process involving ruthenium. The isomerization is stopped at low temperatures, both in the solid state and in solution. Therefore, it is possible to obtain the NMR of **2a**−**c** by dissolving the complexes in acetone-d_6 at −50 °C. The hydride resonance appear as one high-field triplet in the ^1H NMR spectra, whereas the $^{31}P\{^1H\}$ consists of one sharp singlet. The spectral data are consistent with a transoid "four-legged" piano-stool structure for these compounds. The isomerization to vinylidene in solution prevented initially to grow crystals of these materials, until we discovered that the rearrangement process is inhibited in solution by small amounts of a strong acid, such as $HBF_4{\cdot}OEt_2$. In this fashion, careful recrystallization of **2a** from THF/ethanol in the presence of one drop of $HBF_4{\cdot}OEt_2$ afforded colorless crystals, which were subjected to X-ray structure analysis, taking advantage of the stability as solid of this compound, which does not isomerize at room temperature. An ORTEP view of the cation $[Cp^*RuH(C{\equiv}CCOOMe)(dippe)]^+$ is shown in Figure 2. Selected bond lengths and angles are listed in Table 3. The complex cation has a transoid "four-legged" piano-stool structure, consistent with spectral data. The P(1)−Ru(1)−P(2) plane forms an angle of 101.21° with the plane defined by the C_5 ring of the Cp* group. This arrangement is very similar to that adopted by ruthenium dihydrides such as $[Cp^*RuH_2(dippe)][BPh_4]$[18] and $[CpRuH_2(PMe_3)_2][BF_4]$,[25] but in our case, the angle deviates from the ideal value of 90°, possibly to minimize steric

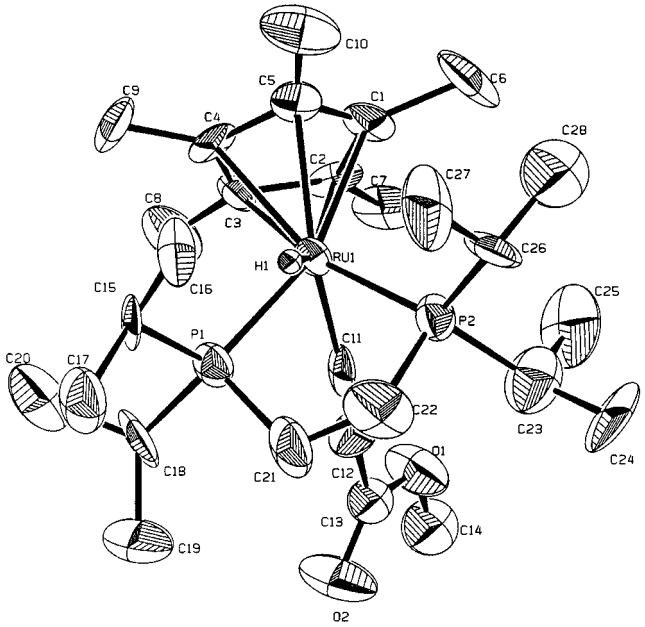


Figure 2. ORTEP drawing of the cation $[Cp^*RuH(C{\equiv}CCOOMe)(dippe)]^+$ with 50% probability thermal ellipsoids. Hydrogen atoms, except hydride, are omitted.

interactions with the substituents of the alkynyl group. This ligand appears linearly assembled to ruthenium, with a Ru(1)−C(11)−C(12) angle of 175(2)°. The bond lengths Ru(1)−C(11), 2.04(2) Å and C(11)−C(12), 1.18(2) Å, compare well with those found in the only structurally characterized ruthenium hydrido−alkynyl complex, *cis*-$[RuH(C{\equiv}CPh)(pp_3)]{\cdot}C_6H_6$, 2.078 and 1.16(1) Å, respectively.[26] These parameters also match those found in the alkynyl−dihydrogen complex $[Ru(H_2)(C{\equiv}CPh)(dippe)_2][BPh_4]$, 2.01(1) and 1.19(2) Å.[27] The hydride atom was localized in a Fourier difference map, and it was not refined. The Ru(1)−H(1) separation was found to be 1.35 Å, rather short compared to 1.57(8) Å in *cis*-$[RuH(C{\equiv}CPh)(pp_3)]{\cdot}C_6H_6$,[26] but similar to the values reported for other ruthenium hydride complexes, such as $[CpRuH(PMe_3)_2]$ (1.36(8) Å)[25] or $[RuH(C_6H_6)(dippe)][BPh_4]$ (1.32 Å).[28] All other bond lengths and angles are in the expected range and are unexceptional. The kinetics of the hydrido−alkynyl to vinylidene isomerization have been studied by NMR spectroscopy, following an experimental procedure analogous to that used by Chinn and Heinekey for the study of the dihydrogen to dihydride tautomerization in half-sandwich ruthenium complexes.[29] Samples of complexes **2a**−**c** were prepared in acetone-d_6 at −80 °C, and then inserted into the spinner and lowered into the NMR precooled probe. At temperatures below −50 °C, the main product observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy was almost exclusively the hydrido−alkynyl tautomer, being also present very minor amounts of the corresponding vinylidene complex. As the temperature rises, the signals corresponding to the hydrido−alkynyl species decrease and the signals attributable to the vinylidene tautomer increase their intensities with time. Kinetic data acquired following the rate of disappearance of the phosphorus resonance of the hydrido−alkynyl complex in the $^{31}P\{^1H\}$ NMR spectra were consistent with a first-order process. Data were collected over 3 half-lives or more at different temperatures, and rate constants were obtained from the slope of the least-squares best-fit lines of the ln(intensity) *vs* time

