Alkyne Coupling Reactions Mediated by Tris(pyrazolyl)borate Ruthenium Vinylidene Complexes: X-Ray Crystal Structures of $[TpRu{=}C{=}CHPh(PEt_3)_2][BPh_4]$ and $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2][BPh_4]$

Miguel Angel Jiménez Tenorio, Manuel Jiménez Tenorio, M. Carmen Puerta,* and Pedro Valerga

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain

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A series of cationic vinylidene complexes of the type $[TpRu{=}C{=}CHR(PR_3)_2][BPh_4]$ (Tp = hydrotris(pyrazolyl)borate; $PR_3 = PEt_3$, PMe^iPr_2; R = Ph, Bu^t, COOMe) have been prepared. The reaction of $[TpRu{=}C{=}CHCOOMe(PEt_3)_2][BPh_4]$ with a further HC≡CCOOMe molecule yields the *E*-stereoisomer of the vinylvinylidene derivative $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2][BPh_4]$, which has been structurally characterized. This C−C coupling reaction has been interpreted in terms of a [2 + 2] cycloaddition of the alkyne to the $C_\alpha-C_\beta$ bond of the vinylidene ligand to yield a cyclobutenylidene intermediate, followed by a concerted ring opening. The neutral σ-η^1-butadienyl complex $[TpRu(CH{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2]$ was prepared by reaction of the vinylvinylidene complex with $NaBH_4$ in MeOH. The reaction of $[TpRuCl(PMe^iPr_2)_2]$ with 1-alkynes leads to neutral vinylidene derivatives $[TpRu{=}C{=}CHR(Cl)(PMe^iPr_2)]$ (R = Ph, Bu^t, $SiMe_3$, H). These complexes react with LDA and diphenylacetylene yielding the enynyl species $[TpRu(PhC{=}C(Ph)C{\equiv}CR)(PMe^iPr_2)]$ (R = Ph, Bu^t). These complexes, which were isolated and characterized, are efficient catalysts for alkyne dimerization reactions, as well as for cross-coupling reaction of terminal alkynes.

Introduction

Transition metal vinylidene complexes are known to be involved in the oligomerization and polymerization of alkynes.[1−3] One of the key steps in such processes is considered to be the cycloaddition of alkyne to the M=C bond to yield a metallocyclobutene intermediate, which upon ring opening leads to polymerization.[1,4] A related reaction that may also have implications in the polymerization of alkynes is the cycloaddition of alkynes to the C=C bond of the vinylidene moiety to form cyclobutenylidene intermediates, which may also undergo ring-opening reactions,[5,6] being known examples of both types of cycloaddition reactions. Olefins may also add to M=C bonds,[7] and very recently the formation of η^3-butadienyl complexes has been described by reaction of [TpRuCl(COD)] (COD = 1,5-cyclooctadiene) or $[TpRuCl(\kappa^3(P,C,C)\text{-}Ph_2PCH{=}CHC(Ph){=}CH_2)]$ with a terminal alkyne in refluxing methanol in the presence of 1 equiv of sodium ethoxide.[8] This process has been interpreted in terms of a [2 + 2] cycloaddition reaction of one of the double bonds of the COD to the Ru=C bond of a vinylidene complex formed in situ, followed by ring opening. This reaction is very relevant to olefin ring-opening metathesis polymerization (ROMP), and in this sense TpRu complexes have shown to catalyze the ROMP of norbornene.[9,10] On the other hand, some ruthenium complexes containing the hydrotris(pyrazolyl)borate ligand have shown to catalyze efficiently several alkyne-coupling reactions in which new C−C bonds are formed.[11] All of these processes involve the participation of vinylidene complexes. Thus, the catalytic dimerization and oligomerization reactions of several terminal alkynes have been studied by Kirchner and co-workers.[3,10,11] The catalysts have been generally compounds of the type $[TpRuCl(PPh_3)(L)]$ (L = weakly bound P-, N-, or O-donor ligand). In the case of using $[TpRuCl(PPh_3)_2]$[12] as catalyst, the conversion factor depends strongly on the solvent, whereas the stereo-

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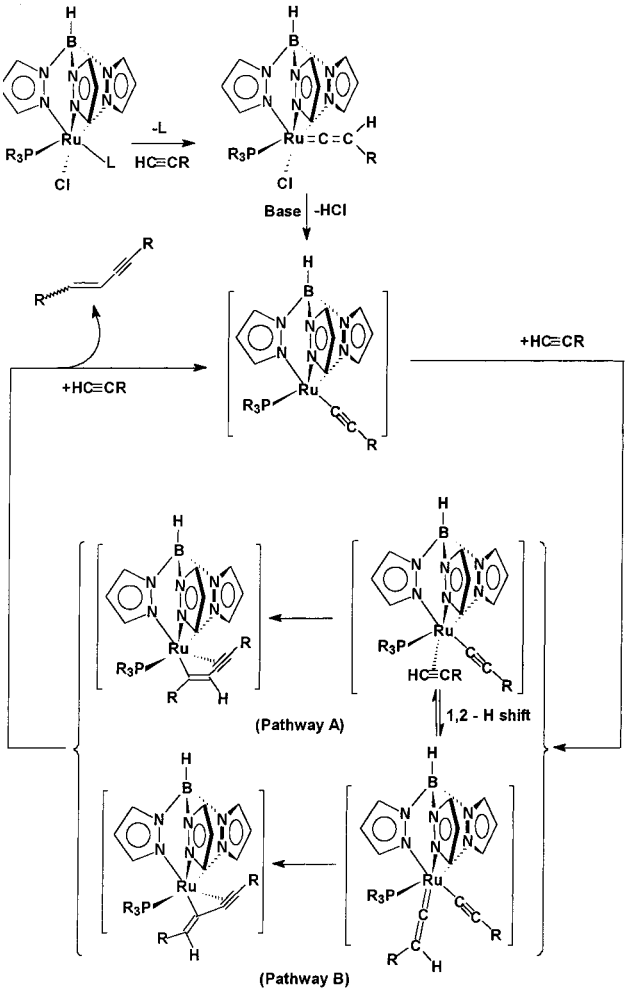
Scheme 1. Proposed Mechanism for the Catalytic Cycle of Alkyne Dimerization Mediated by TpRu Phosphine Complexes[a]



[a] None of the species in square brackets, considered intermediate complexes in the overall catalytic cycle, have been so far isolated or detected.

isomer ratio appears to be independent. It has been suggested that the catalytic cycle starts with the loss of the weakly bound ligand L (PPh_3 in the case of $[TpRuCl(PPh_3)_2]$) and subsequent formation of neutral vinylidene species of the type $[TpRu{=}C{=}CHR(Cl)(PPh_3)]$. The elimination of HCl from this compound generates a 16-electron alkynyl complex, namely, $[TpRu(C{\equiv}CR)(PPh_3)]$, which appears to be the true catalytically active species in the cycle shown in Scheme 1.[3] The subsequent reaction sequence is consistent with the mechanisms proposed by several authors to rationalize the catalytic dimerization of terminal alkynes leading to enynyl or butatrienyl complexes.[13,14] A similar mechanistic proposal has also been made for explaining the catalytic dimerization of terminal alkynes catalyzed by $[Cp^*RuH_3(PR_3)]$[15] or even the cross-coupling of terminal and internal alkynes to yield functionalized enynes catalyzed by $[Cp^*Ru{=}C{=}CHPh(Cl)(PPh_3)]$.[16] Also in these two cases, the catalytically active species are coordinatively unsaturated alkynyl complexes of the type $[Cp^*Ru(C{\equiv}CR)(PPh_3)]$, formal homologues of $[TpRu(C{\equiv}CR)(PPh_3)]$.

Within this context, we have prepared and characterized a series of new ruthenium hydrotris(pyrazolyl)borate phosphine complexes containing ligands resulting from the coupling of alkynes by different reaction pathways, namely, a formal [2 + 2] cycloaddition reaction followed by ring opening and direct insertion of alkyne into the Ru−C bond of a coordinatively unsaturated alkynyl complex generated in situ. This study adds experimental support to some of the mechanistic proposals suggested by several authors in order to explain the role of the metal complex in catalytic alkyne-coupling processes such as dimerization or oligomerization.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk 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. Triethylphosphine was purchased from Aldrich, whereas PMe^iPr_2 was obtained by reaction of PCl^iPr_2 (Aldrich) with MeMgI in diethyl ether. KTp,[17] $[TpRuCl(PEt_3)_2]$, and $[TpRuCl(PMe^iPr_2)_2]$ were obtained according to published procedures.[18] IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). The coupling constants $^3J_{HH}$ within the Tp ligand were all in the range 2−2.5 Hz. Microanalyses were by the Serveis Científico-Tècnics, Universitat de Barcelona.

$[TpRu{=}C{=}CHR(PEt_3)_2][BPh_4]$ (R = Ph 1a; Bu^t 1b). To a suspension of $[TpRuCl(PEt_3)_2]$ (0.12 g, ca. 0.2 mmol) in MeOH (15 mL) were added an excess of solid $NaBPh_4$ (0.3 g) and of the appropriate 1-alkyne (0.1 mL). The mixture was heated smoothly using a warm water bath for 30 min, and then it was stirred at room temperature for another 30 min. The resulting microcrystalline precipitate was filtered off, washed with EtOH and petroleum ether, and dried in vacuo. The products were recrystallized from an acetone/ethanol mixture. **1a:** Yield: 85%. Anal. Calcd for $C_{53}H_{66}N_6B_2P_2Ru$: C, 65.5; H, 6.80; N, 8.7. Found: C, 65.3; H, 6.93; N, 8.4. IR: ν(BH) 2484 cm^{-1}; ν(C=C) 1620 cm^{-1}. NMR ($CDCl_3$) δ: (^1H) 0.75 (m, $P(CH_2CH_3)_3$), 1.76 (m, $P(CH_2CH_3)_3$); 5.14 (t, J_{HP} = 3.6 Hz, Ru=C=C*H*Ph); 6.17 (t, 2H), 6.45 (t, 1H), 7.44 (d, 1H), 7.69 (d, 2H), 7.71 (d, 2H), 7.92 (d, 1H). $^{31}P\{^1H\}$: 20.0 (s). $^{13}C\{^1H\}$: 7.6 (s, $P(CH_2CH_3)_3$), 18.7 (t, $P(CH_2CH_3)_3$); 106.5, 107.5, 137.3, 138.0, 144.3, 145.0 6 (s, $HB(C_3H_3N_2)_3$); 114.0 (s, Ru=C=*C*HPh); 126.4, 127.0, 129.0 (s, Ru=C=CH(C_6H_5)); 373.0 (m, Ru=*C*). **1b:** Yield: 85%. Anal. Calcd for $C_{51}H_{70}N_6B_2P_2Ru$: C, 64.4; H, 7.36; N, 8.8. Found: C, 64.1; H, 7.49; N, 8.5. IR: ν(BH) 2467 cm^{-1}; ν(C=C) 1639 cm^{-1}. NMR (CD_2Cl_2) δ: 0.82 (m, $P(CH_2CH_3)_3$), 1.82 (m, $P(CH_2CH_3)_3$); 1.03 (s, Ru=C=CHC(CH_3)$_3$); 3.94 (t, J_{HP}

