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Reactivity of [TpRuCl(dippe)] toward 1-Alkynes. X-ray Crystal Structures of [TpRu=C(OMe)CH$_2$COOMe(dippe)][BPh$_4$] and [TpRu(C$\equiv$CC(Ph)=CH$_2$)(dippe)] (dippe = 1,2-Bis(diisopropylphosphino)ethane; Tp = Hydrotris(pyrazolyl)borate)

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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The complex [TpRuCl(dippe)] (Tp = hydrotris(pyrazolyl)borate) reacts with 1-alkynes in MeOH in the presence of NaBPh$_4$ yielding vinylidene complexes [TpRu=C=CHR(dippe)]-[BPh$_4$]. When R = COOMe, the vinylidene derivative reacts further with MeOH furnishing the corresponding methoxy−carbene complex [TpRu=C(OMe)CH$_2$COOMe(dippe)][BPh$_4$]. The X-ray crystal structure of this compound was determined. The vinylidene complexes, as well as the methoxy−carbene derivative, react with KOBu^t yielding neutral alkynyls [TpRu(C$\equiv$CR)(dippe)]. The reaction of [TpRuCl(dippe)] with propargyl alcohols HC$\equiv$CCRR′-(OH) leads to different products depending on the R groups. Thus, with HC$\equiv$CCMePh-(OH), the allenylidene complex [TpRu=C=C=CMePh(dippe)][BPh$_4$] was obtained. This compound is deprotonated by strong bases at the δ carbon, yielding the enynyl derivative [TpRu(C$\equiv$CC(Ph)=CH$_2$)(dippe)], which was studied by X-ray diffraction. The reaction of [TpRuCl(dippe)] with HC$\equiv$CCMe$_2$(OH) leads to a deep red binuclear vinylidene−carbene complex of composition [{TpRu(dippe)}$_2$(μ-C$_{10}$H$_{12}$)][PF$_6$]$_2$, formally derived from the coupling of one isoprenyl−vinylidene species, generated *in situ*, to an allenylidene moiety. This coupled product is readily deprotonated by weak bases furnishing the blue binuclear allenylidene/alkynyl−carbene complex [{TpRu(dippe)}$_2$(μ-C$_{10}$H$_{11}$)]$^+$, which was isolated as a [BPh$_4$]$^-$ salt. All compounds were characterized by microanalysis, IR, and NMR spectroscopy.

Introduction

In a recent work, we have shown that the complex [TpRuCl(dippe)][1] exhibits a chemical reactivity toward small molecules similar in many aspects to that of the related half-sandwich derivatives [CpRuCl(dippe)] and [Cp*RuCl(dippe)] (Cp = C$_5$H$_5$, Cp* = C$_5$Me$_5$),[2] although significant differences in chemical behavior were also observed. Following our studies on the reactivity of these half-sandwich ruthenium complexes toward alkynes,[3] we became interested in carrying a parallel study on the formally homologous TpRu system. It is well-known that a wide range of complexes can be readily derived from [(C$_5$R$_5$)RuClP$_2$] (R = H, Me; P$_2$ = two monodentate phosphines or one bidentate phosphine) and terminal acetylenes,[4] but until now, such a rich chemistry was virtually unknown for ruthenium complexes containing the Tp ligand. Very recently, Kirchner and co-workers[5−9] have reported that certain TpRu compounds display a versatile chemical reactivity toward alkynes, which converts them in efficient catalyst precursors in processes such as the dimerization of terminal acetylenes[6,9] or the coupling of phenylacetylene with benzoic acid or allyl alcohols.[5] We have now shown that [TpRuCl(dippe)] reacts with terminal alkynes yielding cationic vinylidene complexes, which undergo typical transfomations of such species, namely formation of alkoxy−carbene complexes and deprotonation to yield neutral alkynyls. On the other hand, the final product of the reaction of [TpRuCl(dippe)] with substituted propargyl alcohols HC$\equiv$CC(OH)RR′ has been shown to be a function of the R and R′ substituents. Thus, when R = Me and R′ = Ph, an allenylidene complex is obtained, but for R = R′ = Me, the coupling of two

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allenylidene units formally occurs to yield a novel binuclear complex, an interesting process which has only one precedent in cyclopentadienylruthenium chemistry.[10] The characterization and properties of all of these species is described, and analogies and differences with related Cp and Cp* derivatives are also discussed.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere 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[11] was prepared according to reported procedures. [TpRuCl(dippe)] was obtained by thermal displacement of PPh_3 from $[TpRuCl(PPh_3)_2]$[12] by dippe, as recently described.[1] 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 ppm from $SiMe_4$ (^{1}H and ^{13}C{^{1}H}) or 85% H_3PO_4 (^{31}P{^{1}H}). The phosphine protons for all of the compounds appeared as a series of overlapping multiplets in the range 0.5−3 ppm, and were not assigned. Microanalyses were performed by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

Preparation of Vinylidene Complexes [TpRu=C=CHR(dippe)][BPh$_4$] (R = COOMe (1a), Ph (1b), H (1c)). In a typical preparation, a suspension of [TpRuCl(dippe)] (0.2 g, *ca.* 0.3 mmol) in MeOH (15 mL) was treated with an excess of the corresponding 1-alkyne ($HC{\equiv}CSiMe_3$ in the case of **1c**) and solid $NaBPh_4$ (0.3 g, excess). The mixture was heated gently using a heat gun for several minutes, and then it was stirred at room temperature until a microcrystalline precipitate was formed (*ca.* 1 h). The precipitate was filtered off, washed with EtOH and petroleum ether, and dried *in vacuo*. These compounds can be recrystallized from acetone/EtOH or CH_2Cl_2. **1a**: Yield 0.2 g, 75%. Anal. Calcd for $C_{51}H_{66}N_6B_2O_2P_2Ru$: C, 62.5; H, 6.74; N, 8.6. Found: C, 62.4; H, 6.87; N, 8.7. IR (Nujol): ν(BH) 2507 cm^{-1}; ν(C=O) 1730 cm^{-1}; ν(C=C) 1589 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 3.61 (s, $Ru{=}C{=}CHCOOC\mathit{H}_3$), 5.14 (t, *J*(H,P) = 3.6 Hz, $Ru{=}C{=}C\mathit{H}COOCH_3$), 6.37 (t, *J*(H,H) = 2 Hz, 2H), 6.48 (t, *J*(H,H) = 2 Hz, 1H), 7.96 (d, 2H), 8.13 (d, 1H), 8.15 (d, 2H), 8.30 (d, 1H). ^{31}P{^{1}H} NMR: 68.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): 18.2, 18.9, 19.5 (s, $P(CH(\mathit{C}H_3)_2)_2$), 20.3 (m, $P\mathit{C}H_2$), 26.8, 29.4 (m, $P(\mathit{C}H(CH_3)_2)_2$), 51.6 (s, $COO\mathit{C}H_3$), 106.5 (s, $Ru{=}C{=}\mathit{C}HCOOMe$), 106.5, 106.9, 136.5, 137.7, 145.2, 145.5 (s, $HB(\mathit{C}_3H_3N_2)_3$); 352.7 (t, *J*(C,P) = 16.14 Hz, $Ru{=}\mathit{C}$). **1b:** Yield 0.24 g, 80%. Anal. Calcd for $C_{55}H_{68}N_6B_2P_2Ru$: C, 66.2; H, 6.82; N, 8.4. Found: C, 65.9; H 6.95; N, 8.2. IR (Nujol): ν(BH) 2475 cm^{-1}; ν(C=C) 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.15 (t, *J*(H,P) = 3.2 Hz, $Ru{=}C{=}C\mathit{H}Ph$), 6.41, 7.01 (m, $Ru{=}C{=}CHC_6\mathit{H}_5$), 6.18 (t, *J*(H,H) = 2 Hz, 2H), 6.38 (t, *J*(H,H) = 2.4 Hz, 1H), 7.44 (d, 1H), 7.72 (d, 2H), 7.80 (d, 2H), 7.84 (d, 1H). ^{31}P{^{1}H} NMR: 69.1 (s). ^{13}C{^{1}H} NMR: 18.3, 18.5, 19.3, 19.6 (s, $P(CH(\mathit{C}H_3)_2)_2$), 20.8 (m, $P\mathit{C}H_2$), 26.4, 29.4 (m, $P(\mathit{C}H(CH_3)_2)_2$), 106.1, 106.7, 126.7, 127.0, 144.9, 145.3 (s, $HB(\mathit{C}_3H_3N_2)_3$), 113.4 (s, $C{=}\mathit{C}HPh$), 354.9 (m, $Ru{=}\mathit{C}$). **1c:** Yield 0.22 g, 77%. Anal. Calcd for $C_{53}H_{72}N_6B_2P_2Ru$: C, 65.1; H, 7.37; N, 8.6. Found: C, 65.0; H, 7.35; N, 8.4. IR: ν(BH) 2486 cm^{-1}; ν(C=C) 1637 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.61 (t, *J*(H,P) = 3.2 Hz); 6.21 (t, *J*(H,H) = 2 Hz, 2H), 6.36 (t, *J*(H,H) = 2 Hz, 1H), 7.51 (d, 1H), 7.58 (d, 2H), 7.6 (d, 2H), 7.81 (d, 1H). ^{31}P{^{1}H} NMR: 71.3 (s). ^{13}C{^{1}H} NMR: 18.1, 18.5, 19.1, 19.5 (s, $P(CH(\mathit{C}H_3)_2)_2$), 20.5 (m, $P\mathit{C}H_2$), 26.5, 28.1 (m, $P(\mathit{C}H(CH_3)_2)_2$), 91.3 (s, $Ru{=}C{=}\mathit{C}H_2$), 106.4, 106.7, 136.3, 137.4, 144.1, 145.3 (s, $HB(\mathit{C}_3H_3N_2)_3$), 358.5 (t, $Ru{=}\mathit{C}$, *J*(C,P) = 16.1 Hz).