(24) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089.
(25) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980.
(26) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.
(27) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1750.
(28) de los Ríos, I.; Jiménez-Tenorio, M.; Jiménez-Tenorio, M. A.; Puerta, M.C.; Valerga, P. *J. Organomet. Chem.* **1996**, *525*, 57.
(29) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *113*, 5166.

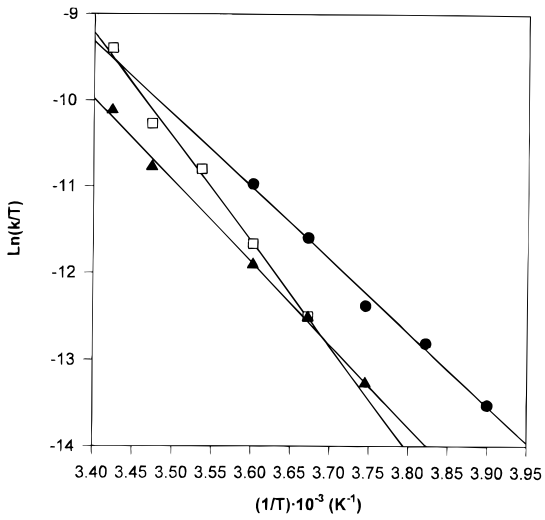
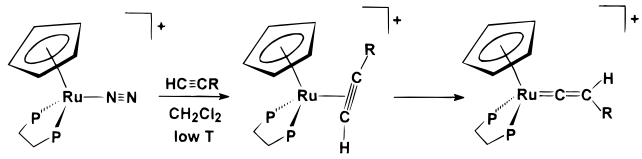


Figure 3. Plot of ln(k/T) vs $1/T$ (K^{-1}) for the irreversible isomerization of [Cp*RuH(C≡CR)(dippe)]$^+$ to [Cp*Ru=C=CHR(dippe)]$^+$ (R = COOMe (●); $SiMe_3$ (▲); Ph (□)).

Table 4. Activation Parameters for the Hydrido−Alkynyl to Vinylidene and η^2-Alkyne to Vinylidene Rearrangements Studied in this Work

process	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (kcal mol^{-1})	ΔG^{298} (kcal mol^{-1})
2a → 1a	17 ± 1	−9 ± 1	20 ± 1
2b → 1b	24 ± 1	17 ± 1	19 ± 1
2c → 1c	21 ± 2	4 ± 1	20 ± 2
4a → 3a	26.6 ± 0.5	21 ± 1	20.3 ± 0.5
4e → 3e	29 ± 2	26 ± 1	21 ± 2
2e → 1e	25 ± 2	10 ± 1	22 ± 2
6e → 1e	26 ± 2	12 ± 1	22 ± 2