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= 3.2 Hz, Ru=C=C*H*C(CH$_3$)$_3$); 6.27 (t, 2H), 6.43 (t, 1H), 7.66 (d, 1H), 7.71 (d, 2H), 7.87 (d, 2H), 7.96 (d, 2H). ^{31}P{^{1}H}: 19.1 (s). ^{13}C{^{1}H}: 7.8 (s, P(CH$_2$*C*H$_3$)$_3$), 18.5 (t, J_{CP}= 13.7 Hz, P(*C*H$_2$-CH$_3$)$_3$); 32.0 (s, Ru=C=CH*C*(CH$_3$)$_3$); 32.4 (s, Ru=C=CHC-(*C*H$_3$)$_3$); 106.2, 107.1, 120.1, 137.0, 137.6, 144.5 (s, HB-(*C*$_3$H$_3$N$_2$)$_3$); 120.1 (s, Ru=C=*C*HC(CH$_3$)$_3$); 367.1 (br, Ru=*C*).

[TpRu=C=CHCOOMe(PEt$_3$)$_2$][BPh$_4$] (1c). To a solution of [TpRu(N$_2$)(PEt$_3$)$_2$][BPh$_4$] (0.15 g, 0.17 mmol) in tetrahydrofuran or dichloromethane was added an excess of HC≡CCOOMe. The solution turned orange immediately. It was stirred at room temperature for 15 min. Then, the solvent was removed in vacuo, and the residue was washed with several portions of petroleum ether and dried in vacuo. It was recrystallized from dichloromethane/petroleum ether. Yield: 0.12 g, 75%. Anal. Calcd for $C_{49}H_{64}N_6B_2O_2P_2Ru$: C, 61.7; H, 6.72; N, 8.8. Found: C, 61.4; H, 6.69; N, 8.5. IR: ν(BH) 2506 cm^{-1}; ν(C=O) 1702 cm^{-1}; ν(C=C) 1603 cm^{-1}. NMR ($CDCl_3$) δ: (^{1}H) 0.75 (m, P(CH$_2$C*H*$_3$)$_3$), 1.75 (m, P(C*H*$_2$CH$_3$)$_3$); 3.65 (s, Ru=C=CHCOOC*H*$_3$); 4.80 (t, J_{HP} = 3.4 Hz, Ru=C=C*H*-COOMe); 6.24 (t, 2H), 6.41 (t, 1H), 7.67 (d, 2H), 7.73 (s br), 7.90 (d, 1H). ^{31}P{^{1}H}: 17.4 (s). ^{13}C{^{1}H}: 7.6 (s, P(CH$_2$*C*H$_3$)$_3$), 18.8 (m, P(*C*H$_2$CH$_3$)$_3$); 51.8 (s, Ru=C=CHCOO*C*H$_3$); 106.4 (s, Ru=C=*C*HCOOCH$_3$); 106.9, 107.7, 137.1, 144.5, 145.0, 145.5 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 352.8 (br, Ru=*C*).

[TpRu=C=CHR(PMe^{i}Pr$_2$)$_2$][BPh$_4$] (R = Ph 2a, Bu^t 2b). These compounds were obtained by a procedure analogous to that for compounds **1a**,**b**, starting from [TpRuCl(PMe^{i}Pr$_2$)$_2$] and the corresponding alkyne. **2a:** Yield: 85%. Anal. Calcd for $C_{55}H_{70}N_6B_2P_2Ru$: C, 66.1; H, 7.01; N, 8.4. Found: C, 65.9; H, 7.13; N, 8.2. IR: ν(BH) 2491 cm^{-1}; ν(C=C) 1626 cm^{-1}. NMR ($CDCl_3$) δ: (^{1}H) −0.28, 0.92, 1.27, 1.35 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.18 (d, J_{HP} = 8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.10, 2.41 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 5.16 (t, J_{HP} = 3.6 Hz, Ru=C=C*H*Ph); 6.12 (t, 2H), 6.44 (t, 1H), 7.65 (d, 1H), 7.67 (d, 2H), 7.77 (d, 2H), 7.90 (d, 1H). ^{31}P{^{1}H}: 21.3 (s). ^{13}C{^{1}H}: 6.5 (t, J_{CP} = 11.6 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 15.1, 17.9, 18.8, 19.1 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 24.7, 30.9 (t, J_{CP} = 13 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 106.6, 107.2, 137.1, 138.0, 144.5, 145.8 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 114.7 (s, Ru=C=*C*HPh); 124.7, 126.6, 126.8, 128.8 (Ru=C=CH*C*$_6$H$_5$); 373.0 (br, Ru=*C*). **2b:** Yield: 85%. Anal. Calcd for $C_{53}H_{74}N_6B_2P_2Ru$: C, 65.0; H, 7.56; N, 8.6. Found: C, 64.8; H, 7.64; N, 8.4. IR: ν(BH) 2491 cm^{-1}; ν(C=C) 1665, 1634 cm^{-1}. NMR ($CDCl_3$) δ: (^{1}H) −0.21, 0.92, 1.29, 1.38 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 0.93 (s, Ru=C=CHC(C*H*$_3$)$_3$); 1.16 (d, J_{HP} = 8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.20, 2.35 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 3.80 (t, J_{HP} = 4 Hz, Ru=C=C*H*C-(CH$_3$)$_3$); 6.22 (t, 2H), 6.38 (t, 1H), 7.60 (d, 1H), 7.61 (d, 2H), 7.85 (d, 1H), 7.94 (d, 2H). ^{31}P{^{1}H}: 20.0 (s). ^{13}C{^{1}H}: 6.6 (t, J_{CP} = 11 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 16.0, 18.0, 18.1, 19.3 (s, P(CH-(*C*H$_3$)$_2$)$_2$CH$_3$); 24.7, 30.6 (t, J_{CP} = 12.4 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 32.0 (s, Ru=C=CH*C*(CH$_3$)$_3$); 32.1 (s, Ru=C=CHC(*C*H$_3$)$_3$); 106.2, 106.9, 136.9, 137.8, 144.3, 145.7 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 121.9 (s, Ru=C=*C*HC(CH$_3$)$_3$); 367.8 (br, Ru=*C*).

[TpRu=C=CHCOOMe(PMe^{i}Pr$_2$)$_2$][BPh$_4$] (2c). This compound was obtained by the same procedure used for the preparation of **1c**, starting from [TpRu(N$_2$)(PMe^{i}Pr$_2$)$_2$][BPh$_4$]. However, it was obtained always impurified with other unidentified substances, according to ^{1}H and ^{31}P{^{1}H} NMR spectra. Attempts to purify the complex by recrystallization led to decomposition, and accurate microanalysis could not be obtained. The spectral data given correspond to the vinylidene complex in an impure sample (ca. 80%). Yield (crude): 87%. IR: ν(BH) 2516 cm^{-1}; ν(C=O) 1691 cm^{-1}; ν(C=C) 1605 cm^{-1}. NMR ($CDCl_3$) δ: (^{1}H) -0.34, 0.95, 1.35, 1.36 (m, P(CH(C*H*$_3$)$_2$)$_2$-CH$_3$); 1.19 (d, J_{HP} = 7.2 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.21, 2.35 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 3.86 (s, Ru=C=CHCOOC*H*$_3$); 4.90 (t, J_{HP} = 4 Hz, Ru=C=C*H*COOCH$_3$); 6.24 (t, 2H), 6.37 (t, 1H), 7.59 (d, 1H), 7.63 (d, 2H), 7.87 (d, 1H), 7.94 (d, 2H). ^{31}P{^{1}H}: 19.4 (s). ^{13}C{^{1}H}: 6.5 (t, J_{CP} = 14 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 16.3, 18.2, 18.5, 19.3 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 25.3, 30.5 (t, J_{CP} = 14 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 51.8 (s, Ru=C=CHCOO*C*H$_3$); 106.8, 107.6, 137.1, 138.2, 145.4, 151.0 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 106.9 (s, Ru=C=*C*HCOOCH$_3$); 362.6 (t, $^2J_{CP}$ = 17.1 Hz, Ru=*C*).