[TpRu=C(OMe)CH$_2$COOMe(dippe)][BPh$_4$] (2). To a suspension of [TpRuCl(dippe)] (0.2 g, 0.3 mmol) in MeOH (15 mL), an excess of $HC{\equiv}CCOOMe$ and solid $NaBPh_4$ (0.3 g, excess) were added. The mixture was refluxed for 2 h. At the end of this time, a red solution was obtained. It was concentrated until a red, crystalline solid began to precipitate. Cooling to −20 °C, in order to complete the precipitation, afforded a red-pink crystalline material, which was filtered off, washed with EtOH and petroleum ether, and dried *in vacuo*. This compound was recrystallized from an acetone/EtOH mixture, yielding crystals suitable for X-ray structure analysis. Yield: 0.2 g, 66%. Anal. Calcd for $C_{52}H_{70}N_6B_2O_3P_2Ru$: C, 61.7; H, 6.92; N, 8.3. Found: C, 61.5; H, 7.01; N, 8.0. IR (Nujol): ν(BH) 2463 cm^{-1}; ν(C=O) 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.54 (s, $Ru{=}C(OC\mathit{H}_3)$), 3.65 (s, $Ru{=}C(OMe)CH_2COOC\mathit{H}_3$), 3.68 (s, $Ru{=}C(OMe)C\mathit{H}_2COOCH_3$), 6.20 (t, *J*(H,H) = 2.4 Hz, 2H), 6.24 (t, *J*(H,H) = 2.4 Hz, 1H), 7.44 (d, 1H), 7.46 (d, 2H), 7.75 (d, 2H), 7.78 (d, 1H). ^{31}P{^{1}H} NMR: 69.8 (s). ^{13}C{^{1}H} NMR: 18.3, 18.8, 20.0, 20.3 (s, $P(CH(\mathit{C}H_3)_2)_2$), 22.1 (t, *J*(C,P) = 18.6 Hz,$P\mathit{C}H_2$), 26.1 (t, *J*(C,P) = 9.5 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 26.9 (t, *J*(C,P) = 11.06 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 52.6 (s, $Ru{=}C(O\mathit{C}H_3)$), 54.7 (s, $\mathit{C}H_2COOCH_3$), 62.9 (s, $CH_2COO\mathit{C}H_3$), 106.0, 106.3, 136.5, 136.7, 144.4, 145.6 (s, $HB(\mathit{C}_3H_3N_2)_3$), 166.2 (s, $CH_2\mathit{C}OOCH_3$), 309.7 (t, *J*(C,P) = 13 Hz, $Ru{=}\mathit{C}$).

