Activation of alkynes by {[Cp*Ru(CO)(PMe^iPr_2)]^+}: X-ray crystal structures of [Cp*Ru=C=CH^tBu(CO)(PMe^iPr_2)][BAr'_4] and [Cp*Ru(CO)_2(PMe^iPr_2)][BAr'_4]

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Dedicated to Prof. J.J. Vicente Soler (Universidad de Murcia, Spain) on the occasion of his 60 birthday

Abstract

The complex $[Cp^*Ru\{OCMe_2\}(CO)(PMe^iPr_2)][BAr'_4]$ $(2, Ar'_4 = 3, 5 - C_6H_3(CF_3)_2)$ reacts with $HC\equiv CPh$ at -40 °C in CD_2Cl_2 furnishing the π-alkyne adduct $[Cp^*Ru(\eta^2-HC\equiv CPh)(CO)(PMe^iPr_2)][BAr'_4]$ (3), which rearranges to the vinylidene complex $[Cp^*Ru=C=CHPh(CO)(PMe^iPr_2)][BAr'_4]$ (4a) when the temperature is raised to 25 °C. $[Cp^*Ru=C=CHR(CO)(PMe^iPr_2)][BAr'_4]$ (R = Ph 4a, ^tBu 4b, H 4c) were obtained by reaction of $[Cp^*RuCl(CO)(PMe^iPr_2)]$ (1) with $NaBAr'_4$ and alkyne in fluorobenzene. Addition of water to the vinylidene complexes leads to the dicarbonyl $[Cp^*Ru(CO)_2(PMe^iPr_2)][BAr'_4]$ (5), whereas deprotonation yields neutral σ-alkynyl complexes $[Cp^*Ru(C\equiv CR)(CO)(PMe^iPr_2)]$ (R = ^tBu 6b, H 6c). The allenylidene complex $[Cp^*Ru=C=C=CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ (7) was prepared by reaction of 1 with $HC\equiv CC(OH)Ph_2$ and $NaBAr'_4$ in fluorobenzene.
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Keywords: π-alkyne complexes; Vinylidene complexes; Allenylidene complexes

1. Introduction

The activation of alkynes by transition metal complexes continues attracting a great deal of attention. The involvement of transition metal vinylidene and allenylidene complexes in the stoichiometric and catalytic transformations of alkynes is well established [1–4]. We have previously reported the isolation of metastable half-sandwich Ru^{IV} alkynylhydrido complexes of the type $[Cp^*RuH(C\equiv CR)(P)_2]^+$ ((P)$_2$ = 1,2-bis(diisopropylphosphino)ethane (dippe) [5,6], (PEt$_3$)$_2$ [7,8], (PMe^{i}Pr$_2$)$_2$ [9]) as intermediates in the formation of vinylidene com-

plexes. Our research group has reported very recently the isolation and structural characterization of three isomers of the acetylene adduct $[Cp^*Ru(C_2H_2)(PEt_3)_2][BPh_4]$, namely the η²-acetylene, hydridoacetylide and vinylidene forms [10]. DFT and QM/MM calculations performed, respectively, for the systems $[CpRu(C_2H_2)-(PH_3)_2]^+$ and $[Cp^*Ru(C_2H_2)-(PEt_3)_2]^+$ have shown that Cp*, a better π-donor than Cp, and basic, strong electron-releasing phosphines stabilize the hydridoacetylide form. Besides, bulky alkyl substituents at the phosphorus atom contribute to the destabilization of the π-alkyne form due to the increased steric repulsions [10].