[TpRu(C≡CR)(PEt$_3$)$_2$] (R = Ph 3a, Bu^t 3b, COOMe 3c). To a solution of the corresponding cationic vinylidene complex **1a**−**c** (ca. 0.2 mmol) in tetrahydrofuran (15 mL) was added an excess of solid KOBu^t. The mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue extracted with toluene. The Schlenk tube containing this mixture was immersed into an ultrasonic bath for a few seconds. Then, the mixture was filtered through Celite and concentrated. Addition of petroleum ether and cooling to −20 °C afforded the yellow microcrystalline products. **3a:** Yield: 65%. Anal. Calcd for $C_{29}H_{45}N_6BP_2Ru$: C, 53.5; H, 6.91; N, 12.1. Found: C, 53.2; H, 7.03; N, 12.0. IR: ν(BH) 2449 cm^{-1}; ν(C≡C) 2064 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) 0.71 (m, P(CH$_2$C*H*$_3$)$_3$), 1.71 (m, P(C*H*$_2$CH$_3$)$_3$); 5.85 (t, 2H), 5.97 (t, 1H), 7.43 (d, 2H), 7.55 (d, 1H), 7.61 (d, 1H), 8.18 (d, 2H). ^{31}P{^{1}H}: 30.3 (s). ^{13}C{^{1}H}: 8.1 (s, P(CH$_2$*C*H$_3$)$_3$), 19.6 (t, J_{CP}= 12.2 Hz, P(*C*H$_2$CH$_3$)$_3$); 105.2, 105.6, 135.0, 135.4, 145.1, 145.3 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 122.8, 128.3, 131.3 (s, RuC≡C*C*$_6$H$_5$); 108.7 (s, RuC≡*C*Ph); 137.2 (t, J_{CP} = 16 Hz, Ru*C*≡CPh). **3b:** Yield**:** 65%. Anal. Calcd for $C_{27}H_{49}N_6BP_2Ru$: C, 51.4; H, 7.77; N, 13.3. Found: C, 51.1; H, 7.73; N, 13.6. IR: ν(BH) 2465 cm^{-1}; ν(C≡C) 2079 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) 0.77 (m, P(CH$_2$C*H*$_3$)$_3$), 1.77 (m, P(C*H*$_2$CH$_3$)$_3$); 1.47 (s, RuC≡CC(C*H*$_3$)$_3$); 5.92 (t, 2H), 5.97 (t, 1H), 7.47 (d, 2H), 7.52 (d, 1H), 7.65 (d, 1H), 8.25 (d, 2H). ^{31}P{^{1}H}: 31.3 (s). ^{13}C{^{1}H}: 8.1 (s, P(CH$_2$*C*H$_3$)$_3$), 19.3 (t, J_{CP} = 12 Hz, P(*C*H$_2$CH$_3$)$_3$); 33.9 (s, RuC≡CC(*C*H$_3$)$_3$); 104.7, 105.3, 134.8, 135.3, 144.8, 147.7 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 105.2 (s, RuC≡*C*C(CH$_3$)$_3$); 138.0 (t, J_{CP} = 18 Hz, Ru*C*≡CC(CH$_3$)$_3$). **3c:** Yield: 59%. Anal. Calcd for $C_{25}H_{43}N_6BP_2O_2Ru$: C, 47.4; H, 6.80; N, 13.3. Found: C, 47.6; H, 6.68; N, 13.1. IR: ν(BH) 2470 cm^{-1}; ν(C≡C) 2041 cm^{-1}; ν-(C=O) 1659 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) 0.69 (m, P(CH$_2$C*H*$_3$)$_3$), 1.77 (m, P(C*H*$_2$CH$_3$)$_3$); 3.60 (s, RuC≡CCOOC*H*$_3$); 5.81 (t, 2H), 5.95 (t, 1H), 7.39 (d, 2H), 7.41 (d, 1H), 7.58 (d, 1H), 8.14 (d, 2H). ^{31}P{^{1}H}: 28.9 (s). ^{13}C{^{1}H}: 7.4 (s, P(CH$_2$*C*H$_3$)$_3$), 18.7 (t, J_{CP} = 12.2 Hz, P(*C*H$_2$CH$_3$)$_3$); 50.3 (s, RuC≡CCOO*C*H$_3$); 104.9, 105.5, 135.1, 135.6, 145.1, 145.2 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 102.7 (s, RuC≡*C*CCOOMe); 137.5 (t, Ru*C*≡CCCOOMe).

[TpRu(C≡CR)(PMe^{i}Pr$_2$)$_2$] (R = Ph 4a, Bu^t 4b). These compounds were obtained in a fashion analogous to that for **3a**−**c**, by deprotonation of the corresponding cationic vinylidene complexes **2a**,**b**. **4a:** Yield: 65%. Anal. Calcd for $C_{31}H_{49}N_6BP_2Ru$: C, 54.8; H, 7.22; N, 12.4. Found: C, 55.3; H, 7.12; N, 12.2. IR: ν(BH) 2459 cm^{-1}; ν(C≡C) 2063 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) −0.18, 0.67, 1.32, 1.59 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.09 (d, J_{HP} = 6 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.12, 2.87 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 5.85 (t, 2H), 5.97 (t, 1H), 7.43 (d, 2H), 7.56 (d, 1H), 7.59 (d, 1H), 8.33 (d, 2H). (^{31}P{^{1}H}) 30.9 (s). ^{13}C{^{1}H}: 7.8 (m, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 17.0, 18.1, 19.2, 19.4 (s, P(CH-(*C*H$_3$)$_2$)$_2$CH$_3$); 24.6, 30.0 (t, J_{CP} = 9.9 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 100.2 (s, Ru(C≡*C*Ph); 104.9, 105.3, 135.0, 135.8, 145.3, 145.6 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 131.9 (t, J_{CP} = 15 Hz, Ru*C*≡CPh). **5b:** Yield: 55%. Anal. Calcd for $C_{29}H_{53}N_6BP_2Ru$: C, 52.8; H, 8.04; N, 12.8. Found: C, 53.0; H, 8.09; N, 12.5. IR: ν(BH) 2485 cm^{-1}; ν(C≡C) 2081 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) −0.12, 0.78, 1.39, 1.61 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.14 (d, J_{HP} = 6.4 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.90, 2.18 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 1.47 (s, RuC≡CC(C*H*$_3$)$_3$); 5.95 (t, 2H), 6.00 (t, 1H), 7.47 (d, 2H), 7.54 (d, 1H), 7.63 (d, 1H), 8.37 (d, 2H). ^{31}P{^{1}H}: 32.6 (s). ^{13}C{^{1}H}: 8.0 (m, P(CH-(CH$_3$)$_2$)$_2$*C*H$_3$); 14.8, 17.1, 18.3, 19.7 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 24.7, 29.8 (t, J_{CP} = 12.4 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 33.7 (s, RuC≡CC-(*C*H$_3$)$_3$); 104.8, 134.8, 135.7, 145.3, 145.4 (s, HB(*C*$_3$H$_3$N$_2$)$_3$); 107.0 (s, RuC≡*C*Bu^t); 131.0 (t, J_{CP} = 19.5 Hz, Ru*C*≡CBu^t).

[TpRu=C=C(COOMe)CH=CHCOOMe(PEt$_3$)$_2$][BPh$_4$] (5). To a solution of **1c** in tetrahydrofuran was added an excess of HC≡CCOOMe. The mixture was heated under reflux for 2 h. Then, it was cooled to room temperature and concentrated using reduced pressure. Addition of ethanol and cooling to −20 °C afforded a red precipitate, which was filtered off, washed with petroleum ether, and dried in vacuo. Red crystals of the

dichloromethane solvate **5**·0.6CH_2Cl_2 were obtained by recrystallization from dichloromethane/petroleum ether. Yield: 80%. Anal. Calcd for $C_{53}H_{68}N_6B_2O_4P_2Ru\cdot C_{0.62}H_{1.24}Cl_{1.24}$: C, 61.4; H, 6.56; N, 8.1. Found: C, 61.5; H, 6.45; N, 8.3. IR: ν(BH) 2505 cm^{-1}; ν(C=O) 1702 cm^{-1}; ν(C=C) 1603 cm^{-1}. NMR ($CDCl_3$) δ: (^{1}H) 0.73 (m, P(CH_2CH_3)$_3$), 1.81 (m, P(CH_2CH_3)$_3$; 3.63, 3.65 (s, Ru=C=C(COOCH_3)CH=CHCOOCH_3); 5.57, 6.91 (d, $^3J_{HH}$ = 16 Hz, Ru=C=C(COOMe)C*H*=C*H*COOMe); 6.24 (t, 2H), 6.93 (t, 1H), 7.53 (d, 1H), 7.68 (d, 2H), 7.70 (d, 2H), 7.88 (d, 2H). ^{31}P{^{1}H}: 19.5 (s). ^{13}C{^{1}H}: 7.5 (s, PCH_2CH_3); 18.7 (m, PCH_2-CH_3); 51.5 (s, COOCH_3), 52.0 (s, COOCH_3); 107.0, 107.9, 137.6, 138.1, 144.3, 145.2 (s, HB($C_3H_3N_2$)$_3$); 117.8, 128.6 (s, *C*H=*C*HCOOMe); 361.5 (t, $^2J_{CP}$ = 22 Hz, Ru=*C*).

[TpRuCH=C(COOMe)CH=CHCOOMe(PEt$_3$)$_2$] (6). A slurry of **5** in MeOH was treated with an excess of solid $NaBH_4$. The color changed immediately to yellow. The mixture was stirred at room temperature for 1 h. By concentration and cooling this solution at −20 °C, yellow crystals were deposited. They were filtered off and dried in vacuo. Alternatively, the solvent was removed using reduced pressure. The residue was extracted with petroleum ether, and the solution filtered through Celite. Removal of the solvent afforded **6** as a yellow powder. Spectral data are given for the final isomer (vide infra). Yield: 66%. Anal. Calcd for $C_{29}H_{47}N_6BO_4P_2Ru$: C, 48.5; H, 6.56; N, 11.7. Found: C 48.7; H, 6.51; N, 11.4. IR: ν(BH) 2478 cm^{-1}; ν(C=O) 1723 cm^{-1}; ν(C=C) 1665 cm^{-1}. NMR (CD_3COCD_3) δ: (^{1}H) 0.49 (m, P(CH_2CH_3)$_3$), 1.50 (m, P(CH_2CH_3)$_3$); 3.33, 3.63 (s, RuCH=C(COOCH_3)CH=CHCOOCH_3); 6.22, 6.68 (d, $^3J_{HH}$ = 16 Hz, RuCH=C(COOMe)C*H*=C*H*COOMe); 5.93 (t, 2H), 6.01 (t, 1H), 7.61 (d, 1H), 7.62 (d, 2H), 8.12 (br, 3H); 12.67 (t, J_{HP} = 11.2 Hz, RuC*H*=C(COOCH$_3$)CH=CHCOOCH$_3$). ^{31}P-{^{1}H}: 26.9 (s). ^{13}C{^{1}H}: 6.9 (s, PCH_2CH_3); 18.1 (t, J_{CP} = 10.9 Hz, PCH_2CH_3); 61.6, 62.2 (s, COOCH_3); 105.1, 105.5, 135.5, 135.8, 145.4, 145.7 (s, HB($C_3H_3N_2$)$_3$); 109.0, 149.2 (s, *C*H=*C*HCOOMe); 209.6 (t, $^2J_{CP}$ = 23.6 Hz, Ru*C*H=C(COOCH$_3$)CH=CHCOOCH$_3$).