Neutral Alkynyl Complexes [TpRu(C≡CR)(dippe)] (R = COOMe (3a), Ph (3b), H (3c)). A thf solution of the corresponding vinylidene complex **1a**−**c** 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 was filtered through Celite. Concentration, addition of petroleum ether and cooling to −20 °C afforded yellow crystals of **3a**−**c**. **3a:** Yield 60%. Anal. Calcd for $C_{27}H_{45}N_6BO_2P_2Ru$: C, 49.1; H, 6.83; N, 12.8. Found: C, 48.9; H, 6.76; N, 12.2. IR (Nujol): ν(BH) 2494 cm^{-1}; ν(C≡C) 2054 cm^{-1}; ν(C=O) 1657 cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.53 (s, $COOC\mathit{H}_3$), 5.87 (two overlapping triplets, 3H), 7.00 (d, 1H), 7.44 (d, 2H), 7.54 (d, *J*(H,H) = 2.4 Hz, 1H), 8.33 (d, *J*(H,H) = 1.6 Hz, 2H). ^{31}P{^{1}H} NMR: 79.9 (s). ^{13}C{^{1}H} NMR: 18.6, 19.3, 19.9, 20.0 (s, $P(CH(\mathit{C}H_3)_2)_2$), 22.0 (t, *J*(C,P) = 19.1 Hz, $P\mathit{C}H_2$), 26.3 (t, *J*(C,P) = 9.9 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 28.4 (m, $P(\mathit{C}H(CH_3)_2)_2$), 50.6 (s, $RuC{\equiv}CCOO\mathit{C}H_3$), 103.3 (s, $RuC{\equiv}\mathit{C}COOMe$), 104.6, 105.4, 134.7, 135.6, 144.3, 145.7 (s, $HB(C_3H_3N_2)_3$), 145.9 (t, *J*(C,P) = 16.8 Hz, $Ru\mathit{C}{\equiv}CCOOMe$), 153.2 (s, $RuC{\equiv}C\mathit{C}OOMe$). **3b:** Yield 53%. Anal. Calcd for $C_{31}H_{47}N_6BP_2Ru$: C, 54.9; H, 6.94; N, 12.4. Found: C, 55.2; H, 7.03; N, 12.1. IR (Nujol): ν(BH) 2464 cm^{-1}; ν(C≡C) 2067 cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.89 (t, *J*(H,H) = 2 Hz, 1H), 5.91 (t, 2H), 7.04 (d, *J*(H,H) = 1.6 Hz, 1H), 7.47 (d, 2H), 7.57 (d, *J*(H,H) = 2.4 Hz, 1H), 8.37 (d, 2H), 6.90 (t, 1H), 7.12 (t, 2H), 7.124 (m, 2H, $RuC{\equiv}CC_6\mathit{H}_5$). ^{31}P{^{1}H} NMR: 81.6 (s). ^{13}C{^{1}H} NMR: 18.7, 19.4, 19.9, 20.0 (s, $P(CH(\mathit{C}H_3)_2)_2$), 22.3 (t, *J*(C,P) = 18.1 Hz, $P\mathit{C}H_2$), 26.5 (t, *J*(C,P) = 8.1 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 28.4 (t, *J*(C,P) = 11.1 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 104.5, 105.1, 134.6, 135.5, 144.4, 145.5 (s, $HB(\mathit{C}_3H_3N_2)_3$), 109.5 (s, $RuC{\equiv}\mathit{C}Ph$), 122.9, 128.1, 131.2 (s, $RuC{\equiv}C\mathit{C}_6H_5$), 130.9 (t, *J*(C,P) = 17.6 Hz, $Ru\mathit{C}{\equiv}CPh$). **3c:** Yield 55%. Anal. Calcd for $C_{25}H_{43}N_6BP_2Ru$: C, 49.9; H, 7.16; N, 14.0. Found: C, 50.1; H, 7.22; N, 13.8. IR (Nujol): ν(BH) 2460 cm^{-1}; ν(C≡C) 1922 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.07 (s, $RuC{\equiv}C\mathit{H}$), 5.87 (t, *J*(H,H) = 2.2 Hz, 1H), 5.90 (t, 1H), 7.02 (d, 1H), 7.47 (d, *J*(H,H) = 1.6 Hz, 2H), 7.56 (d, *J*(H,H) = 2.4 Hz, 1H), 8.41 (d, 2H). ^{31}P{^{1}H} NMR: 81.4 (s). ^{13}C{^{1}H} NMR: 18.7, 19.5, 20.2, 20.3 (s, $P(CH(CH_3)_2)_2$), 22.3 (t, *J*(C,P) = 17.6 Hz, $P\mathit{C}H_2$), 26.5 (t, *J*(C,P) = 7.4 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 28.0 (t, *J*(C,P) = 11.8 Hz, $P(\mathit{C}H(CH_3)_2)_2$), 91.6 (s, $RuC{\equiv}\mathit{C}H$), 120.3 (t, *J*(C,P) = 16.3 Hz, $Ru\mathit{C}{\equiv}CH$), 104.5, 104.9, 134.5, 135.4, 144.4, 145.6 (s, $HB(C_3H_3N_2)_3$).

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[TpRu=C=C=CMePh(dippe)][BPh_4] (4). A suspension of [TpRuCl(dippe)] (0.2 g, 0.3 mmol) in MeOH (15 mL) was treated with an excess of HC≡CC(OH)MePh and $NaBPh_4$ (0.3 g, excess). The mixture was heated using a water bath. The initial yellow color of the suspension changes to a dark red-brown. It was stirred for 15 min and then allowed to cool to room temperature. The red-brown precipitate was filtered off, washed with EtOH and petroleum ether, and dried *in vacuo*. This product can be recrystallized from acetone/EtOH. Yield: 0.24 g, 78%. Anal. Calcd for $C_{57}H_{70}N_6B_2P_2Ru$: C, 66.9; H, 6.85; N, 8.2. Found: C, 66.7; H, 6.79; N, 8.0. IR (Nujol): ν(C=C=C) 1937 cm^{-1}; ν(BH) 2480 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.91 (s, CH_3), 6.09 (t, J(H,H) = 2 Hz, 2H), 6.45 (t, J(H,H) = 2 Hz, 1H), 7.43 (d, 2H), 7.70 (d, 2H), 7.34 (d, 1H), 7.91 (d, 1H), 7.16 (t, J(H,H) = 7.6 Hz, C_6H_5), 7.61 (t, J(H,H) = 7.2 Hz, C_6H_5), 7.90 (d, J(H,H) = 7.2 Hz, C_6H_5). $^{31}P\{^1H\}$ NMR: 72.1 (s). $^{13}C\{^1H\}$ NMR: 18.2, 18.5, 18.9, 19.5 (s, $P(CH(CH_3)_2)_2$), 20.8 (m, PCH_2); 26.6 (m, $P(CH(CH_3)_2)_2$), 28.6 (m, $P(CH(CH_3)_2)_2$), 30.3 (s, Ru=C=C=CCH_3Ph), 105.9, 107.0, 135.9, 137.2, 144.2, 145.8 (s, $HB(C_3H_3N_2)_3$), 128.6, 129.5, 132.4 (s, Ru=C=C=$CCH_3(C_6H_5)$), 156.3 (s, Ru=C=C=CCH_3Ph), 205.1 (s, Ru=C=C=CCH_3Ph), 312.9 (t, J(C,P) = 17.2 Hz, Ru=C=C=CCH_3Ph).

[TpRu−C≡C−C(Ph)=CH_2(dippe)] (5). This compound was obtained following an experimental procedure similar to that used for the preparation of the neutral alkynyls **3a**−**c**. To a solution of **4** (0.1 g, *ca.* 0.1 mmol) in thf, excess solid $KOBu^t$ was added. An immediate color change from deep red to orange was observed. The mixture was stirred for 30 min at room temperature and then taken to dryness. The residue was extracted with diethyl ether and centrifuged. Addition of petroleum ether, concentration, and cooling to −20 °C afforded well-formed orange crystals of **5** suitable for X-ray structure analysis. Yield: 0.05 g, 71%. Anal. Calcd for $C_{33}H_{49}N_6BP_2Ru$: C, 56.3; H, 6.97; N, 12.0. Found: C, 56.4; H, 7.02; N, 11.9. IR (Nujol): ν(BH) 2457 cm^{-1}; ν(C≡C) 2056 cm^{-1}. ^1H NMR (C_6D_6): δ 5.463 (d, J(H,H) = 2.4 Hz, RuC≡CC(Ph)=CH_aH_b), 5.60 (d, J(H,H) = 2.4 Hz, RuC≡CC(Ph)=CH_aH_b), 5.89 (t, 1H), 5.91 (t, 2H), 7.03 (d, 1H), 7.50 (d, J(H,H) = 2.4 Hz, 2H), 7.58 (d, J(H,H) = 2 Hz, 1H), 8.33 (d, 2H), 7.07, 7.90 (m, RuC≡$CC(C_6H_5)$=CH_2). $^{31}P\{^1H\}$ NMR: 81.3 (s). $^{13}C\{^1H\}$ NMR: 18.7, 19.4, 19.9, 20.0 (s, $P(CH(CH_3)_2)_2$), 22.4 (m, PCH_2), 26.5 (m, $P(CH(CH_3)_2)_2$), 28.3 (m, $P(CH(CH_3)_2)_2$), 104.5, 104.8, 134.6, 135.5, 144.4, 145.8 (s, $HB(C_3H_3N_2)_3$), 109.8 (s, RuC≡CC(Ph)=CH_2), 126.8, 127.3, 127.8 (s, RuC≡$CC(C_6H_5)$=CH_2), 133.5 (t, J(C,P) = 17.7 Hz, RuC≡CC(Ph)=CH_2), 135.9 (s, RuC≡CC(Ph)=CH_2).