Hydroxyalkynylhydrido complexes have been also characterized as intermediate species in the formation of hydroxyvinylidene complexes, which by subsequent dehydration alternatively lead to allenylidene, vinylvinylidene

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or hydrido-enynyl derivatives [5–9,11]. In the context of our studies in the chemistry of pentamethylcyclopentadienylruthenium complexes, we have recently reported the complexes [Cp*RuCl(CO)(PMe^{i}Pr$_2$)] and the cationic acetone adduct [Cp*Ru{OC(CH$_3$)$_2$}(CO)-(PMe^{i}Pr$_2$)]$^+$ [12]. In this work we report the outcome of our investigations on the activation of alkynes by the fragment {[Cp*Ru(CO)(PMe^{i}Pr$_2$)]$^+$}. Here, we compare the results with those previously obtained with the {[Cp*Ru(P)$_2$]$^+$} ((P)$_2$ = dippe [6,7,11], (PEt$_3$)$_2$ [7,8,10], (PMe^{i}Pr$_2$)$_2$ [9]) fragments and the analogous less electron rich {[CpRu(CO)(P^{i}Pr$_3$)]$^+$} fragment [13].

2. Experimental

2.1. General consideration

All synthetic operations were performed under a dry dinitrogen or argon atmosphere, using conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. Fluorobenzene was purchased from Aldrich (0.01% water max.). All solvents were deoxygenated immediately before use. The complexes [Cp*RuCl(CO)(PMe^{i}Pr$_2$)] **1** and [Cp*Ru{OC(CH$_3$)$_2$}(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] (**2**, Ar$'_4$ = 3,5 − C$_6$H$_3$(CF$_3$)$_2$) were prepared according to recently reported procedures [12]. IR spectra were recorded in Nujol mulls on a Perkin–Elmer Spectrum 1000 spectrophotometer. NMR spectra were taken on a Varian Unity 400 MHz or a Varian Gemini 300 MHz spectrometer. Chemical shifts are given in ppm from SiMe$_4$ (^{1}H and ^{13}C{^{1}H}), or 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Microanalyses were performed by the Serveis Científico-Tècnics, Universitat de Barcelona.

2.2. Characterization of [Cp*Ru(η^2-HC≡CPh)(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] (3)

[Cp*Ru{OC(CH$_3$)$_2$}(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] **2** (ca. 70 mg) was dissolved in CD$_2$Cl$_2$ in a NMR tube. The solution was cooled to −40 °C using an ethanol bath cooled with liquid N$_2$, then an excess of alkyne was added. The sample was inserted into the precooled NMR probe, and ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 233 K): δ 0.95–1.2 (m, 15 H, PCH(CH_3)$_2$, PCH_3), 1.67 (d, 15 H, $^4J_{HP}$ = 1.1 Hz, C$_5$(CH_3)$_5$), 2.04 (m, 2 H, PCH(CH$_3$)$_2$), 4.65 (d, 1 H, $^3J_{HP}$ = 13.7 Hz, HC≡CPh), 7.32–7.61 (m, 5 H, Ph); ^{31}P{^{1}H} NMR (161.89 MHz, CD$_2$Cl$_2$, 233 K): δ 42.13 (s).

2.3. Synthesis of [Cp*Ru=C=CHR(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] (R = Ph (4a), ^{t}Bu (4b), H (4c))

To a solution of [Cp*RuCl(CO)(PMe^{i}Pr$_2$)] **1** (100 mg, 0.23 mmol) in fluorobenzene (8 ml), the stoichiometric amount of the corresponding alkyne was added. After addition of NaBAr$'_4$ (206 mg, 0.23 mmol) the mixture was stirred for 30 min at room temperature and then filtered through celite. The solution was layered with petroleum ether. The resulting crystalline solids were filtered off, washed with petroleum ether and dried in vacuo.