[TpRu=C=CHR(Cl)(PMe^{i}Pr$_2$)] (R = Ph 7a, Bu^t 7b, SiMe$_3$ 7d). To a solution of [TpRuCl(PMe^{i}Pr$_2$)$_2$] (0.15 g, 0.2 mmol) in tetrahydrofuran (10 mL) was added an excess of the corresponding 1-alkyne. The mixture was heated at the reflux temperature for 1 h. Then, it was stirred for a further 12 h at room temperature. The resulting red solution was concentrated to ca. 1−2 mL, and petroleum ether was added. Cooling to −20 °C afforded a microcrystalline precipitate, which was filtered off, washed with cold petroleum ether, and dried in vacuo. These compounds can be recrystallized from diethyl ether/petroleum ether mixtures. **7a:** Yield: 80%. Anal. Calcd for $C_{23}H_{30}N_6BClPRu$: C, 48.6; H, 5.28; N, 14.8. Found: C, 48.4; H, 5.23; N, 14.5. IR: ν(BH) 2484 cm^{-1}; ν(C=C) 1623, 1651 cm^{-1}. NMR (CD_3COCD_3) δ: (^{1}H) 0.53, 0.96, 1.21, 1.32 (m, P(CH-(CH_3)$_2$)$_2$CH$_3$); 1.65 (d, J_{HP} = 8.8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.08, 2.27 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 5.06 (d, J_{HP} = 4 Hz, Ru=C=C*H*Ph); 6.06 (m, 1H), 6.27 (t, 1H), 6.37 (t, 1H), 7.48 (d, 1H), 7.54 (d, 1H), 7.66 (m, 1H), 7.91 (d, 1H), 7.94 (d, 1H), 8.15 (d, 1H); 6.95, 7.17, 7.31 (m, Ru=C=CH(C_6H_5). ^{31}P{^{1}H}: 31.9 (s). ^{13}C{^{1}H}: 4.0 (d, J_{CP} = 27 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 16.3, 16.6, 17.3, 19.5 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 24.9, 28.2 (d, J_{CP} = 24.7 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 106.0, 106.2, 106.4, 133.9, 135.3, 136.5, 144.0, 144.4, 145.1 (s, HB($C_3H_3N_2$)$_3$); 113.2 (s, Ru=C=*C*HPh); 356.5 (br, Ru=C=*C*HPh). **7b:** Yield: 80%. Anal. Calcd for $C_{21}H_{34}N_6BClPRu$: C, 46.0; H, 6.20; N, 15.3. Found: C, 46.2; H, 6.15; N, 15.0. IR: ν(BH) 2470 cm^{-1}; ν(C=C) 1644 cm^{-1}. NMR (C_6D_6) δ: (^{1}H) 0.58, 0.70, 1.03, 1.11 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.24 (d, J_{HP} = 8.4 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 1.90, 1.81 (m, P(C*H*(CH$_3$)$_2$)$_2$-CH$_3$); 1.16 (s, Ru=C=CHC(C*H*$_3$)$_3$); 3.66 (d, J_{HP} = 3.6 Hz, Ru=C=C*H*Bu^t); 5.74 (t, 1H), 5.84 (t, 1H), 5.95 (t, 1H), 7.19 (d, 1H), 7.27 (d, 1H), 7.32 (d, 1H), 7.47 (d, 1H), 8.16 (d, 1H), 8.26 (d, 1H). ^{31}P{^{1}H}: 32.7 (s). ^{13}C{^{1}H}: 3.8 (d, J_{CP} = 26 Hz, P(CH-(CH$_3$)$_2$)$_2$*C*H$_3$); 16.6, 16.7, 17.0, 17.1 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 26.6 (t, J_{CP} = 25.7 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 32.8 (s, Ru=C=CHC-(*C*H$_3$)$_3$); 33.1 (s, Ru=C=CH*C*(CH$_3$)$_3$); 105.2, 105.5, 105.6, 133.7, 134.8, 136.1, 143.2, 143.5, 144.7 (s, HB($C_3H_3N_2$)$_3$); 119.4 (s, Ru=C=*C*HC(CH$_3$)$_3$); 339.4 (d, J_{CP} = 17 Hz, Ru=*C*=CHBu^t). **7d:** Yield: 75%. Anal. Calcd for $C_{18}H_{28}N_6BClPRuSi$: C, 40.0; H, 5.28; N, 15.8. Found: C, 40.2; H, 5.17; N, 15.5. IR: ν(BH) 2477 cm^{-1}; ν(C=C) 1629 cm^{-1}. NMR (CD_3COCD_3) δ: (^{1}H) −0.08 (s, Ru=C=CH(Si(C*H*$_3$)$_3$); 0.56, 0.94, 1.24 (m, P(CH-(C*H*$_3$)$_2$)$_2$CH$_3$); 1.55 (d, J_{HP} = 8.8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 2.20 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 3.59 (d, J_{HP} = 3.6 Hz, Ru=C=C*H*(SiMe$_3$)); 6.17 (t, 1H), 6.25 (t, 1H), 6.27 (t, 1H), 7.66 (d, 1H), 7.661 (d, 1H), 7.84 (d, 1H), 7.85 (d, 1H), 7.92 (d, 1H), 7.93 (d, 1H). ^{31}P{^{1}H}: 35.0 (s). ^{13}C{^{1}H} (C_6D_6): 1.4 (s, Ru=C=CHSi-(*C*H$_3$)$_3$); 4.1 (d, J_{CP} = 26.1 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 16.6, 16.9, 17.2, 17.8 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 25.3, 28.3 (d, J_{CP} = 25.6 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 92.4 (s, Ru=C=*C*HSi(CH$_3$)$_3$); 105.7, 106.0, 134.1, 134.2, 135.3, 136.3, 143.6 (2H), 145.2 (s, HB($C_3H_3N_2$)$_3$); 339.4 (d. J_{CP} = 17, Ru=*C*=CHSi(CH$_3$)$_3$).

[TpRu=C=CH$_2$(Cl)(PMe^{i}Pr$_2$)] (7e). A certain amount of the neutral vinylidene complex **7d** was refluxed in MeOH for 2 h. After this time, the solvent was removed in vacuo. The product was washed with one portion of ethanol and several portions of petroleum ether and dried in vacuo. Yield: 92%. Anal. Calcd for $C_{17}H_{26}N_6BClPRu$: C, 41.8; H, 5.32; N, 17.2. Found: C, 42.0; H, 5.25; N, 17.5. IR: ν(BH) 2461 cm^{-1}; ν(C=C) 1605 cm^{-1}. NMR (CD_3COCD_3) δ: (^{1}H) 0.38, 0.93, 1.15, 1.33 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.62 (d, J_{HP}= 8.8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 1.97, 2.24 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 3.45 (d, J_{HP}= 4 Hz, Ru=C=C*H*$_2$); 6.13 (t, 1H), 6.23 (t, 1H), 6.32 (t, 1H), 7.51 (d, 1H), 7.63 (d, 1H), 7.66 (d, 1H), 7.86 (d, 1H), 7.90 (d, 1H), 8.06 (d, 1H). ^{31}P{^{1}H}: 35.2 (s). ^{13}C{^{1}H} ($CDCl_3$): 3.7 (d, J_{CP} = 26.3 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 15.8, 16.1, 16.9, 17.3 (s, P(CH(*C*H$_3$)$_2$)$_2$CH$_3$); 23.5, 28.6 (d, J_{CP} = 25.6 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 105.5 (s, Ru=C=*C*H$_2$); 105.6, 105.7, 106.1, 134.1, 135.7, 136.3, 142.0, 143.2, 145.0 (s, HB($C_3H_3N_2$)$_3$); 355.8 (d, J_{CP} = 17.2 Hz, Ru=*C*=CH$_2$).

[TpRu(R^{1}C=C(R^2)C≡CR^3)(PMe^{i}Pr$_2$)] (R^1 = R^2 = R^3 = Ph 8a; R^1 = R^2 = Ph, R^3 = Bu^t 8b; R^1 = R^3 = Ph, R^2 = H 8c). To a solution of the corresponding neutral vinylidene complex **7a** or **7b** (0.5 mmol) in tetrahydrofuran was added the stoichiometric amount of either diphenylacetylene (for **8a**,**b**) or phenylacetylene (**8c**). The mixture was immersed in a liquid N_2/ethanol bath, and then LDA (0.3 mL of a 1.5 M solution in cyclohexane, ca. 0.5 mmol) was added. The color changed from orange to yellow. The mixture was warmed to room temperature and then stirred at room temperature for 2 h. A darkening of the solution was observed during this period. The solvent was removed in vacuo, and the residue extracted with petroleum ether. The orange solution was filtered through Celite, concentrated, and cooled to −20 °C, affording a yellow-orange microcrystalline material, which was filtered off, washed with cold petroleum ether, and dried in vacuo. These compounds were recrystallized from petroleum ether. **8a:** Yield: 80%. Anal. Calcd for $C_{38}H_{42}N_6BPRu$: C, 62.9; H, 5.79; N, 11.6. Found: C, 62.7; H, 5.83; N, 11.5. IR: ν(BH) 2476 cm^{-1}; ν(C≡C) 2026 cm^{-1} (weak). NMR (C_6D_6) δ: (^{1}H) 0.01, 0.69, 0.87, 1.27 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 1.00 (d, J_{HP} = 6.8 Hz, P(CH(CH$_3$)$_2$)$_2$C*H*$_3$); 1.86, 1.93 (m, P(C*H*(CH$_3$)$_2$)$_2$CH$_3$); 5.63 (m, 1H), 5.64 (t, 1H), 5.84 (t, 1H), 6.83 (m, 1H), 7.28 (d, 1H), 7.45 (m, 1H), 7.54 (d, 1H), 7.55 (d, 1H), 7.69 (d, 1H), (HB($C_3H_3N_2$)$_3$); 6.64, 6.75, 6.82, 6.84, 6.87, 6.89, 7.61, 7.68 (m, RuC(C_6H_5)=C(C_6H_5)C≡CC_6H_5). ^{31}P{^{1}H}: 31.9 (s). ^{13}C{^{1}H}: 6.6 (d, J_{CP} = 11 Hz, P(CH(CH$_3$)$_2$)$_2$*C*H$_3$); 17.2, 17.3, 18.0, 18.3 (s, P(CH-(*C*H$_3$)$_2$)$_2$CH$_3$); 25.9, 27.9 (d, J_{CP} = 12 Hz, P(*C*H(CH$_3$)$_2$)$_2$CH$_3$); 60.1, 65.8 (s, RuC(Ph)=C(Ph)*C*≡*C*Ph) 105.2, 105.4, 105.6, 135.4, 135.9, 136.4, 138.6, 147.4, 147.5 (s, HB($C_3H_3N_2$)$_3$); 137.5 (s, RuC(Ph)=*C*(Ph)C≡CPh) 125.1, 125.2, 125.3, 126.4, 127.1, 127.8, 128.2, 128.3, 128.9, 129.2, 129.5, 130.4, 131.9, 132.1, 145.0, 148.0 (s, RuC(C_6H_5)=C(C_6H_5)C≡CC_6H_5); 180.5 (d, J_{CP} = 12 Hz, Ru*C*(Ph)=C(Ph)C≡CPh). **8b:** Yield: 75%. Anal. Calcd for $C_{36}H_{50}N_6BPRu$: C, 60.9; H, 7.10; N, 11.9. Found: C, 61.1; H, 7.01; N, 11.6. IR: ν(BH) 2454 cm^{-1}. NMR (CD_3COCD_3) δ: (^{1}H) 0.05, 0.98, 1.12, 1.30 (m, P(CH(C*H*$_3$)$_2$)$_2$CH$_3$); 0.86 (s, 9H, RuC(Ph)=C(Ph)C≡CC(C*H*$_3$)$_3$); 1.22 (d, J_{HP} = 7.2 Hz, P(CH-