plots. These constants are invariant with the starting concentration of the complex. The rate constants at 273 K are (2.5 ± 0.3) × 10^{-3} s^{-1} for the isomerization of **2a**, (1.01 ± 0.02) × 10^{-3} s^{-1} for **2b**, and (1.0 ± 0.3) × 10^{-3} s^{-1} for **2c**. Thus, the rearrangement is faster for **2a**, which bears on the alkynyl ligand the R group having the most electron-attracting effect. Activation parameters for these systems were derived from an Eyring plot for each of the series of rate constants determined at different temperatures (Figure 3), yielding values which are listed in Table 4. It has been previously noted for the isomerization of hydrido−alkynyl complexes of cobalt that the activation energy of the rate-determining step seems to be influenced by the 1-alkyne substituent.[7] This fact, together with the lack of data in the literature apart from those on the cobalt system, makes difficult the comparison of the thermodynamic functions. However, the values obtained for **2b** are similar in magnitude to those for the rearrangement of [CoH(C≡CPh)(pp$_3$)][BPh_4] to [Co=C=CHPh(pp$_3$)][BPh_4] ($\Delta H^{\ddagger}$ = 31 ± 1 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 28 ± 1 cal K^{-1} mol^{-1}, ΔG^{298} = 22 ± 2 kcal mol^{-1}).[7] No hydrido−alkynyl complexes have been isolated or detected in the reaction of the cyclopentadienyl derivative [CpRuCl(dippe)] with 1-alkynes, and only vinylidene species [CpRu=C=CHR(dippe)][BPh_4] (R = COOMe, **3a**; Ph, **3b**; Bu^t, **3d**) have been obtained. These vinylidene complexes have spectral properties which match those of their Cp* homologues, including the presence of one ν(C=C) band in the IR spectra and of one low-field signal in the $^{13}C\{^1H\}$ NMR spectra due to the C_α of the vinylidene group. The structure for these compounds is hence assumed to be similar to that found by X-ray diffraction for **1a**, but having Cp instead of Cp*. It is interesting to note that, in the course of the reaction of [CpRuCl(dippe)] with HC≡$CSiMe_3$, the C−Si bond is cleaved, presumably by the alcohol used as the solvent, yielding the primary vinylidene complex [CpRu=C=CH_2(dippe)][BPh_4] (**3e**) as the final product of this reaction. This behavior has precedents in the literature, i.e. the formation of [CpFe=C=CH_2(dppm)][BF_4] from [CpFeC≡$CSiMe_3$(dppm)],[30] but this process does not occur for the related Cp* complex **1c**, which is stable. None of the vinylidene complexes prepared in this work react with alcohols to yield alkoxy−carbene species, as it commonly occurs in other cases.[31] The fact that no Cp hydride−alkynyl derivatives were isolated indicates that, if these are intermediates in the formation of the corresponding vinylidene complexes, they should be short-lived species that rearrange at room temperature before precipitation as tetraphenylborate salts takes place. In an attempt to detect possible intermediates, the reaction of 1-alkynes with the labile acetone adduct [CpRu(Me_2CO)(dippe)][BPh_4][18] at low temperature was monitored by NMR spectroscopy. This compound was chosen because it has shown to be an excellent precursor for the preparation of complexes [CpRu(L)(dippe)]$^+$ (L = neutral donor molecule), being readily converted to the dinitrogen complex [CpRu(N_2)(dippe)]$^+$ in dichloromethane solution under N_2.[18] Thus, upon addition of HC≡CR (R = COOMe, Ph) and examination of the CD_2Cl_2 solution by $^{31}P\{^1H\}$ NMR spectroscopy at −50 °C, the resonances due to the dinitrogen adduct dissappear, being replaced by a new, broad signal which does not correspond to the vinylidene complex. This signal splits into two separate broad resonances when the temperature is lowered. For phenylacetylene, these resonances resolve into doublets at 183 K, having a J(P,P) coupling constant of 21.5 Hz (Figure 4). No signals attributable to hydridic protons were observed in the relevant region of the ^1H NMR spectrum. These spectral data are consistent with the formation in solution of the π-alkyne adducts [CpRu(η^2-HC≡CR)(dippe)]$^+$ (R = COOMe, **4a**; Ph, **4b**).



The fluxional behavior arises from the rotation of the 1-alkyne ligand around the metal−carbon bond. When the temperature decreases, this movement is "frozen", causing the nonequivalence of the phosphorus atoms. The rotation barrier around the Ru−alkyne bond has been estimated from the variable-temperature $^{31}P\{^1H\}$ NMR data,[32] being 8 kcal mol^{-1} for **4a** and 11 kcal mol^{-1} for **4b**. All attempts to isolate these π-alkyne complexes as solids were unsuccessful, due to the fact that they rearrange irreversibly to their vinylidene isomers **3a**,**3b** as temperature is raised. At variance with the hydrido−alkynyl complexes, addition of a strong acid does not inhibit these rearrangement processes in solution. The kinetics of the isomerization **4a** → **3a** was studied by NMR spectroscopy. The process is first order, with rate constants varying from (6.1 ± 0.1) × 10^{-4} s^{-1} at 283 K to (1.4 ± 0.1) × 10^{-2} s^{-1} at 303 K. From the studies at different temperatures activation parameters were obtained (Figure 5): $\Delta H^{\ddagger}$ = 26.6 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 21 ± 1 cal K^{-1} mol^{-1}, and ΔG^{298} = 20.3 ± 0.5 kcal mol^{-1}. These values, which appear also in Table 4, resemble those

(30) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Blanca, M. M. *Organometallics* **1992**, *11*, 1373.