[{TpRu(dippe)}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$ (6). To a suspension of [TpRuCl(dippe)] (0.2 g, 0.3 mmol) in MeOH (15 mL), NH_4PF_6 (0.1 g) and a slight excess of HC≡CC(OH)Me_2 were added. The mixture was stirred at room temperature for 24 h. During this time, the color of the mixture changes from yellow to dark red, passing through green and blue. The solvent was removed *in vacuo*, and the residue was extracted with dichloromethane (10 mL) and centrifuged. The deep red solution was concentrated, and then diethyl ether (10 mL) was added. Cooling to −20 °C yielded a dark red microcrystalline product, which was filtered off, washed with petroleum ether, and dried *in vacuo*. It was recrystallized from dichloromethane/petroleum ether in the form of dark red plates. Yield: 0.3 g, 63%. Anal. Calcd for $C_{56}H_{96}N_{12}B_2F_{12}P_6Ru_2$: C, 42.7; H, 6.10; N, 10.7. Found: C, 42.5; H, 6.21; N, 10.5. IR (Nujol): ν(BH) 2477 cm^{-1}; ν(C=C) 1578 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 0.27 (s, 6H, $(CH^a{}_3)_2$), 0.57 (s, 2H, $CH^c{}_2$), 2.21 (s, 2H, $CH^b{}_2$), 5.49 (t, J(H,P) = 3.6 Hz, 1H, Ru=C=CH^e), 6.17 (t, 2H), 6.29 (t, 1H), 6.35 (t, 2H), 6.42 (t, 1H), 7.23 (d, 2H), 7.60 (d, 1H), 7.68 (d, 1H), 7.77 (d, 2H), 7.80 (d, 2H), 7.82 (d, 1H), 7.92 (d, 1H), 8.08 (d, 2H); 7.09 (s, 1H, CH^d). $^{31}P\{^1H\}$ NMR: 65.6 (s), 64.3 (s). $^{13}C\{^1H\}$ NMR: 17.7, 18.3, 18.5, 18.6, 18.9, 19.0, 19.8, 20.2 (s, $P(CH(CH_3)_2)_2$), 19.8 (m, PCH_2), 22.4 (t, J(C,P) = 18.6 Hz, PCH_2), 25.1 (t, J(C,P) = 10.8 Hz, $P(CH(CH_3)_2)_2$), 26.2 (t, J(C,P) = 10.9 Hz, $P(CH(CH_3)_2)_2$), 27.7 (t, J(C,P) = 10.7 Hz, $P(CH(CH_3)_2)_2$), 31.6 (t, J(C,P) = 13.9 Hz, $P(CH(CH_3)_2)_2$), 28.9 (s, $(CH^a{}_3)_2$), 43.2 (s, $CH^c{}_2$), 66.4 (s, $CH^b{}_2$), 114.4 (s, Ru=C=CH^e), 103.7, 104.6, 105.3, 105.3, 133.3, 133.9, 135.2, 135.3, 141.1, 141.8, 142.8, 142.9 (s, $HB(C_3H_3N_2)_3$), 138.7 (s, CH^d), 311.8 (br, Ru=C), 355.5 (br, Ru=C=CH); remaining quaternary carbons not observed.

Table 1. Summary of Data for the Crystal Structure Analysis of 2 and 5[a]

	2	**5**
formula	$C_{52}H_{69}N_6B_2O_3P_2Ru$	$C_{33}H_{49}N_6BP_2Ru$
fw	1010.79	703.62
cryst size (mm)	0.21 × 0.05 × 0.49	0.19 × 0.12 × 0.34
cryst system	monoclinic	triclinic
space group	Pn (No. 7)	$P\bar{1}$ (No. 2)
cell param	a = 13.877(3) Å b = 12.309(2) Å c = 15.296(3) Å β = 99.87(2)°	a = 17.842(4) Å b = 17.914(4) Å c = 11.659(4) Å α = 94.08(2)° β = 104.00(2)° γ = 104.04(2)°
volume	2574(2) $Å^3$	3474(3) $Å^3$
Z	2	4
ρ_{calcd}	1.304 g cm^{-3}	1.345 g cm^{-3}
λ(Mo Kα)	0.710 69 Å	0.710 69 Å
μ(Mo Kα)	4.0 cm^{-1}	5.6 cm^{-1}
F(000)	956	1472
transmision factors	0.91−1.00	0.92−1.00
scan speed (ω)	8 deg min^{-1}	8 deg min^{-1}
2θ interval	$5° < 2\theta < 50°$	$5° < 2\theta < 50°$
no. of measd reflns	5006	10 571
no. of unique reflns	4797 (R_{int} = 0.094)	10246 (R_{int} = 0.041)
no. of obsd reflns ($I > 3\sigma I$)	2247	6332
no. of params	458	773
no. of refln/param ratio	8.73	8.19
R^a	0.053	0.043
R_w ($w = \sigma_F{}^{-2}$)^b	0.058	0.049
max Δ/σ in final cycle	0.49	5.28
gof	1.47	1.32

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

[{TpRu(dippe)}$_2$(μ-$C_{10}H_{11}$)][BPh_4] (7). **6** (0.15 g, *ca.* 0.1 mmol) was dissolved in THF (10 mL). To this dark red solution, a few drops of NEt_3 was added. The color of the solution changed immediately to deep blue. The solvent was removed *in vacuo*, and the residue was extracted with dichloromethane. Centrifugation, concentration, followed by addition of a solution of $NaBPh_4$ (0.15 g, excess) in EtOH and cooling to −20 °C afforded a dark blue precipitate, which was filtered off, washed with petroleum ether, and dried *in vacuo*. Yield: 0.08 g, 50%. Anal. Calcd for $C_{80}H_{115}N_{12}B_3P_4Ru_2$: C, 60.0; H, 7.18; N, 10.5. Found: C, 59.7; H, 6.96; N, 10.4. IR (Nujol): ν(BH) 2482 cm^{-1}; ν(C≡C) 1941 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.12 (t, 2H), 6.13 (t, 2H), 6.20 (t, 1H), 6.21 (t, 1H), 7.26 (s br, 1H), 7.27 (d, 2H), 7.51 (s br, 1H), 7.65 (d, 2H), 7.72 (d, 2H), 7.73 (d, 1H), 7.76 (d, 1H), 7.85 (d, 2H), 0.77 (s, 6H, $(CH^a{}_3)_2$), 1.64 (s, 2H, $CH^c{}_2$), 2.36 (s, 2H, $CH^b{}_2$), CH^d hidden by $[BPh_4]^-$ resonance. $^{31}P\{^1H\}$ NMR: 79.0 (s), 67.7 (s). $^{13}C\{^1H\}$ NMR: 18.3, 18.4, 18.9, 19.0, 19.1, 19.6, 19.9, 20.3 (s, $P(CH(CH_3)_2)_2$), 21.5 (m, PCH_2), 23.0 (m, PCH_2), 26.3, 26.4, 26.6 (overlapping multiplets, $P(CH(CH_3)_2)_2$), 28.5 (m, $P(CH(CH_3)_2)_2$), 28.5 (s, $(CH^a{}_3)_2$), 49.1 (s, $CH^c{}_2$), 63.2 (s, $CH^b{}_2$), 104.9, 105.0, 105.3, 105.9, 134.4, 134.9, 135.2, 135.7, 143.9, 144.4, 144.6, 145.8 (s, $HB(C_3H_3N_2)_3$), 136.1 (s, CH^d), quaternary carbons not observed.