Table 1. Summary of Data for the Crystal Structure Analysis of 1a and 5[a]

	1a	5
formula	$C_{53}H_{66}N_6B_2P_2Ru$	$C_{53}H_{68}N_6B_2O_4P_2Ru\cdot 0.62\ CH_2Cl_2$
fw	971.78	1090.45
cryst size (mm)	0.29 × 0.25 × 0.22	0.35 × 0.26 × 0.20
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cell params	a = 11.512(4) Å	a = 14.545(3) Å
	b = 13.474(4) Å	b = 17.197(4) Å
	c = 32.432(9) Å	c = 12.785(4) Å
		α = 98.51(2)°
	β = 94.15(3)°	β = 113.99(2)°
		γ = 92.58(2)°
volume	5017(2) Å^3	2869(1) Å^3
Z	4	2
ρ_{calcd}	1.286 g cm^{-3}	1.262 g cm^{-3}
λ(Mo Kα)	0.71069 Å	0.71069 Å
μ(Mo Kα)	4.08 cm^{-1}	4.25 cm^{-1}
F(000)	2040	1140
transmision factors	0.60−1.24	0.86−1.00
scan speed (ω)	4° min^{-1}	4° min^{-1}
2θ interval	5° < 2θ < 50.1°	5° < 2θ < 50.1°
no. of measd reflns	7778	8939
no. of unique reflns	7778 (R_{int} = 0.23)	8939 (R_{int} = 0.15)
no. of obsd reflns	3930 ($I > 3\sigma_I$)	5065 ($I > 3\sigma_I$)
no. of params	532	613
refln/param ratio	7.39	8.26
R^a	0.085	0.063
R_w ($w = \sigma_F^{-2}$)^b	0.107	0.073
gof	2.77	2.05

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

($CH_3)_2)_2CH_3$); 2.28 (m, P(C*H*($CH_3)_2)_2CH_3$); 5.77 (t, 1H), 6.10 (t, 1H), 6.34 (t, 1H), 6.64 (d, 1H), 7.39 (d, 1H), 7.71 (d, 1H), 7.75 (d, 1H), 7.93, 8.28 (br, 1H); 6.40, 6.98, 7.00, 7.14, 7.31 (m, RuC(C_6H_5)=C(C_6H_5)C≡CBu^t). ^{31}P{^{1}H}: 31.1 (s). ^{13}C{^{1}H}: 6.2 (d, J_{CP} = 11 Hz, P(CH($CH_3)_2)_2CH_3$); 16.7, 16.9, 17.9, 18.0 (s, P(CH($CH_3)_2)_2CH_3$); 24.6, 27.3 (d, J_{CP} = 11 Hz, P(*C*H($CH_3)_2)_2CH_3$); 31.2 (s, RuC(Ph)=C(Ph)C≡CC($CH_3)_3$); 32.2 (s, RuC(Ph)=C(Ph)C≡C*C*($CH_3)_3$); 76.1, 78.1 (s, RuC(Ph)=C(Ph)*C*≡*C*Bu^t); 103.9, 104.2, 104.7, 134.3, 135.3, 135.4, 146.7, 147.3, 147.4 (s, HB($C_3H_3N_2)_3$); 138.2 (s, RuC(Ph)=*C*(Ph)C≡CBu^t); 124.1, 124.2, 124.5, 125.7, 127.2, 127.8 (s, RuC(C_6H_5)=C(C_6H_6)C≡CBu^t); 183.6 (d, J_{CP} = 14 Hz, Ru*C*(Ph)=C(Ph)C≡CBu^t). **8c:** Yield: 86%. Anal. Calcd for $C_{32}H_{38}N_6BPRu$: C, 59.2; H, 5.86; N, 12.9. Found: C, 59.0; H, 6.10; N, 12.5. IR: ν(BH) 2445 cm^{-1}; ν(C≡C) 2036 cm^{-1} (weak). NMR (C_6D_6) δ: (^{1}H) 0.18, 0.77, 0.82, 1.22 (m, P(CH(C*H*$_3)_2)_2CH_3$); 1.02 (d, J_{HP} = 6.8 Hz, P(CH($CH_3)_2)_2CH_3$); 1.93 (m, P(C*H*($CH_3)_2)_2CH_3$); 5.77 (t, 1H), 5.78 (t, 1H), 5.91 (t, 1H), 7.26 (d, 1H), 7.51 (d, 1H), 7.52 (d, 1H), 7.62 (d, 1H), 7.64 (d, 1H), 7.73 (d, 1H); 7.36 (s, RuC(Ph)=C*H*C≡CPh); 7.15, 7.31, 7.32, 7.33 (m, RuC(C_6H_5)=CHC≡CC$_6H_5$). ^{31}P{^{1}H}: 32.6 (s). ^{13}C{^{1}H}: 6.4 (d, J_{CP} = 11 Hz, P(CH($CH_3)_2)_2CH_3$); 17.0, 17.2, 17.7, 17.9 (s, P(CH($CH_3)_2)_2CH_3$); 25.6, 26.9 (d, J_{CP} = 12 Hz, P(*C*H($CH_3)_2)_2CH_3$); 67.8, 69.1 (s, RuC(Ph)=CH*C*≡*C*Ph); 104.8, 105.0, 105.3, 134.7, 135.2, 135.8, 145.8, 146.7, 147.7 (s, HB($C_3H_3N_2)_3$); 139.4 (s, RuC(Ph)=*C*HC≡CPh); 121.1, 123.1, 125.4, 126.3, 126.4, 126.7, 127.5, 128.7, 132.0 (s, RuC(C_6H_5)=CHC≡CC_6H_5); 175.6 (d, J_{CP} = 14 Hz, Ru*C*(Ph)=CHC≡CPh).

Alkyne-Coupling Reactions Catalyzed by 8a. In a typical experiment, a Schlenk tube was charged with toluene (5 mL), the corresponding 1-alkyne (ca. 5 mmol), and the catalyst (2%). In the case of the cross-coupling experiment, equimolar amounts of HC≡CSiMe$_3$ and HC≡CBu^t (2.5 mmol of each) were mixed. The sealed tube was heated in an oil bath at 110 °C for 12−16 h. At the end of this period, volatiles were removed in vacuo. The residue was dissolved in C_6D_6 or $CDCl_3$ and checked by NMR spectroscopy.

***cis*-PhC≡CCH=CHPh:** ^{1}H NMR (C_6D_6) δ 5.80 (d, 1H), 6.42 (d, 1H, J_{HH} = 12 Hz), 7.0−7.5 (m, C_6H_5).

***trans*-PhC≡CCH=CHPh:** ^{1}H NMR (C_6D_6) δ 6.28 (d, 1H), 6.95 (d, 1H, J_{HH} = 16 Hz), 7.0−7.5 (m, C_6H_5).

***cis*-Me$_3$SiC≡CCH=CHSiMe$_3$:** ^{1}H NMR (C_6D_6) δ 0.16 (s, 9H, Si($CH_3)_3$), 0.23 (s, 9H, Si($CH_3)_3$), 6.01 (d, 1H), 6.23 (d, 1H, J_{HH} = 12 Hz).

***trans*-EtOOCC≡CCH=CHCOOEt:** ^{1}H NMR ($CDCl_3$) δ 1.27, 1.29 (t, 6 H, COOCH_2CH_3), 4.21, 4.23 (q, 4H, COOCH_2-CH_3), 6.42 (d, 1H), 6.74 (d, 1H, J_{HH} = 16 Hz).

***cis*-^{t}BuC≡CCH=CHBu^t:** ^{1}H NMR (C_6D_6) δ 1.18, 1,23 (s, 9H, C($CH_3)_3$), 5,56 (d, 1H), 5.43 (d, 1H, J_{HH} = 12 Hz).

***cis*-Me$_3$SiC≡CCH=CHBu^t:** ^{1}H NMR (C_6D_6) δ 0.16 (s, 9H, Si($CH_3)_3$), 1.19 (s, 9H, C($CH_3)_3$), 5.39 (d, 1H), 5.79 (d, 1H, J_{HH} = 12 Hz).

Experimental for the X-ray Crystal Structure Analysis of 1a and 5. Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to an AFC6S-Rigaku automatic diffractometer (T = 290 K, Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix in each case were determined by least-squares fitting from the settings of 25 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 1. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standard reflections every 100 measurements. Decay and absorption correction were also applied. The structures were solved by Patterson methods and subsequent expansion of the models using DIRDIF.[19] Reflections having $I > 3\sigma(I)$ were used for structure refinement. For **1a** all non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included at idealized positions and not refined. For **5**·0.6 CH_2Cl_2 the non-hydrogen atoms in the cation and in the anion were anisotropically refined. Hydrogen atoms were included in calculated positions and not refined. The solvent CH_2Cl_2 was found to be disordered, and its occupation factor was allowed to refine to get a final value of 0.62. 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[20] software system and ORTEP[21] for plotting. Maximum and minimum peaks in the final difference

(19) Beurkens, P. T. *DIRDIF. Technical report 1984/1*; Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

Fourier maps were +0.91 and -1.31 e Å $^{-3}$ for **1a** and +1.17 and −1.02 e Å^{-3} for **5**·0.6 CH_2Cl_2.