(31) Bruce. M. I.; Duffy, D. N.; Humphrey, M. G.; Swincer, A. G. *J. Organomet. Chem* **1985**, *282*, 383. Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis R. C. *Aust. J. Chem.* **1980**, *33*, 2605. Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.

(32) Günther, H. *NMR Spectroscopy*, 2nd ed.; John Wiley & Sons: Chichester, U.K., 1995.

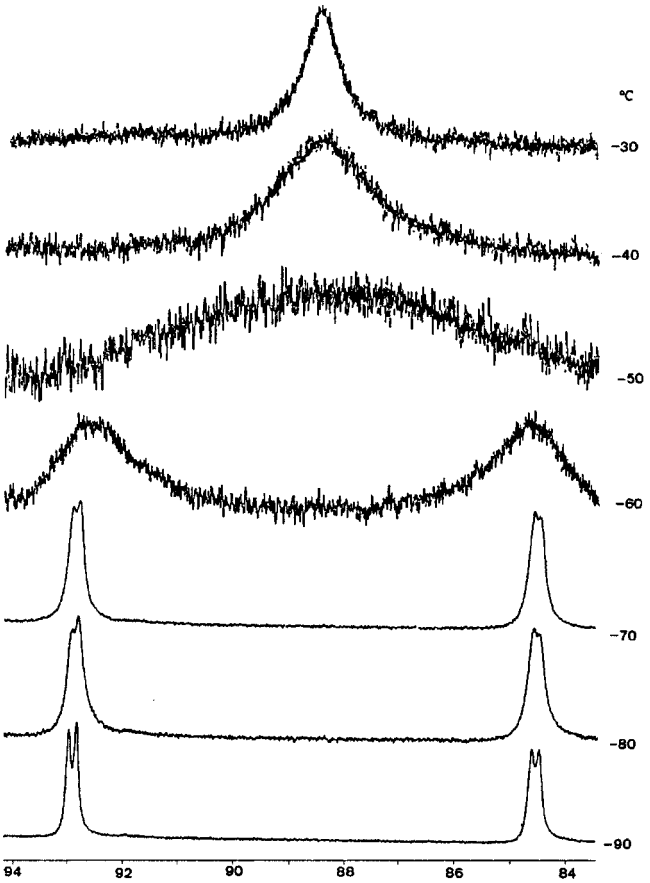


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectrum of [CpRu(η^2-HC≡CPh)(dippe)][BPh_4] (**4b**) in CD_2Cl_2.

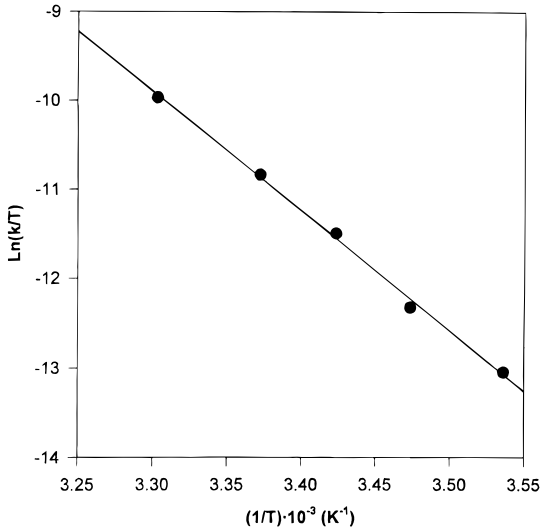


Figure 5. Plot of ln(*k*/*T*) vs 1/*T* (K^{-1}) for the irreversible isomerization of [CpRu(η^2-HC≡CCOOMe)(dippe)]$^+$ to [CpRu=C=CHCOOMe-(dippe)]$^+$.