Experimental Data for the X-ray Crystal Structure Determinations. A summary of crystallographic data for compounds **2** and **5** 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 ω-2θ scan method. Lorentz, polarization, and absorption (ψ-scan method) corrections were applied. A small decay correction was also applied for each of the compounds.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[TpRu{=}C(OMe)CH_2COOMe(dippe)][BPh_4]$

Intramolecular Distances			
Ru(1)−P(1)	2.332(5)	Ru(1)−N(32)	2.26(1)
Ru(1)−P(2)	2.356(5)	Ru(1)−C(1)	1.86(2)
Ru(1)−N(12)	2.12(2)	O(1)−C(1)	1.43(2)
Ru(1)−N(22)	2.16(1)	C(1)−C(3)	1.45(2)
Intramolecular Bond Angles			
P(1)−Ru(1)−P(2)	84.7(2)	N(12)−Ru(1)−N(22)	83.2(5)
P(1)−Ru(1)−N(12)	175.4(6)	N(12)−Ru(1)−N(32)	83.3(6)
P(1)−Ru(1)−N(22)	95.7(3)	N(12)−Ru(1)−C(1)	88.6(8)
P(1)−Ru(1)−N(32)	92.1(4)	N(22)−Ru(1)−N(32)	85.5(5)
P(1)−Ru(1)−C(1)	95.9(7)	N(22)−Ru(1)−C(1)	90.4(7)
P(2)−Ru(1)−N(12)	96.3(4)	N(32)−Ru(1)−C(1)	171.3(8)
P(2)−Ru(1)−N(22)	179.5(4)	Ru(1)−C(1)−O(1)	120(1)
P(2)−Ru(1)−N(32)	94.6(4)	Ru(1)−C(1)−C(3)	129(1)
P(2)−Ru(1)−C(1)	89.4(6)	O(1)−C(1)−C(3)	111(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[TpRu(C{\equiv}CC(Ph){=}CH_2)(dippe)]$

Intramolecular Distances			
Ru(1)−P(1)	2.303(2)	Ru(2)−N(9)	2.176(5)
Ru(1)−P(2)	2.283(2)	Ru(2)−N(11)	2.168(5)
Ru(1)−N(1)	2.165(5)	Ru(2)−C(34)	2.005(7)
Ru(1)−N(3)	2.173(5)	C(1)−C(2)	1.194(8)
Ru(1)−N(5)	2.185(5)	C(2)−C(3)	1.439(9)
Ru(1)−C(1)	2.004(6)	C(3)−C(4)	1.327(9)
Ru(2)−P(3)	2.294(2)	C(34)−C(35)	1.203(8)
Ru(2)−P(4)	2.295(2)	C(35)−C(36)	1.43(1)
Ru(2)−N(7)	2.152(5)	C(36)−C(37)	1.33(1)
Intramolecular Bond Angles			
P(1)−Ru(1)−P(2)	85.19(7)	P(3)−Ru(2)−N(9)	92.4(2)
P(1)−Ru(1)−N(1)	176.0(1)	P(3)−Ru(2)−N(11)	98.8(2)
P(1)−Ru(1)−N(3)	96.8(1)	P(3)−Ru(2)−C(34)	91.5(2)
P(1)−Ru(1)−N(5)	95.6(1)	P(4)−Ru(2)−N(7)	96.6(1)
P(1)−Ru(1)−C(1)	90.0(2)	P(4)−Ru(2)−N(9)	95.0(2)
P(2)−Ru(1)−N(1)	98.5(2)	P(4)−Ru(2)−N(11)	175.6(1)
P(2)−Ru(1)−N(3)	178.0(1)	P(4)−Ru(2)−C(34)	90.2(2)
P(2)−Ru(1)−N(5)	92.2(2)	N(7)−Ru(2)−N(9)	87.5(2)
P(2)−Ru(1)−C(1)	92.6(2)	N(7)−Ru(2)−N(11)	79.1(2)
N(1)−Ru(1)−N(3)	79.5(2)	N(7)−Ru(2)−C(34)	88.4(2)
N(1)−Ru(1)−N(5)	85.9(2)	N(9)−Ru(2)−N(11)	86.0(2)
N(1)−Ru(1)−C(1)	88.2(2)	N(9)−Ru(2)−C(34)	173.8(2)
N(3)−Ru(1)−N(5)	87.2(2)	N(11)−Ru(2)−C(34)	88.6(2)
N(3)−Ru(1)−C(1)	87.8(2)	Ru(1)−C(1)−C(2)	176.0(6)
N(5)−Ru(1)−C(1)	172.9(2)	C(1)−C(2)−C(3)	176.7(7)
P(3)−Ru(2)−P(4)	85.45(7)	Ru(2)−C(34)−C(35)	175.5(6)
P(3)−Ru(2)−N(7)	177.9(1)	C(34)−C(35)−C(36)	177.5(7)

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[13] software system and ORTEP[14] program for plotting. All of the structures were solved by the Patterson method and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. Most of the hydrogen atoms were included at idealized positions and not refined. Maximum and minimum peaks in the final difference Fourier maps were +0.83 and −0.54 e Å^{-3} for **2** and +0.61 and −0.42 e Å^{-3} for **5**. Selected bond lengths and angles for each compound are listed in Tables 2 and 3, respectively.

Results and Discussion

[TpRuCl(dippe)] reacts with $HC{\equiv}CR$ (R = Ph, COOMe, Bu^t) in MeOH in the presence of $NaBPh_4$ furnishing the corresponding vinylidene complexes $[TpRu{=}C{=}CHR(dippe)][BPh_4]$ (R = Ph (**1a**), COOMe (**1b**)). When the reaction is carried out with $HC{\equiv}CSiMe_3$, the final product is the primary vinylidene complex $[TpRu{=}C{=}CH_2(dippe)][BPh_4]$ (**1c**), formed presumably by protonolisis of the C-Si bond as it occurs in the course of the reaction of [CpRuCl(dippe)] with $HC{\equiv}CSiMe_3$ to yield $[CpRu{=}C{=}CH_2(dippe)]^{+}$ [3] as well as in many other cases.[15,16] These vinylidene complexes are microcrystalline materials which display one medium−strong IR band near 1600 cm^{-1}, attributable to ν(C=C) in the vinylidene ligand, apart from one weak ν(BH) band near 2500 cm^{-1}, characteristic of the Tp group. The protons of the pyrazole rings of this ligand appear as one set of six separate resonances in the ^{1}H NMR spectra of most compounds prepared in this work, a pattern which has been previously observed for derivatives of the type $[TpRuXL_2]$[1,5,7,12,17] and needs no further comment. One triplet signal is observed for the hydrogen atoms attached at the β-carbon of each of the vinylidene ligands, due to coupling to two equivalent phosphorus atoms. Accordingly, the $^{31}P\{^1H\}$ NMR spectra consist of one sharp singlet. The most relevant feature of the $^{13}C\{^1H\}$ NMR spectra of these compounds is the extremely low-field resonance for the carbon atom of the vinylidene fragment directly attached to ruthenium, which appears as one triplet due to coupling with two phosphorus atoms. This signal appears at even lower field for these Tp derivatives than for their homologues having Cp or Cp* as coligands.[3] These spectral data suggest an octahedral structure in which two of the pyrazole rings are *trans* to the bidentate dippe ligand, the other being *trans* to the vinylidene group. A similar arrangement has been found very recently by X-ray crystallography for the Tp vinylidene complexes $[TpRu{=}C{=}CHPh(TMEDA)][BPh_4]$ (TMEDA = $Me_2NCH_2CH_2NMe_2$)[7] and $[TpRu{=}C{=}CHPh(PN)][CF_3SO_3]$ (PN = $Ph_2PCH_2CH_2NMe_2$).[8] Compounds **1a**−**c** are formal homologues of the vinylidene derivatives $[CpRu{=}C{=}CHR(dippe)][BPh_4]$ and $[Cp^*Ru{=}C{=}CHR(dippe)][BPh_4]$ recently reported by us.[3] We have observed that the formation of the C_5Me_5 vinylidenes involves hydrido−alkynyl complexes of the type $[Cp^*RuH(C{\equiv}CR)(dippe)]^+$ as intermediates, whereas π-alkyne adducts $[CpRu(\eta^2\text{-}HC{\equiv}CR)(dippe)]^+$ have been detected in the case of Cp derivatives.[3] No intermediates have been isolated or detected in the course of the reaction of [TpRuCl(dippe)] with 1-alkynes. However, it seems likely that the reaction may proceed *via* a π-alkyne intermediate rather than through a hydrido−alkynyl complex, since the latter implies a seven-coordinate species which is not favored by the Tp ligand. Furthermore, there are no reports of genuine seven-coordinate Ru−Tp compounds.[5,18] **1b** reacts slowly with MeOH at reflux temperature to yield the alkoxy−carbene complex $[TpRu{=}C(OMe)CH_2COOMe(dippe)][BPh_4]$ (**2**), at variance with its Cp or Cp* homologues but consistent with the observation that such compounds are readily derived from the attack of alcohols