2.3.1. Compound 4a

Yield: 240 mg, 75%. Anal. Calc. for C$_{58}$H$_{50}$BF$_{24}$OPRu: C, 51.1; H, 3.70. Found: C, 51.4; H, 3.75%. IR (Nujol): ν(CO) 2011 (s) cm^{-1}, ν(C=C) 1659 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 0.98 and 1.13 (m, 12 H, PCH(CH_3)$_2$), 1.52 (d, 3 H, $^2J_{HP}$ = 8.9 Hz, PCH_3), 2.06 (m, 2 H, PCH(CH$_3$)$_2$), 1.90 (d, 15 H, $^4J_{HP}$ = 1.2 Hz, C$_5$(CH_3)$_5$), 6.04 (d, $^4J_{HP}$ = 2.5 Hz, 1 H, (C=CHPh), 6.97, 7.24 and 7.33 (m, 5 H, Ph); ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): δ 51.56 (s); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 298 K) δ: 9.75 (d, $^1J_{CP}$ = 24.0 Hz, PCH$_3$), 10.45 (s, C$_5$(CH$_3$)$_5$), 17.43, 17.70 and 18.26 (m, PCH(CH$_3$)$_2$), 27.27 (d, $^1J_{CP}$ = 27.6 Hz, PCH(CH$_3$)$_2$), 28.44 (d, $^1J_{CP}$ = 26.9 Hz, PCH(CH$_3$)$_2$), 106.57 (s, C_5(CH$_3$)$_5$), 117.87 (d, $^3J_{CP}$ = 2.0 Hz, Ru=C=CHPh), 122–133 (s, Ph), 199.22 (d, $^2J_{CP}$ = 16.7 Hz, CO), 369.03 (d, $^2J_{CP}$ = 15.1 Hz, Ru=C).

2.3.2. Compound 4b

Yield: 200 mg, 65%. Anal. Calc. for C$_{56}$H$_{54}$BF$_{24}$OPRu: C, 50.1; H, 4.06. Found: C, 50.4; H, 4.11%. IR (Nujol): ν(CO) 2001 (s) cm^{-1}, ν(C=C) 1674 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 0.92 and 1.09 (m, 12 H, PCH(CH_3)$_2$), 1.13 (s, 9 H, C(CH_3)$_3$), 1.47 (d, 3 H, $^2J_{HP}$ = 8.9 Hz, PCH_3), 1.96 and 2.05 (m, 2 H, PCH(CH$_3$)$_2$), 1.90 (d, 15 H, $^4J_{HP}$ = 1.4 Hz, C$_5$(CH_3)$_5$), 4.84 (d, $^4J_{HP}$ = 2.5 Hz, 1 H, (C=CHBu^t); ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): δ 49.97 (s); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 298 K) δ: 8.35 (d, $^1J_{CP}$ = 34.8 Hz, PCH$_3$), 10.42 (s, C$_5$(CH$_3$)$_5$), 17.14, 17.38, 17.70 and 18.33 (s, PCH(CH$_3$)$_2$), 27.15 (d, $^1J_{CP}$ = 27.9 Hz, PCH(CH$_3$)$_2$), 28.42 (d, $^1J_{CP}$ = 28.1 Hz, PCH(CH$_3$)$_2$), 31.67 (s, C(CH$_3$)$_3$), 33.67 (s, C(CH$_3$)$_3$), 106.57 (s, C_5(CH$_3$)$_5$), 124.73 (d, $^3J_{CP}$ = 2.0 Hz, Ru=C=CHBut), 200.17 (d, CO, $^2J_{CP}$ = 16.6 Hz), 359.28 (d, $^2J_{CP}$ = 13.0 Hz, Ru=C).

2.3.3. Compound 4c

Yield: 200 mg, 65%. Anal. Calc. for C$_{52}$H$_{46}$BF$_{24}$OPRu: C, 48.6; H, 3.61. Found: C, 48.7; H, 3.71%. IR (Nujol): ν(CO) 2016 (s) cm^{-1}, ν(C=C) 1633 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 0.95 and 1.09 (m, 12 H, PCH(CH_3)$_2$), 1.46 (d, 3 H, $^2J_{HP}$ = 8.8 Hz, PCH_3), 2.01 (m, 2 H, PCH(CH$_3$)$_2$, 1.89 (br, 15 H, C$_5$(CH_3)$_5$), 4.33 (d, $^4J_{HP}$ = 2.9 Hz, 2 H, (C=CH_2); ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): δ 51.13 (s); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 298 K) δ: 9.35 (d, $^1J_{CP}$ = 33.3 Hz, PCH$_3$), 10.26 (s, C$_5$(CH$_3$)$_5$), 17.10, 17.20, 17.70 and 17.98 (s, PCH(CH$_3$)$_2$), 27.48 (d,