Results and Discussion

Cationic Vinylidene Complexes. The complexes $[TpRuCl(PR_3)_2]$ (PR_3 = PEt_3, PMe^iPr_2)[18] react with HC≡CR (R = Ph, Bu^t) and $NaBPh_4$ in MeOH at 60 °C, affording the cationic vinylidene complexes $[TpRu{=}C{=}CHR(PR_3)_2][BPh_4]$ (PR_3 = PEt_3, R = Ph **1a**, Bu^t **1b**; PR_3 = PMe^iPr_2, R = Ph **2a**, Bu^t **2b**). This procedure has been previously used for the preparation of the related vinylidene complexes $[TpRu{=}C{=}CHR(dippe)][BPh_4]$ (dippe = 1,2-bis(diisopropylphosphino)ethane)[22] starting from [TpRuCl(dippe)]. The derivative $[TpRu{=}C{=}CH\text{-}COOMe(PEt_3)_2][BPh_4]$ (**1c**) was better prepared by reaction of the corresponding dinitrogen complex $[TpRu(N_2)(PEt_3)_2][BPh_4]$[18] with HC≡CCOOMe in tetrahydrofuran or dichloromethane at room temperature, whereas the related compound $[TpRu{=}C{=}CHCOOMe(PMe^iPr_2)_2][BPh_4]$ (**2c**) was not obtained in pure form. Apparently, the reaction of $[TpRu(N_2)(PMe^iPr_2)_2][BPh_4]$[18] with HC≡CCOOMe goes beyond the vinylidene stage, yielding a mixture of uncharacterized products, among which the cationic vinylidene **2c** was detected spectroscopically. All of the vinylidene complexes **1a**−**c** and **2a**−**c** exhibit the typical spectral properties of unsaturated carbenes, namely, the medium strong ν(C=C) band near 1650 cm^{-1} in the IR spectra, the vinylidene proton signal in the ^{1}H NMR spectra, and the characteristic low-field resonance for the metal-bound carbon atom of the vinylidene ligand. Also, complexes **2a**−**c** display one high-field multiplet below 0 ppm, attributable to CH_3 protons of isopropyl groups of the PMe^iPr_2 ligand. Such high-field isopropyl resonance is present in the ^{1}H NMR spectra of a series of cationic derivatives of the type $[TpRu(L)(PMe^iPr_2)_2]^+$ (L = H_2O, N_2, CNBu^t), as well as in the ^{1}H NMR spectrum of $[TpRuCl(PMe^iPr_2)_2]$.[18] The origin of this anomalous chemical shift appears to be the anisotropy resulting from the fact that some of the isopropyl H atoms of the phosphine are forced near the magnetic ring current influence of the pyrazole rings, as a consequence of the steric pressure.[18] Furthermore, this signal is so characteristic that it becomes diagnostic of the presence of a $\{TpRu(PMe^iPr_2)_2\}$ moiety containing phosphines in a cis-disposition. The X-ray crystal structure of **1a** was determined. An ORTEP view of the complex cation is shown in Figure 1. Relevant bond lengths and angles are listed in Table 2. The coordination around ruthenium is distorted octahedral, with the vinylidene ligand almost linearly assembled, with a Ru(1)−C(1)−C(2) angle of 174.0(1)°. The Ru−N separations corresponding to the pyrazole rings positioned cis with respect to the Ru(1)−C(1) bond (Ru(1)−N(12) 2.150(1) Å; Ru(1)−N(32) 2.130(1) Å) are significatively shorter than the bond distance Ru(1)−N(22) of 2.220(1) Å found for the pyrazole ring trans to the vinylidene group. This sequence has been also observed for the complexes $[TpRu{=}C{=}CHPh(pn)][CF_3SO_3]$ (pn = $Ph_2PCH_2CH_2NMe_2$)[23] and $[TpRu{=}C{=}CHPh(tmeda)][BPh_4]$ (tmeda = $Me_2NCH_2CH_2NMe_2$),[24] and it is attributable to the strong π-acceptor ability of the vinylidene ligand. Accordingly, the Ru(1)−C(1) bond length of 1.810(1) Å corresponds to a ruthenium−carbon double bond, being slightly shorter than in $[TpRu{=}C{=}CHPh(pn)][CF_3SO_3]$ (1.821(5) Å)[23] and in $[TpRu{=}C{=}CHPh(tmeda)][BPh_4]$ (1.820(5) Å)[24] and essentially identical to that found in the complex $[Cp^*Ru{=}C{=}CHCOOMe(dippe)][BPh_4]$ (1.807(9) Å).[25] As expected for cationic vinylidene complexes, compounds **1a**−**c** and **2a**,**b** are readily deprotonated by KOBu^t, furnishing the corresponding neutral alkynyls $[TpRu(C{\equiv}CR)(PEt_3)_2]$ (R = Ph **3a**, Bu^t **3b**, COOMe **3c**) and $[TpRu(C{\equiv}CR)(PMe^iPr_2)_2]$ (R = Ph **4a**,

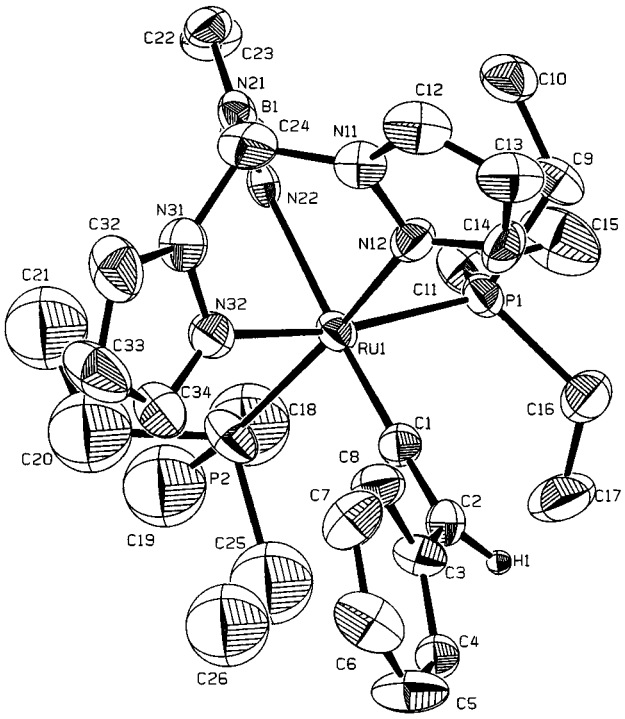


Figure 1. ORTEP view (50% probability) of the cation $[TpRu{=}C{=}CHPh(PEt_3)_2]^+$ showing the atom-labeling scheme. Hydrogen atoms, except the vinylidene proton, have been omitted.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[TpRu{=}C{=}CHPh(PEt_3)_2][BPh_4]$ (1a)

Ru(1)	P(1)	2.384(4)	Ru(1)	C(1)	1.81(1)
Ru(1)	P(2)	2.361(4)	C(1)	C(2)	1.31(2)
Ru(1)	N(12)	2.15(1)	C(2)	C(3)	1.46(2)
Ru(1)	N(22)	2.20(1)	C(2)	H(1)	0.9557
Ru(1)	N(32)	2.13(1)			

P(1)	Ru(1)	P(2)	100.9(1)	N(12)	Ru(1)	N(22)	87.0(4)
P(1)	Ru(1)	N(12)	88.8(3)	N(12)	Ru(1)	N(32)	82.2(4)
P(1)	Ru(1)	N(22)	89.4(3)	N(12)	Ru(1)	C(1)	86.8(5)
P(1)	Ru(1)	N(32)	169.4(3)	N(22)	Ru(1)	N(32)	84.4(5)
P(1)	Ru(1)	C(1)	92.5(4)	N(22)	Ru(1)	C(1)	173.5(5)
P(2)	Ru(1)	N(12)	170.2(3)	N(32)	Ru(1)	C(1)	92.7.0(5)
P(2)	Ru(1)	N(22)	93.5(3)	Ru(1)	C(1)	C(2)	174.0(1)
P(2)	Ru(1)	N(32)	88.2(3)	C(1)	C(2)	C(3)	124.0(1)
P(2)	Ru(1)	C(1)	92.2(4)				

(20) *TEXSAN, Single-Crystal Structure Analysis Software*, version 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989.
(21) Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(22) Jiménez Tenorio, M. A.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1997**, *16*, 5528.
(23) Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**.
(24) Gemel, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1996**, 4071.
(25) de los Ríos, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529.

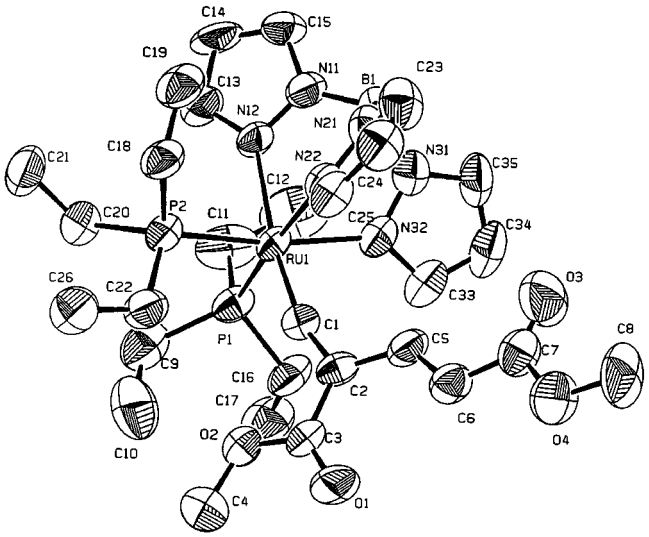


Figure 2. ORTEP view (50% probability) of the cation $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2]^+$ showing the atom-labeling scheme. Hydrogen atoms have been omitted.

Bu^t **4b**). Their spectral properties are given in the Experimental Section and do not require further comment.