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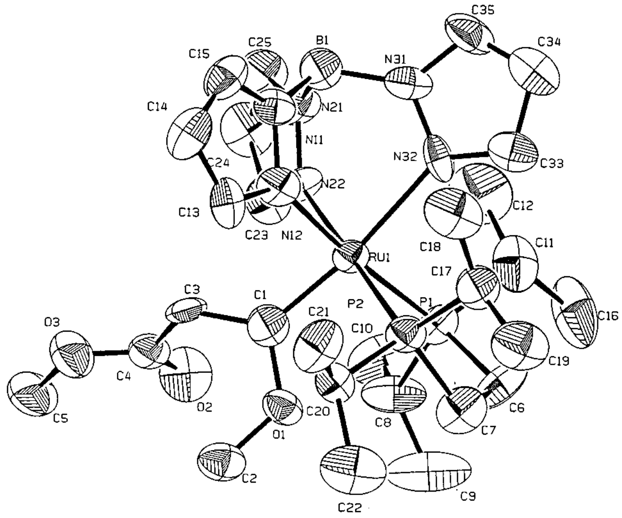
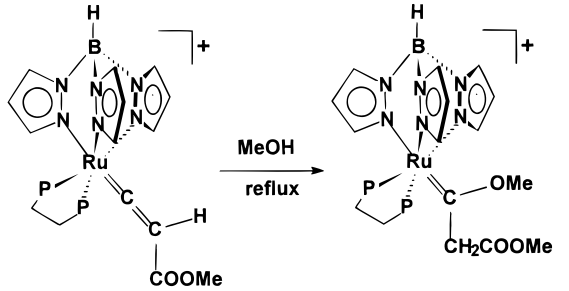


Figure 1. ORTEP drawing of the cation [TpRu=C(OMe)-CH_2COOMe(dippe)]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

at the electrophilic α carbon of monosubstituted vinylidenes in other cases.[4,19−22]



The IR spectrum of **2** displays one single band at 1730 cm^{-1}, attributable to ν(C=O) in the COOMe group, whereas one triplet at 309.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum corresponds to the carbon atom of the carbene ligand directly bound to ruthenium. This chemical shift is similar to that found for the carbene resonance in cyclopentadienylruthenium alkoxy−carbene complexes, i.e., in the range 290−310 ppm. The X-ray crystal structure of **2** was determined. An ORTEP view of the complex cation [TpRu=C(OMe)CH_2COOMe(dippe)]$^+$ is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The coordination around the ruthenium atom is distorted octahedral, very similar to that recently found in the complex [TpRu(H_2)(dippe)]$^+$.[1] The pyrazolyl rings are planar, having dihedral angles close to the ideal value of 120°. The carbene moiety is characterized by a Ru(1)−C(1) bond distance of 1.85(2) Å corresponding to a Ru−C double bond, which is slightly shorter than those found in other cyclopentadienylruthenium carbene complexes such as [CpRu=C(OMe)Et($(PPh_3)_2$)][PF_6] (1.959(6) Å)[20] and [CpRu=C(OMe)CH_2Ph(CHIRAPHOS)][PF_6] (1.93(2) Å, CHIRAPHOS = $Ph_2PCH(CH_3)CH_2PPh_2$).[21] The C(1)−O(1) and C(1)−C(3) bond lengths of 1.43(2) and 1.45(2) Å, respectively are indicative of single bonds. The angle O(1)−C(1)−C(3) is 111(2)°, consistent with sp^2 hybridization for C(1). These three atoms together with Ru are in a plane (max deviation 0.008 Å) almost perpendicular to the plane defined by P(1)−Ru(1)−P(2) and bisecting this angle, a disposition which achieves the maximum π-stabilization between the metal fragment and the carbene moiety, as inferred from MO calculations made for the model compound [CpRu=CH_2-$(PH_3)_2$]$^+$.[23] This arrangement is also adopted by other half-sandwich alkoxy−carbene complexes in the absence of severe steric constraints.[20,21] No alkoxy−carbene complex has been obtained from the reaction of MeOH or EtOH with [TpRu=C=CHR(dippe)]$^+$ for R groups other than COOMe. It has been determined that the attack of an alcohol at the α-carbon of a vinylidene group is influenced by both steric and electronic factors. Thus, bulky phosphine ligands seem to inhibit such a process, as indicated by the inverse relationship between the relative reaction rates of [CpRu=C=CHPh(PPh_3)(PR_3)]$^+$ with MeOH and the cone angle of the phosphine PR_3.[19] On the other hand, electron-withdrawing groups on the vinylidene ligand or on the metal facilitate nucleophilic attack at C_α. On the basis, it is easy to explain why in our case the vinylidene complex having the most electron-withdrawing R group, COOMe, is the only one that reacts with with MeOH to yield the corresponding methoxy−carbene complex. The fact that no homologues of **2** containing Cp or Cp* instead of Tp have been observed could be attributable to the increased electron density at the metal in these Cp and Cp* ruthenium−dippe vinylidene complexes compared to their Tp counterparts, as reflected in the higher values found for ν(CO) and ν(N≡N) in the IR spectra of the complexes [TpRu(L)(dippe)][BPh_4] (L = CO, N_2)[1] in comparison with those for [CpRu(L)(dippe)][BPh_4] and [Cp*Ru(L)-(dippe)][BPh_4] (L = CO, N_2).[24] Attempts made to obtain the neutral vinyl complex [TpRuC(OMe)=CHCOOMe-(dippe)] by deprotonation of the β-carbon of the methoxy−carbene ligand of compound **2**, as done for other ruthenium alkoxy−carbene complexes,[25] led to the elimination of MeOH and formation of the σ-alkynyl derivative [TpRu(C≡CCOOMe)(dippe)] (**3a**). This compound **3a**, as well as the other neutral alkynyls [TpRu(C≡CR)(dippe)] (R = Ph (**3b**), H (**3c**)), are easily accesible by deprotonation of the corresponding vinylidene complex **1a**−**c** using KOBu^t, a procedure which has been extensively used for the preparation of alkynyl complexes starting from cationic vinylidene derivatives.[3,16] Compounds **3a**−**c** are yellow, crystalline materials, soluble in nonpolar solvents that display one strong ν(C≡C) band in their IR spectra, as expected. The main NMR spectral feature of these compounds is the $^{13}C\{^1H\}$ resonance corresponding to C_α of the alkynyl ligand, which appears as one triplet in the range 120−150 ppm. All of these alkynyl complexes are reversibly protonated, yielding the starting vinylidene derivatives.