$^1J_{CP} = 27.2$ Hz, PCH(CH$_3$)$_2$), 28.02 (d, $^1J_{CP} = 28.7$ Hz, PCH(CH$_3$)$_2$), 96.3 (d, $^3J_{CP} = 1.8$ Hz, C=CH$_2$) 105.6 (s, C_5(CH$_3$)$_5$), 198.9 (d, $^2J_{CP} = 15.9$ Hz, CO), 356.25 (d, $^2J_{CP} = 12.3$ Hz, Ru=C).

2.4. Synthesis of [Cp*Ru(CO)$_2$(PMe^{i}Pr$_2$)][BAr'$_4$] (5)

Carbon monoxide was bubbled through a solution of **1** (80 mg, 0.2 mmol) in fluorobenzene (8 ml) and a slight excess of NaBAr'$_4$ was added. The mixture was stirred for 1 h. Removal of solvent until half-volume and layering with petroleum ether, afforded a microcrystalline white solid. Single crystals adequate for X-ray diffraction study were obtained by recrystallization from Et$_2$O/petroleum ether. Yield: 200 mg, 65%. Anal. Calc. for C$_{51}$H$_{44}$BF$_{24}$O$_2$PRu: C, 47.6; H, 3.44. Found: C, 46.7; H, 3.47%. IR (Nujol): v(CO) 2001 (s) cm^{-1}, 2047 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 1.08 (m, 12 H, PCH(CH_3)$_2$, 1.37 (d, 3 H, $^2J_{HP} = 8.5$ Hz, PCH_3), 2.06 (m, 2 H, PCH(CH$_3$)$_2$), 1.91 (d, $^4J_{HP} = 1.5$ Hz, 15 H, C$_5$(CH_3)$_5$); ^{31}P$\{^1$H$\}$ NMR (161.89 MHz, CDCl$_3$, 298 K): δ 45.08 (s); ^{13}C$\{^1$H$\}$ NMR (75.4 MHz, CDCl$_3$, 298 K) δ: 10.74 (d, $^1J_{CP} = 32.1$ Hz, PCH$_3$), 10.77 (s, C$_5$(CH$_3$)$_5$), 17.88, 18.44 (s, PCH(CH$_3$)$_2$), 28.20 (d, $^1J_{CP} = 27.2$ Hz, PCH(CH$_3$)$_2$), 103.29 (s, C_5(CH$_3$)$_5$), 198.68 (d, $^2J_{CP} = 14.63$ Hz, CO).

2.5. Synthesis of [Cp*Ru(C≡CR)(CO)(PMe^{i}Pr$_2$)] (R = ^{t}Bu(6b), H(6c))

To a solution of the corresponding vinylidene complex **4b** or **4c** (200 mg in 5 ml of THF) a slight excess of KO^{t}Bu was added. After stirring the mixture for 3 h at room temperature, the colour changed from orange to yellow. The solvent was removed in vacuo, and the residue extracted with 10 ml of petroleum ether. The solution was filtered through celite, concentrated to ca. 1 ml and cooled to −20 °C. The resulting microcrystalline solid was filtered off and dried in vacuo.