Complex **1c** reacts further with HC≡CCOOMe in refluxing tetrahydrofuran, yielding the vinylvinylidene complex $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2][BPh_4]$ (**5**), which was isolated as dichloromethane solvate in the form of red crystals. This reaction does not take place with other 1-alkynes apart from HC≡CCOOMe, and no coupling has been observed in the case of the other vinylidene complexes **1a**,**b** or **2a**,**b**. However it has already been mentioned that the vinylidene complex **2c** was always obtained accompanied by uncharacterized impurities. These impurities most likely arise from some sort of alkyne-coupling process similar to that observed for **1c**, but going further afterward in this particular case. In compound **5**, the formal insertion of one HC≡CCOOMe into the C−H bond of the vinylidene moiety has taken place. The ^{1}H NMR spectrum of **5** shows two separate resonances for the methyl protons of the COOMe groups, whereas the vinylic protons appear as two doubles at 5.57 and 6.91 ppm. The large value of 16 Hz found for the coupling constant $^3J_{HH}$ suggests that these two protons are in mutually trans-positions, leading to an overall *E*-stereochemistry for the vinylvinylidene fragment. Only one isomer has been observed, and its stereochemistry was unequivocally established by X-ray crystal structure analysis. An ORTEP view of the complex cation is shown in Figure 2. Selected bond lengths and angles are listed in Table 3. The coordination around Ru is distorted octahedral, with the vinylvinylidene ligand trans to one of the pyrazole rings of the Tp ligand. The vinylvinylidene group is planar (mean deviation from the plane 0.05 Å), the substituted vinyl group pointing toward the pyrazole rings and away from the PEt_3 ligands. The Ru(1)−C(1) bond length of 1.791(8) Å is shorter than the Ru=C separation in the carbene complex $[TpRu{=}C(OMe)CH_2COOMe(dippe)][BPh_4]$ (1.86(2) Å),[22] but very similar to that found in the vinylidene complex **1a**. The carbon chain C(1)−C(2)−C(5)−C(6)-C(7) adopts an S-trans-stereochemistry with alternating double C(1)−C(2), C(5)−C(6) and single C(2)−C(5), C(6)−C(7) bonds, and its dimensions compare well in general with those reported in the literature for other vinylvinylidene ruthenium derivatives.[26−28] However, the few vinylvinylidene complexes of ruthenium previously reported in the literature were obtained by dehydration of substituted propargyl alcohols,[26−28] which means that the C−C bond of the vinylvinylidene unit was already present. In our case, the formation of the vinylvinylidene ligand has been interpreted in terms of a [2 + 2] cycloaddition of one HC≡CCOOMe molecule to the C=CHR bond of the vinylidene moiety, as shown in Scheme 2, followed by a concerted ring opening of the resulting undetected cyclobutenylidene intermediate to yield the final product. An analogous mechanism has been proposed for explaining the formation of zerovalent tungsten[5] and chromium[6] vinylvinylidene complexes starting from the corresponding vinylidene species. As far as we are aware, ours is the first report of such a process taking place at a Ru^{II} metal center, although very recently related cycloaddition reactions of aromatic imines to a ruthenium butatrienylidene complex have been reported.[29] Iron(II) vinylidenes also undergo [2 + 2] cycloaddition reactions, which have been successfully used in the synthesis of *β*-lactam.[30] The first stable cyclobutenylidene complex $[CpFe{=}\overline{C-C(Me){=}C(Ph)CH_2}(CO)(P(OMe)_3)][CF_3SO_3]$ was obtained by addition of MeC≡CPh to the primary vinylidene complex $[CpFe{=}C{=}CH_2(CO)(P(OMe)_3)][CF_3SO_3]$, and it was structurally characterized by single-crystal X-ray diffraction.[6b] We carried out deuterium labeling experiments in an attempt to find experimental evidence supporting the formation of a metallocyclobutenylidene as intermediate. Unfortunately, proton−deuterium scrambling prevented the study of the coupling process, and no conclusion could be reached, so the proposed mecha-

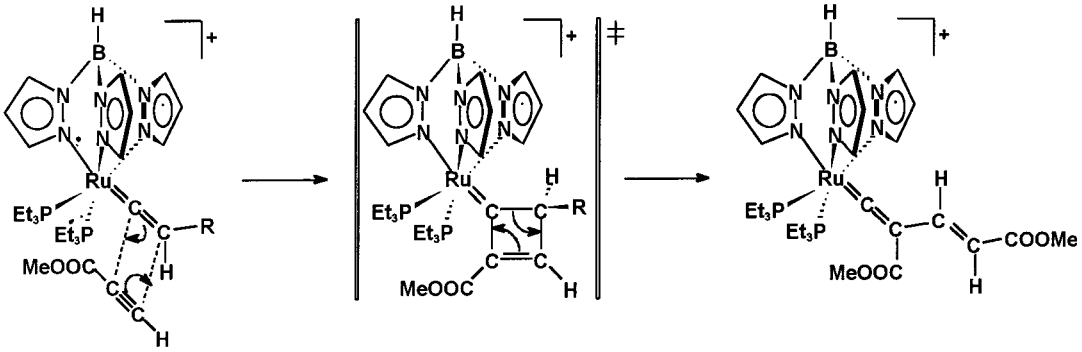
Table 3. Selected Bond Distances (Å) and Angles (deg) for $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2][BPh_4]$ (5)

Ru(1)	P(1)	2.395(2)	C(1)	C(2)	1.33(1)
Ru(1)	P(2)	2.388(2)	C(2)	C(3)	1.46(1)
Ru(1)	N(12)	2.189(6)	C(2)	C(5)	1.45(1)
Ru(1)	N(22)	2.147(7)	C(5)	C(6)	1.34(1)
Ru(1)	N(32)	2.145(7)	C(6)	C(7)	1.47(1)
Ru(1)	C(1)	1.791(8)			

P(1)	Ru(1)	P(2)	99.23(8)	N(22)	Ru(1)	N(32)	80.9(3)
P(1)	Ru(1)	N(12)	91.7(2)	N(22)	Ru(1)	C(1)	87.6(3)
P(1)	Ru(1)	N(22)	170.8(2)	N(32)	Ru(1)	C(1)	88.3(3)
P(1)	Ru(1)	N(32)	90.4(2)	Ru(1)	C(1)	C(2)	163.6(7)
P(1)	Ru(1)	C(1)	95.4(3)	C(1)	C(2)	C(3)	120.0(8)
P(2)	Ru(1)	N(12)	89.0(2)	C(1)	C(2)	C(5)	117.7(8)
P(2)	Ru(1)	N(22)	89.2(2)	C(3)	C(2)	C(5)	122.3(7)
P(2)	Ru(1)	N(32)	169.5(2)	O(1)	C(3)	O(2)	121.1(9)
P(2)	Ru(1)	C(1)	95.0(2)	C(2)	C(5)	C(6)	127.7(8)
N(12)	Ru(1)	N(22)	84.7(3)	C(5)	C(6)	C(7)	119.9(9)
N(12)	Ru(1)	N(32)	86.5(3)	O(3)	C(7)	O(4)	122.0(1)
N(12)	Ru(1)	C(1)	171.3(3)				

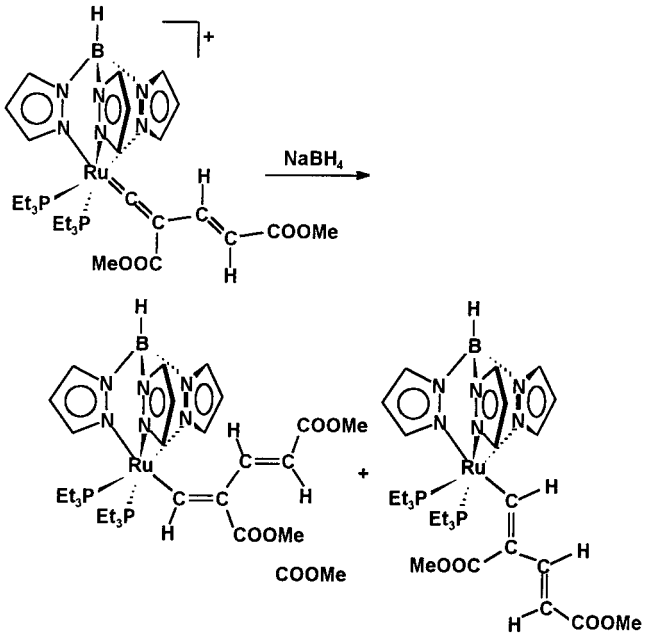
(26) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.
(27) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178.
(28) Bustelo, E.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563.
(29) Bruce, M. I.; Hinterding, P.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1997**, 715.
(30) Barrett, A. G.; Mortier, J.; Sabat, M.; Sturgess, M. A. *Organometallics* **1988**, *7*, 2553.

Scheme 2. Proposed Reaction Sequence for the Formation of the Vinylvinylidene Derivative 5 via Formation of a Cyclobutenylidene Intermediate Complex

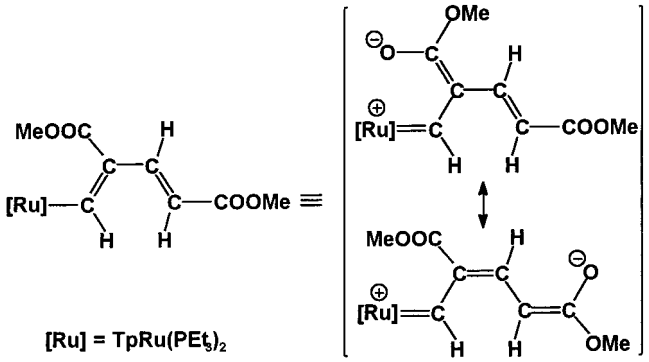


nism, although reasonable, must be considered only as a tentative explanation. However, the fact that only one single stereoisomer is observed seems to be in support of a concerted mechanism, since the opening of the postulated cyclobutenylidene should be either conrotatory or disrotatory, leading to one single isomer, as in our case. As it occurs in the case of the tungsten derivative [W=C=C(COOMe)C(COOMe)=CHPh(CO)$_3$(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane),[5] the presence of the COOMe substituent at the β-carbon apparently deactivates the vinylidene fragment toward further reaction with alkyne, a process that would lead to polymerization.

The α-carbon atom of the vinylvinylidene ligand in **5** is electrophilic, and hence, the reaction with $NaBH_4$ in MeOH led to the neutral σ-η^1-butadienyl complex [TpRu(CH=C(COOMe)CH=CHCOOMe)(PEt$_3$)$_2$] (**6**), which was isolated as a yellow microcrystalline solid.