found for the isomerization of [CpRu(HC≡CMe)(PMe_3)$_2$]$^+$ to [CpRu=C=CHMe(PMe_3)$_2$]$^+$ in MeCN ($\Delta H^{\ddagger} = 23.4 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = 3.9 \pm 0.9$ cal K^{-1} mol^{-1}, and $\Delta G^{298} = 22 \pm 1$ kcal mol^{-1}). For comparison purposes, the stable π-alkyne complex [CpRu(η^2-MeOOCC≡CCOOMe)(dippe)][BPh_4] (**5**) been prepared and characterized in full as a model for the spectral properties of this sort of compounds. **5** was obtained by reaction of [CpRuCl(dippe)] with MeOOCC≡CCOOMe in the presence of $AgBF_4$ acting as chloride scavenger. This compound displays one medium IR band at 1857 cm^{-1} due to ν(C≡C) of the η^2-alkyne ligand, together with another at 1705 cm^{-1} attributable to ν(C=O) in the ester group. The $^{31}P\{^1H\}$ NMR spectrum consists of one singlet at 87.9 ppm, whereas the carbon atoms of the MeOOCC≡CCOOMe group directly attached to Ru appear as one broad signal at 84.87 ppm in the $^{13}C\{^1H\}$ NMR spectrum. No analogous compound has been obtained having Cp* as coligand. Furthermore, no π-alkyne complexes were detected in the course of the reaction of [Cp*Ru(η^2-C_2H_4)(dippe)][BPh_4],[18] which dissociates ethylene very easily, with 1-alkynes at low temperature. The only product observed was the corresponding hydrido−alkynyl derivative, which rearranges to its vinylidene isomer at higher temperatures. These data suggest that the formation of metastable hydrido−alkynyl intermediates is only feasible in the case of Cp* complexes and that for Cp compounds a more standard direct isomerization occurs from the π-alkyne adduct to the corresponding vinylidene complex, consistent with data reported in the literature for other ruthenium complexes.

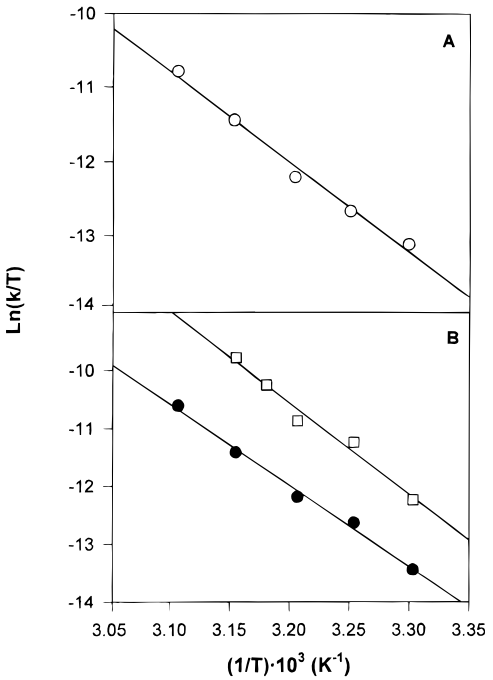
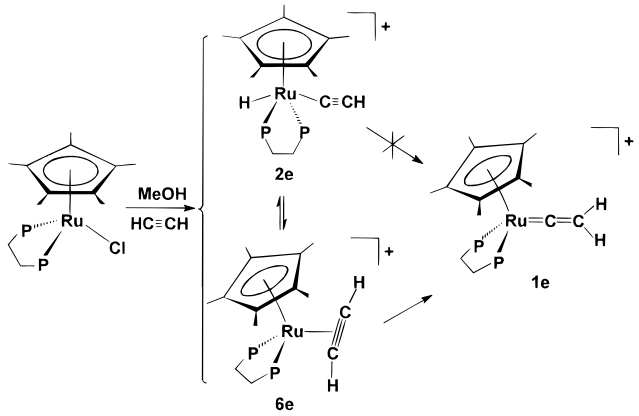


Figure 6. Plot of ln(*k*/*T*) vs 1/*T* (K^{-1}) for the irreversible isomerization of (A) [Cp*RuH(C≡CH)(dippe)]$^+$ to [Cp*Ru=C=CH_2(dippe)]$^+$ (○); (B) [Cp*Ru(η^2-HC≡CH)(dippe)]$^+$ to [Cp*Ru=C=CH_2(dippe)]$^+$ (●); [CpRu(η^2-HC≡CH)(dippe)]$^+$ to [CpRu=C=CH_2(dippe)]$^+$ (□).

The reaction of both [CpRuCl(dippe)] and [Cp*RuCl(dippe)] with acetylene, HC≡CH, deserves a separate, detailed comment. When acetylene is bubbled through a solution of [CpRuCl-(dippe)] in MeOH containing $NaBPh_4$, a precipitate of [CpRu-(η^2-HC≡CH)(dippe)][BPh_4] (**4e**) is immediately obtained. This compound displays one medium IR band at 1747 cm^{-1} corresponding to ν(C≡C) in the η^2-alkyne ligand. The acetylene protons appear in the ^1H NMR spectrum as one triplet at 4.29 ppm, J(H,P) = 4.6 Hz, whereas one singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum. **4e** rearranges to the primary vinylidene complex **3e** both in the solid state and in solution. The rate of rearrangement was measured in solution by $^{31}P\{^1H\}$ NMR spectroscopy, the half-life being 7.9 min at 30 °C, with the activation parameters (Figure 6) shown in Table 4. This process is slower than the isomerization of the π-alkyne adduct **4a** to **3a**, but much faster than similar rearrangements reported in the literature, i.e. [CpRu(η^2-HC≡CH)(PMe_2Ph)$_2$]$^+$ to [CpRu=C=CH_2(PMe_2Ph)$_2$]$^+$ ($t_{1/2}$ = 18 min at 65 °C)[11] or [CpRu(η^2-HC≡CH)(PMe_3)$_2$]$^+$ to [CpRu=C=CH_2(PMe_3)$_2$]$^+$ ($t_{1/2}$ = 5 h at 60 °C).[12]