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The reaction of [TpRuCl(dippe)] with substituted propargyl alcohols $HC\equiv CC(OH)R_2$ has also been studied. It is reasonably well-established now that the reaction of half-sandwich ruthenium complexes with $HC\equiv CC(OH)R_2$ leads to allenylidene species,[26-28] *via* formation of a hydroxyvinylidene complex followed by spontaneous dehydration to form the allenylidene. This is what happens in the course of the reaction of [TpRuCl(dippe)] with $HC\equiv CC(OH)MePh$ in MeOH in the presence of $Na[BPh_4]$, and the final isolated product is the deeply colored allenylidene derivative $[TpRu{=}C{=}C{=}CMePh(dippe)][BPh_4]$ (**4**), which constitutes, as far as we are aware, the first allenylidene complex of ruthenium containing Tp as a coligand. This compound is a dark red-brown crystalline material, which shows an intense IR band at 1973 cm^{-1} adscribed to $\nu(C{=}C{=}C)$ in the allenylidene ligand. The $^{13}C\{^1H\}$ NMR spectrum displays two singlets at 156.3 and 205.1 ppm attributable, respectively, to the C_γ and C_β atoms of the allenylidene unit, whereas one weak triplet at 312.9 ppm corresponds to the C_α atom directly attached to ruthenium and coupled to two equivalent phosphorus atoms (J(C,P) = 17.2 Hz). These spectral properties match those of other ruthenium allenylidene complexes,[27,28] including the Cp and Cp* homologues of **4**, $[CpRu{=}C{=}C{=}CMePh(dippe)][BPh_4]$ and $[Cp^*Ru{=}C{=}C{=}CMePh(dippe)][BPh_4]$.[29] The protons on the δ-carbon atom of the allenylidene ligand in **4** are acidic, and deprotonation at this position occurs readily and in a reversible manner yielding the neutral enynyl derivative $[TpRuC\equiv CC(Ph){=}CH_2(dippe)]$ (**5**). A similar process is known to take place spontaneously in the course of the reaction of $[LRuCl(PPh_3)_2]$ (L = Cp, indenyl) with cyclic propargyl alcohols of the type $HC\equiv C\overline{C(OH)(CH_2)_nC}H_2$, and the corresponding enynyl complexes are the only isolated products.[4,27] Other enynyl complexes have been obtained by direct reaction of $[CpRu(thf)(PPh_3)_2][PF_6]$ with the lithium salts of 3-methylbutenyne or cyclohexenylethyne.[30] Compound **5** is an orange, crystalline material that displays one strong $\nu(C\equiv C)$ band at 2056 cm^{-1} in its IR spectrum. The ^1H NMR spectrum shows two doublets at 5.463 and 5.595 ppm due to the nonequivalent protons of the terminal $=CH_aH_b$ unit of the $C\equiv CC(Ph){=}CH_2$ ligand. The connectivity between the protons and their corresponding carbon resonances was determined by a 2D-HETCOR NMR experiment, which allowed the unequivocal assignment of the signals to each of the carbon atoms in the molecule. The α-carbon atom of the enynyl ligand appears as one triplet at 133.5 ppm. The X-ray crystal structure of **5** was determined. The crystal is triclinic, space group $P\bar{1}$, having an asymmetric unit consisting of two independent, virtually identical molecules. An ORTEP view of one of the two molecules is shown in Figure 2. Selected bond lengths and angles are listed in Table 3. The coordination around ruthenium is octahedral, not too distorted. The arrangement and dimensions of the Tp and dippe ligands are similar to those found for compound **2**, as well as for the complex $[TpRu(H_2)(dippe)][BPh_4]$.[1] The enynyl ligand appears linearly assembled to ruthenium, with mean angles Ru−C−C and C−C−C of 175.7° and 177°, respectively. All of the atoms of the enynyl fragment, including the carbon atoms of the phenyl and methylene substituents, are aproximately in the same plane. The metal−carbon bond distances are Ru(1)−C(1) 2.004(6) Å and Ru(2)−C(34) 2.005(7) Å, which correspond to a single bond, and compare well with other Ru−C separations found in ruthenium alkynyls, i.e., 2.078 Å in *cis*-$[RuH(C\equiv CPh)(PP_3)]\cdot C_6H_6$ ($PP_3 = P(CH_2CH_2PPh_2)_3$)[32] and 2.01(1) Å in $[Ru(C\equiv CPh)(H_2)(dippe)_2][BPh_4]$.[33] The C(1)−C(2) and C(34)−C(35) bond lengths, 1.194(8) and 1.203(8) Å, respectively, correspond to triple bonds, being slightly shorter than the value of 1.22(1) Å that we have found for the related complex $[Cp^*RuC\equiv CC(Ph){=}CH_2(dippe)]$[29] but very similar to the reported $C\equiv C$ separations for most ruthenium alkynyl complexes structurally characterized.[20,32,33] These data suggest that the weakening of the $C\equiv C$ bond occurs to a lesser extent in **5** than in its Cp* homologue, possibly as a consequence of the increased electron density at the metal in the latter. Finally, the C(2)−C(3) and C(3)−C(4) bond lengths, 1.439(9) and 1.327(9) Å, correspond to a single and a double bond, respectively, this sequence of very distinct C−C bond distances in the enynyl fragment suggesting that there is not extensive electron delocalization across this ligand.

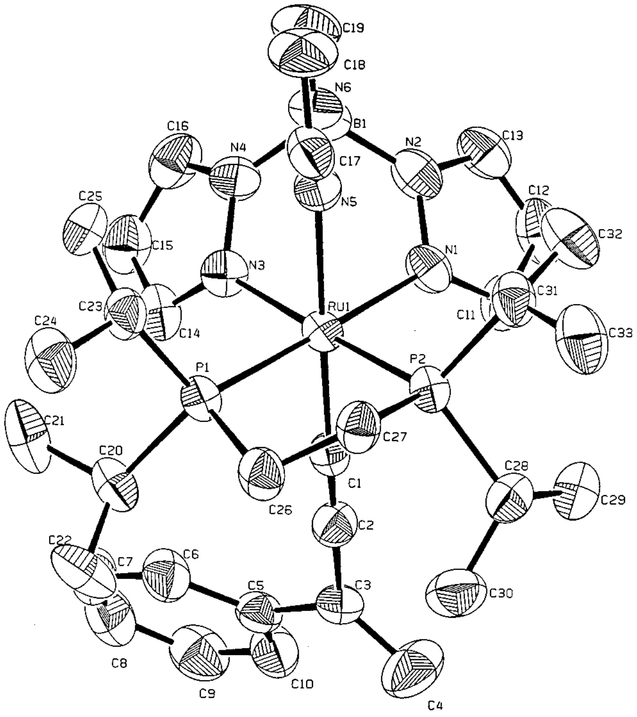

Figure 2. ORTEP drawing (50% probability thermal ellipsoids) of one of the two independent virtually identical molecules of $[TpRu(C\equiv CC(Ph){=}CH_2(dippe)]$ in the crystal structure of **5**. Hydrogen atoms are omitted.