This compound exists as a mixture of two isomers, namely, *Z* and *E*, one of them being clearly predominant as inferred by NMR spectroscopy. Furthermore, it appears that on standing in solution, the minor isomer (probably the kinetic product) converts into the main product, so at the end only one of the two possible isomers is observed. However, it is not possible to distinguish unambiguously on an NMR basis only to which of the two isomers corresponds the structure of the final product. The most relevant feature of the ^{1}H NMR spectrum of **6** is the resonance for the proton at the α-carbon, which appears as a low-field triplet at 12.67 ppm ($^3J_{HP}$ = 11.2 Hz) for the final isomer (at 11.60 ppm for the kinetic products). This chemical shift is unusually low field for an alkenyl complex. For instance, the resonance for the proton at the α-carbon in the σ-η^1-butadienyl complex [(η^5-indenyl)Ru(CH=CH−CH=CH$_2$)(dppm)] appears as one triplet at 7.60 ppm.[31] In fact, this chemical shift falls in the range expected for a carbene complex. From the ^{13}C{^{1}H} NMR spectrum of **6**, the carbene character is also evident after the chemical shift of the α-carbon (triplet at 209.6 ppm, $^2J_{CP}$ = 23.6 Hz). We have explained it by considering that delocalization of π-electron density between the alkenyl and the ester fragments makes an important resonance contribution to the structure of two zwitterionic Schrock-type carbene hybrids, as shown.



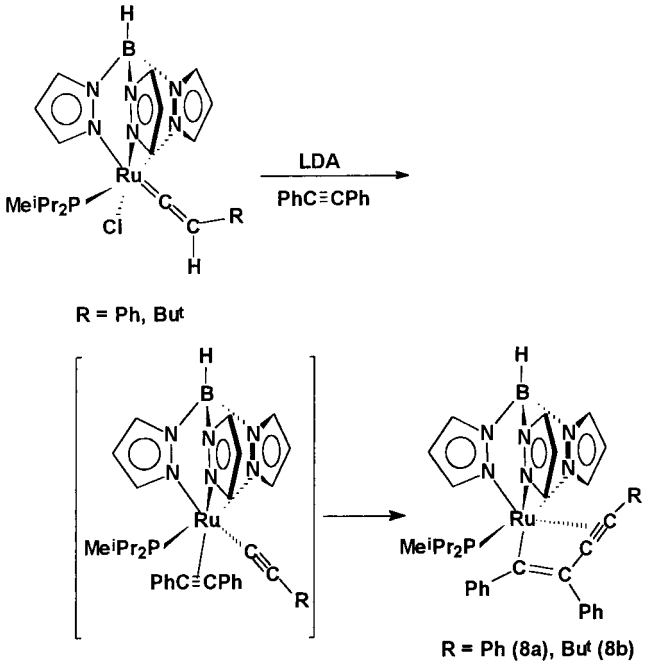
A similar explanation has been invoked for explaining the observed bond length sequence across the vinylvinylidene ligand in the tungsten complex [W=C=C(COOMe)C(COOMe)=CHPh(CO)$_3$(dppe)], although in this particular case the resonance contribution was in the form of carbyne hybrids.[5]

Neutral Vinylidene Complexes and Alkyne Coupling. We have recently noted that as a consequence of its bulkiness, P^{i}Pr$_2$Me in [TpRuCl(PMe^{i}Pr$_2$)$_2$] is substitutionally labile, at variance with PEt$_3$ in [TpRuCl(PEt$_3$)$_2$]. This fact has allowed the preparation of neutral derivatives of the type [TpRuCl(L)(P^{i}Pr$_2$Me)] (L = MeCN, CNBu^t, PEt$_3$).[18] In analogous fashion, the reaction of [TpRuCl(PMe^{i}Pr$_2$)$_2$] with 1-alkynes in re-

(31) Gamasa, M. P.; Gimeno, J.; Martin-Vaca, B. M. *Organometallics* **1998**, *17*, 3707.

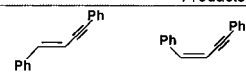
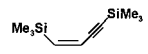
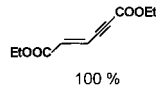
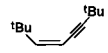
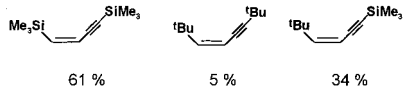
fluxing tetrahydrofuran affords the neutral vinylidene complexes [TpRu(=C=CHR)(Cl)(PMe^iPr_2)] (R = Ph **7a**, Bu^t **7b**, $SiMe_3$ **7d**). The primary vinylidene [TpRu(=C=CH_2)Cl(PMe^iPr_2)] (**7e**) was accessible by methanolysis of the Si−C bond in **7d**, but no neutral vinylidene could be obtained in the case of COOMe as substituent. Complexes **7a**−**e** contain a chiral ruthenium center. As a consequence, the three pyrazole rings of the Tp ligand become chemically and magnetically inequivalent, giving rise to nine separate proton and carbon resonances in their ^1H and $^{13}C\{^1H\}$ NMR spectra. The vinylidene proton appears in all cases as one doublet in the range 3.5−5.1 ppm. One doublet is also observed in the $^{13}C\{^1H\}$ NMR spectra for the carbon atom of the vinylidene ligand attached directly to ruthenium. Compounds of the type [TpRu(=C=CHR)Cl(PR_3)] (PR_3 = PCy_3,[32] PPh_3[33]) have been recently reported. At variance with the behavior observed for compounds **7a**−**e**, the formation of the derivatives [TpRu(=C=CHR)Cl(PPh_3)] has shown to be reversible, the 1-alkyne being easily regenerated upon reaction of these complexes with neutral donor molecules such as PMe_3, CO, PPh_3, MeCN, and pyridine.[33]

7a and **7b** react with LDA and the stoichiometric amount of diphenylacetylene in tetrahydrofuran affording the alkyne-coupling derivatives **8a** and **8b** according to the reaction shown.



The derivative [TpRu(C(Ph)=CH−C≡CPh)(PMe^iPr_2)] (**8c**) was also prepared in analogous fashion, using phenylacetylene instead of diphenylacetylene. Complexes **8a**−**c** are yellow-orange microcrystalline materials, very soluble in polar as well as in nonpolar solvents. Because of this, all efforts to obtain single crystals suitable for X-ray structure analysis were unsuccessful, and hence the characterization was accomplished by NMR spectroscopy and microanalysis. The ^1H NMR spectrum of **8a**−**c** is very complicated in the aromatic region, due to the overlapping of the phenyl ring resonances with those of Tp ligand (nine pyrazole ring protons). The assignation of the signals was made by means of 2D $^1H-^1H$ COSY and $^{13}C\{^1H\}-^1H$ HETCOR spectroscopy. The resonances for the quaternary carbons of the C_4 chain were also identified on the $^{13}C\{^1H\}$ NMR spectra. The σ-bound carbon appears as one doublet at ca. 180 ppm, whereas the carbon atoms of the triply bonded moiety appear in the range 60−75 ppm. These spectral data are consistent with a formulation as σ-enynyls for compounds **8a**−**c**. However, the lack of an X-ray crystal structure for any of these derivatives does not allow the unambiguous confirmation of such structural assignment. Several possible structures have been found for enynyl ruthenium complexes, depending essentially on the fact that alkyne to vinylidene isomerization might take place prior to alkynyl migration (pathway B in Scheme 1).[1,13,14,34−36] If this happens, the stereochemistry of the C_4 chain is different from that resulting from the direct insertion of the alkyne into the metal−alkynyl bond (pathway A in Scheme 1).[1,3,15,16] In this case, there is also the possibility of formation of a σ-enynyl stabilized by means of β-agostic interaction rather than triple-bond coordination, as occurs in [Cp*Ru(C(H−CH_2)=C(CH_3)C≡CBu^t)(PPh_3)].[16] The $^{13}C\{^1H\}$ chemical shifts for the C_4 chain of compounds having any of these possible structures overlap to a great extent, so the structural assignment, made only on spectral grounds, must be regarded with due caution. In any case, the proposed geometries for compounds **8a**,**b** are supported by the fact that a structure derived from pathway B would involve an energetically too costly diphenylacetylene-to-diphenylvinylidene rearrangement. Such a process is more feasible for phenylacetylene, but the similarities in spectral properties

Table 4. Product Distribution for Alkyne-Coupling Reactions Catalyzed by Compound 8a[a]

Alkyne	Products	Yield (%)
HC≡CPh	 81 % 18 %	90
HC≡CSiMe$_3$	 100 %	57
HC≡CCOOEt	 100 %	95
HC≡C^{t}Bu	 100 %	14
HC≡CSiMe$_3$ + HC≡C^{t}Bu	 61 % 5 % 34 %	65

[a] Reaction conditions: toluene, 110 °C, 12−16 h, 2 % catalyst.

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suggest analogous structures for the three derivatives **8a**−**c**. No evidence for agostic interactions, e.g., with ortho-phenyl hydrogen atoms, has been found.

Compounds **8a**−**c** can be regarded as isolable intermediates in the overall catalytic alkyne-coupling cycle. As such, they are efficient catalysts for alkyne dimerization, and also for the cross-coupling reaction of terminal alkynes. Preliminary studies show that the three compounds catalyze the dimerization of phenylacetylene, yielding mixtures of *cis*- and *trans*-PhC≡CCH═CHPh. We have studied in more detail the coupling reactions catalyzed by **8a**, and the results are summarized in Table 4. The conversion factors and the stereoselectivity depend much on the nature of the R groups of the alkyne, a fact that has been previously noted by others.[1,3,15,16,36] In the case of cross-coupling of trimethylsilylacetylene and *tert*-butylacetylene, a 2:1 mixture of the homocoupling product *cis*-Me_3SiC≡CCH═CH$SiMe_3$ and the cross-coupling product *cis*-Me_3-SiC≡CCH═CHBu^t was obtained, accompanied by very small amounts of *cis*-^{t}BuC≡CCH═CHBu^t. The good yield and the stereoselectivity found for the formation of the *E*-isomer of EtOOC−C≡C−CH═CHCOOEt are remarkable. The full study of applications of **8a**−**c** and related compounds as catalysts for alkyne dimerization and oligomerization reactions is currently underway, and the results will be reported in due course.

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Supporting Information Available: Tables of crystal data, bond lengths, bond angles, atomic fractional coordinates and U_{iso} values, and themal parameters and ORTEP views for **1a** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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