The product of the reaction of [Cp*RuCl(dippe)] with acetylene in MeOH containing $NaBPh_4$ is a white microcrystalline material which showed to be a mixture of two isomers,

Scheme 2. Interaction of [Cp*RuCl(dippe)] with HC≡CH

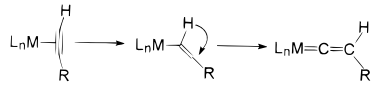


namely the hydrido−alkynyl derivative [Cp*RuH(C≡CH)(dippe)][BPh_4] (**2e**), and the π-alkyne complex [Cp*Ru(η^2-HC≡CH)(dippe)][BPh_4] (**6e**), as inferred from IR and NMR spectral data. Thus, the IR spectrum of this mixture displays bands at 1965 and 1743 cm^{-1} attributable to ν(C≡C) in the hydrido−alkynyl **2e** and π-alkyne **6e**, respectively. The hydride proton of **2e** appears as one triplet at −8.83 ppm in the ^1H NMR spectrum (223 K, acetone-d_6), a pattern similar to that observed for the related hydrido−alkynyl derivatives **2a**−**c**, whereas another triplet at 4.83 ppm, with a smaller coupling constant J(H,P) = 5.2 Hz, corresponds to the protons of the η^2-alkyne ligand. The $^{31}P\{^1H\}$ NMR spectrum displays one singlet for each of the isomers, as expected. Both **2e** and **6e** rearrange to the primary vinylidene [Cp*Ru=C=CH_2(dippe)][BPh_4] (**1e**) in the solid state and in solution. The rearrangement in the solid state is faster for **6e** than for **2e**, and this allows us to obtain solid samples containing only **2e** and **1e,** by just leaving the mixture standing at room temperature for some time. The $^{31}P\{^1H\}$ NMR spectrum of these samples at −50 °C showed initially signals due to the hydrido−alkynyl and vinylidene complexes, but at higher temperatures, the π-alkyne complex **6e** is formed at the expense of **2e**. This observation is supported also by spin saturation transfer experiments. The rearrangement of **2e** and **6e** to **1e** occurs at essentially the same rate, the half-life being 26 min at 303 K. The activation parameters, listed in Table 4, have identical values within the experimental error (Figure 6). At difference with the other hydrido−alkynyl to vinylidene isomerizations presented in this work, the rearrangement **2e** → **1e** does not seem to be inhibited by strong acids. All of these observations suggest that there is possibly an equilibrium between the hydrido−alkynyl and π-alkyne isomers, which is however difficult to study due to the irreversible isomerization to vinylidene. The equilibrium is shifted to the hydrido−alkynyl tautomer, since this is the most abundant species in the mixture in all cases. However, the observed rate of isomerization corresponds probably to that of the π-alkyne adduct. If we assume that this process occurs faster than the direct isomerization of **2e** to vinylidene, this compound would convert to **6e** to maintain the equilibrium and, hence, its rate of disappearance would be the same as that for **6e**. In this fashion, the rearrangement of **2e** to **1e** will occur *via* the formation of **6e** (Scheme 2), and the isomerization of the latter is not inhibited by strong acids, as it has been already observed for **4a**,**4b**.

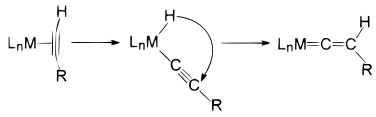
All vinylidene complexes prepared in this work react with a strong base such as $KOBu^t$, yielding the corresponding neutral alkynyl complexes [Cp*RuC≡CR(dippe)] (R = COOMe, **7a**; Ph, **7b**; $SiMe_3$, **7c**; Bu^t, **7d**; H, **7e**) or [CpRuC≡CR(dippe)] (R = COOMe, **8a**; Ph, **8b**; Bu^t, **8d**; H, **8e**), as has been observed for most reported cationic vinylidene complexes.[12,13,33] The IR spectra ot these compounds are dominated by the strong ν(C≡C) absorption band near 2000 cm^{-1}, having unexceptional NMR spectral properties that do not require further comment. All these compunds are protonated by HBF_4·OEt_2, yielding back the corresponding vinylidene complex in all cases, irrespective of the solvent and the temperature. In no case has the formation of a hydrido−alkynyl derivative as the product of the protonation of neutral alkynyl complexes been detected by NMR spectroscopy.