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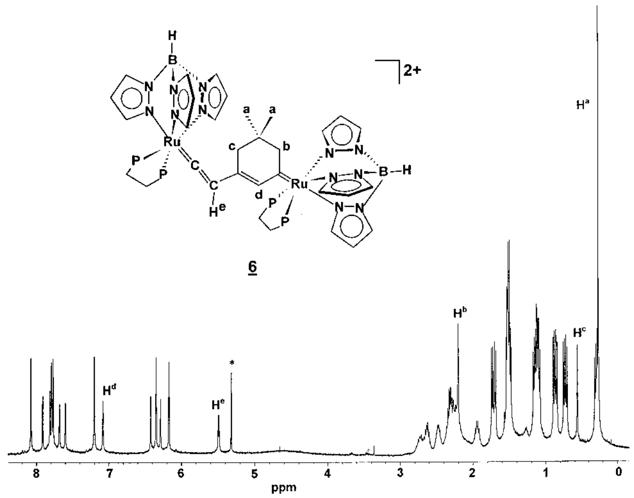
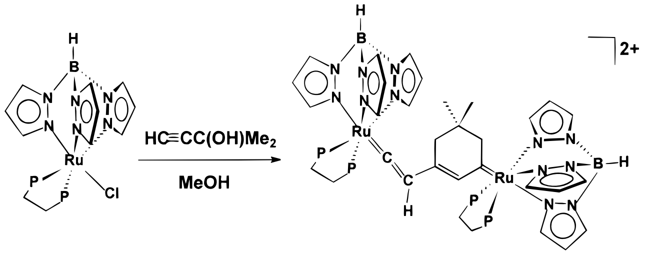


Figure 3. ^1H NMR spectrum of compound **6** in CD_2Cl_2 (solvent peak marked with an asterisk).

Whereas the allenylidene complex **4** is the product of the reaction of [TpRuCl(dippe)] with HC≡CC(OH)MePh in MeOH, the reaction takes a different course when the substrate is dimethylpropargyl alcohol, HC≡CC(OH)Me_2. Thus, when [TpRuCl(dippe)] is allowed to react with HC≡CC(OH)Me_2 in MeOH in the presence of NH_4PF_6 for 24 h, a deep red color is developed. Workup of the reaction mixture yielded a red microcrystalline material having a microanalysis consistent with the composition [TpRu=C=C=CMe_2(dippe)][PF_6]. However, the spectral properties of this compound do not correspond to those expected for a simple allenylidene complex. For instance, the expected ν(C=C=C) band is absent from the IR spectrum. Instead, one medium band at 1578 cm^{-1}, typical of a vinylidene complex, is present. The ^1H NMR spectrum (CD_2Cl_2) is very complex (Figure 3), consisting of 12 separate resonances for pyrazole ring protons. Two singlets of the same intensity are observed in the $^{31}P\{^1H\}$ NMR spectrum. These spectral data suggest that the red compound contains two nonequivalent TpRu(dippe) moieties and has been interpreted in terms of a dimerization process involving a dimethylallenylidene complex. This reaction leads to the formation of new C−C bonds, and the final product in our case is the binuclear vinylidene−carbene complex [{TpRu(dippe)}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$ (**6**) having the structure shown based upon spectral data.



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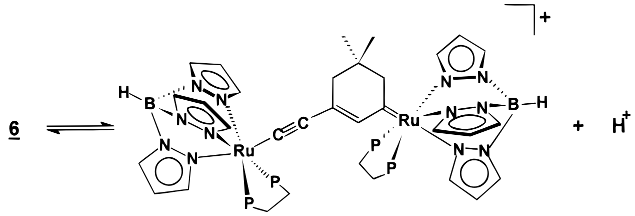
There is only one precedent for such a coupling process: the reaction of [CpRuCl(PPh_3)$_2$] with HC≡CC(OH)Me_2 to yield the binuclear complex [{CpRu(PPh_3)$_2$}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$, which was structurally characterized.[10] The spectral properties of **6** match those of the related Cp compound. Unfortunately, all attempts to grow crystals of **6** suitable for X-ray structure analysis were unsuccessful. The $^{13}C\{^1H\}$ NMR resonances of the carbon atoms of the μ-$C_{10}H_{12}$ ligand were assigned by means of a DEPT experiment. The α-carbon of the vinylidene fragment appears as a broad signal at 355.5 ppm, whereas the resonance corresponding to the carbene atom is observed at 311.8 ppm, also as a broad signal. The formation of **6** possibly follows the same reaction pathway suggested for the formation of the related compound [{CpRu(PPh_3)$_2$}$_2$(μ-$C_{10}H_{12}$)]$^{2+}$: the coupling of a dimethylallenylidene complex and a isopropenylvinylidene cation, both generated *in situ* by the spontaneous dehydration of an intermediate hydroxyvinylidene complex.[10] This mechanism is supported by the fact that in the case of the reaction of [CpRuCl(PMe_3)$_2$] with certain alkynols, stable vinylvinylidene complexes rather than allenylidene complexes have been isolated as products of the dehydration of the hydroxyvinylidene intermediate,[33] although no vinylvinylidene complex has been detected in our Tp system. As it occurs for the Cp dimer, **6** shows a great tendency to dissociate the proton attached to the β-carbon of the vinylidene fragment, yielding deep blue solutions containing the cation [{TpRu(dippe)}(μ-$C_{10}H_{11}$)]$^+$, according to the reaction.



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This complex cation, which can be regarded as the resonance hybrid of an allenylidene−vinyl complex and an alkynyl−alkylidene complex can be obtained by treatment of **6** with NEt_3 in thf, being isolable as the [BPh_4]$^-$ salt **7**. This blue microcrystalline solid displays one strong band at 1941 cm^{-1} attributable to the carbon−carbon stretching in the alkynyl/allenylidene fragment. The NMR spectra of this compound are essentially similar to those of **6**, including the 12 resonances for the protons of the pyrazole rings and the two singlets in the $^{31}P\{^1H\}$ NMR spectrum. The intense red and blue coloration displayed by compounds **6** and **7** has also been observed in the case of the related CpRu complexes,[10] as well as in other organometallic systems having π-conjugated bridging ligands, such as [Cp*(dppe)Ru=C=C=CHCH=C=Ru-(dppe)Cp*]$^{2+}$ and its deprotonated form [Cp*(dppe)Ru-C≡C-(CH)=C=C=Ru-(dppe)Cp*]$^+$.[34]

Conclusion

From this study, it is demonstrated that ruthenium phosphine tris(pyrazolyl)borate complexes exhibit a chemical reactivity toward 1-alkynes which is comparable to that of their half-sandwich homologues. The ability of these systems to promote the coupling of dimethylpropargyl alcohol derivatives leading to the formation of new C−C bonds is especially interesting, an observation which is consistent with the very recent

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report that TpRu compounds catalyze the dimerization (and even trimerization) of terminal alkynes[6,9] as well as other coupling reactions involving alkynes.[5]

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Supporting Information Available: Tables of positional parameters, *U* values, intramolecular distances, intramolecular bond angles, and least-squares planes and ORTEP diagram (30 pages). Ordering information is given on any current masthead page.

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