Discussion

The isomerization of 1-alkynes to vinylidene complexes at the moieties {[Cp*Ru(dippe)]$^+$} and {[CpRu(dippe)]$^+$} has been shown to occur by two alternative pathways, either *via* Ru^{IV} hydrido−alkynyl complexes or through the formation of π-alkyne adducts as intermediates. These two pathways of isomerization have been previously observed for other transition metal complexes,[6,7,11,13] but this is the first report in which metastable Ru^{IV} hydrido−alkynyl complexes have been detected and characterized as intermediates in the rearrangement of 1-alkyne to vinylidene complexes. The tautomerization *via* the π-alkyne adducts is thought to occur by a slippage of the η^2-alkyne ligand leading to $\sigma-\eta^1$ coordination, followed by a subsequent 1,2-hydrogen migration to yield the vinylidene complex (mechanism A):[2−5,9]



In our case, kinetic data for the rearrangement of η^2-alkyne complexes to vinylidene are similar to those reported in the literature for the isomerization of related compounds,[11,12] and hence, it is likely that these processes take place according to the concerted mechanism shown above. However, a different mechanism operates when the tautomerization occurs *via* hydrido−alkynyl complexes and a concerted 1,3-hydrogen shift has been proposed (mechanism B):[2,3,9]



However, this mechanism was found to be energetically too costly for Ru^{II} (d^6) complexes.[3,5] This affirmation has been supported by the fact that all hydrido−alkynyl complexes of ruthenium reported until now were stable species which do not rearrange to their vinylidene isomers.[7,27] For the hydrido−alkynyl complexes **2a**−**c**, a number of experimental facts suggest that the isomerization proceeds in a nonconcerted fashion, so the mechanism B proposed above is not strictly applicable. As shown in Scheme 1, once the hydrido−alkynyl complex is formed, the hydride ligand dissociates as a proton, yielding the corresponding neutral alkynyl complex. Protonation of this compound at the β-carbon yields the vinylidene complex. Addition of a strong acid inhibits the dissociation of the hydride as proton and, therefore, the isomerization, as a consequence of the common ion effect. This is a thermodynamic (not kinetic) effect, since it only depends on the relative strength as acid of the hydrido−alkynyl complex and that of the added acid. The isomerization by a concerted mechanism would not be affected by the addition of acid. On the other hand, the isomerization of a 1:1 mixture of **2a** or **2c** with the labeled derivative [Cp*Ru-

(33) Haquette, P.; Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 163.

(D)(C≡CPh)(dippe)][BPh_4] occurs with scrambling of deuterium, and mixtures of [Cp*Ru=C=CHR(dippe)]$^+$/[Cp*Ru=C=CDR(dippe)]$^+$ (R = COOMe or $SiMe_3$) and [Cp*Ru=C=CHPh(dippe)]$^+$/[Cp*Ru=C=CDPh(dippe)]$^+$ are observed by NMR spectroscopy, indicative of the dissociative nature of the process. Consistent with this, the activation entropy is positive in all cases except for the isomerization of **2a**, which is negative. This negative value could be a consequence of the errors affecting the determination of the thermodynamic functions, particularly the activation entropy, and may have no mechanistic significance, but it could also result from the fact that the isomerization takes place in two steps, the first one being dissociative and the second one associative. This seems to be consistent with the absence of isotopic effect observed for the isomerization of [Cp*Ru(D)(C≡CPh)(dippe)]$^+$ to [Cp*Ru=C=CDPh(dippe)]$^+$. Thus, the overall rearrangement process occurs according to a dissociative 1,3-hydrogen shift, which appears to be the same as that proposed for the isomerization of [Co(H)(C≡CR)(PP_3)]$^+$ to [Co=C=CHR-(PP_3)]$^+$.[7]

We can consider now the factors that determine which of the isomerization mechanisms is going to operate for half-sandwich ruthenium complexes. The mechanism involving the formation of a hydrido−alkynyl intermediate requires C−H activation in the 1-alkyne and oxidative addition, this being unnecessary if the isomerization occurs via slippage in the π-alkyne adduct. This may explain why the latter mechanism seems to be more common than the former. For complexes of the type [CpRuXP_2] (Cp = C_5H_5 or C_5Me_5; X = halide; P_2 = one bidentate or two monodentate phosphine ligands), dissociation of halide leads to 16-electron species of the type [CpRuP_2]$^+$,[14,34] which have been isolated in some instances,[35] these being reactive toward 1-alkynes. For these species, there is a competition between oxidative addition and direct side-on coordination of the alkyne to achieve the 18-electron configuration. For the series of compounds prepared in this work, only those having the stronger electron releasing Cp* ligand undergo oxidative addition. If the R group on the alkyne has a strong electron-attracting effect, i.e. COOMe or Ph, the C−H is more activated toward cleavage and therefore the oxidative addition is expected to occur more easily. The $SiMe_3$ may have a similar effect, due to the presence of empty d-orbitals at the silicon atom, although at this stage it is not possible to establish the extent to which these orbitals are involved. Interestingly, in the case of R = Bu^t, which has the inverse effect, no hydrido−alkynyl or η^2-alkyne complexes have been detected, and therefore, little can be said about its possible mechanism of isomerization. For acetylene, a mixture of both the hydrido−alkynyl and η^2-alkyne complexes is observed. These two species seem to be in equilibrium, suggesting that their stability is comparable. However, the isomerization possibly occurs through a concerted 1,2-hydrogen shift in the η^2-acetylene adduct (Scheme 2), which should be the minimum energy reaction pathway to the vinylidene complex. Bianchini *et al.* have observed for the isomerization of [Co(η^2-HC≡CR)(PP_3)]$^+$ to [Co=C=CHR(PP_3)]$^+$ that the π-alkyne adduct rearranges first to [CoH(C≡CR)(PP_3)]$^+$ and then to vinylidene.[7] This is possibly due to the fact that no equilibrium exists between the hydrido−alkynyl and the η^2-alkyne tautomers, the former being much more stable than the latter given the strong tendency of Co^I complexes to undergo oxidative addition leading to Co^{III} (d^6) complexes, but this does not seems to be the case for Ru^{II}/Ru^{IV} systems. The competition between oxidative addition and side-on coordination of the alkyne is affected not only by electronic factors but also by steric ones. The Cp* ligand is bulkier than Cp, and hence, the steric interactions are more important in its complexes. Thus, the η^2-coordination of an alkyne, specially for those bearing bulky R groups is sterically more demanding than the η^1-bonding mode found in hydrido−alkynyl complexes. Only small alkyne substituents would make possible the isolation of η^2-alkyne complexes with the Cp* ligand, i.e. in case of C_2H_2, leading to [Cp*Ru(η^2-C_2H_2)(dippe)]-[BPh_4]. This is also consistent with the observations made on the literature regarding the effect of steric interactions in the stabilization of half-sandwich η^2-alkyne complexes, such as [CpRu(η^2-C_2H_2)(PMe_2Ph)$_2$][BF_4][11] or [CpRu(η^2-alkyne)(^{i}Pr-DAB)][CF_3SO_3] (^{i}Pr-DAB = 1,4-diisopropyl-1,4-diaza-1,3 -butadiene, ^{i}PrN=CH-CH=N^{i}Pr).[36] The bulkiness of the substituents of the phosphine ligand is also important. No Cp*Ru hydrido−alkynyl complexes have been detected with phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis-(dimethylphosphino)ethane (dmpe). Dppe has steric requirements similar to those of dippe, but it is a poorer donor, whereas dmpe has electron releasing capabilities similar to dippe, but it is sterically much less demanding. However, it has been possible to isolate hydrido−alkynyl complexes of the type [Cp*RuH(C≡CR)(PR_3)$_2$][BPh_4], containing large, strong electron-releasing monodentate phosphines, which will be reported elsewhere.[37] It appears clear that bulky ligands, good donors of electron density, favor the mechanism of isomerization to vinylidene involving oxidative addition, specially in case of alkynes bearing electron-attracting groups, whereas for complexes with poorer donor and less bulky ligands, the rearrangement will occur through a concerted 1,2-hydrogen shift in the π-alkyne adduct.

The mechanisms of isomerization to vinylidene of either π-alkyne and hydrido−alkynyl derivatives in the solid state might be related to the processes observed in solution but are more complex and difficult to study due to the larger number of factors affecting the structural changes in the solid state associated with the isomerization. We are currently studying these rearrangement processes by a number of spectral techniques, and the results will be reported in due course.

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(34) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem*. **1990**, *30*, 1. Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Inorg. Chim. Acta* **1984**, *88*, 151.

(35) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmidt, R. *J. Chem. Soc., Chem. Commun*. **1993**, 892. Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.

(36) de Klerk-Engels, B.; Delis, J. G. P.; Vrieze, K.; Goubitz, K.; Fraanje, J. *Organometallics* **1994**, *13*, 3269.

(37) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. Manuscript in preparation.