2.5.1. Compound 6b

Yield: 50 mg, 68%. Anal. Calc. for C$_{24}$H$_{41}$OPRu: C, 60.3; H, 8.65. Found: C, 60.5; H, 8.70%. IR (Nujol): (CO) 2006 (s) cm^{-1}, v(C≡C) 2070 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 0.93 and 1.18 (m, 12 H, PCH(CH_3)$_2$), 1.30 (d, 3 H, $^2J_{HP} = 8.0$ Hz, PCH_3), 1.42 (s, 9 H, C(CH_3)$_3$, 1.82 (m, 2 H, PCH(CH$_3$)$_2$), 1.77 (d, $^4J_{HP} = 1.3$ Hz, 15 H, C$_5$(CH_3)$_5$); ^{31}P$\{^1$H$\}$ NMR (161.89 MHz, C$_6$D$_6$, 298 K): δ 50.05 (s); ^{13}C$\{^1$H$\}$ NMR (75.4 MHz, C$_6$D$_6$, 298 K) δ: 9.12 (d, $^1J_{CP} = 30.8$ Hz, PCH$_3$), 10.90 (s, C$_5$(CH$_3$)$_5$), 17.47, 18.20, 18.72, 19.15 (s, PCH(CH$_3$)$_2$), 26.68 (d, $^1J_{CP} = 22.2$ Hz, PCH(CH$_3$)$_2$), 28.33 (d, $^1J_{CP} = 27.7$ Hz, PCH(CH$_3$)$_2$), 29.73 (s, C(CH$_3$)$_3$), 33.67 (s, C(CH$_3$)$_3$), 96.28 (d, $^3J_{CP} = 2.3$ Hz, C_5(CH$_3$)$_5$), 113.7 (s, RuC≡C), 90.54 (d, $^2J_{CP} = 23.6$ Hz, RuC≡C), 208.8 (d, $^2J_{CP} = 19.7$ Hz, CO).

2.5.2. Compound 6c

Yield: 40 mg, 65%. Anal. Calc. for C$_{20}$H$_{33}$OPRu: C, 56.9; H, 7.89. Found: C, 58.8; H, 7.80%. IR (Nujol): v(CO) 1996 (s) cm^{-1}, v(C≡C) 2050 cm^{-1}. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ 0.96 (m, 12 H, PCH(CH_3)$_2$), 1.06 (d, 3 H, $^2J_{HP} = 8.4$ Hz, PCH_3), 1.70 (m, 2 H, PCH(CH$_3$)$_2$), 1.73 (s, 15 H, C$_5$(CH_3)$_5$), 2.74 (d, $^4J_{HP} = 0.71$ Hz, 1 H, (RuC≡CH); ^{31}P$\{^1$H$\}$ NMR (161.89 MHz, C$_6$D$_6$, 298 K): δ 47.70 (s); ^{13}C$\{^1$H$\}$ NMR (75.4 MHz, C$_6$D$_6$, 298 K) δ: 9.12 (d, $^1J_{CP} = 24.8$ Hz, PCH$_3$), 10.46 (s, C$_5$(CH$_3$)$_5$), 18.10, 18.56, 18.65, 19.02 (s, PCH(CH$_3$)$_2$), 25.87 (d, $^1J_{CP} = 21.5$ Hz, PCH(CH$_3$)$_2$), 27.87 (d, $^1J_{CP} = 21.5$ Hz, PCH(CH$_3$)$_2$), 83.01 (s, RuC≡C), 97.8 (s, C_5(CH$_3$)$_5$), 117.74 (d, $^2J_{CP} = 22.1$ Hz, RuC≡C), 202.5 (d, $^2J_{CP} = 17.7$ Hz, CO).

2.6. Synthesis of [Cp*Ru=C=C=CPh$_2$(CO)(PMe^{i}Pr$_2$)][BAr'$_4$] (7)

Solid NaBAr'$_4$ (150 mg, 1.67 mmol) was added to a solution of compound **1** (720 mg, 1.67 mmol) and 1,1-diphenylpropyn-1-ol (350 mg, 1.7 mmol) in 10 ml of fluorobenzene. The mixture was stirred for 8 h at room temperature and the colour changed from yellow-orange to dark purple. The solution was filtered through celite and the solvent was removed in vacuo. The residue was dissolved in methanol and the solvent was evaporated to dryness. The solid was washed with petroleum ether affording a dark purple solid. Yield: 1.9 g, 80%. Anal. Calc. for C$_{65}$H$_{54}$BF$_{24}$OPRu: C, 53.8; H, 3.75. Found: C, 53.7; H, 3.85%. IR (Nujol): v(CO) 1936 (s) cm^{-1}, v(C=C=C) 2004 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 1.05 (m, 12 H, PCH(CH_3)$_2$), 1.36 (d, 3 H, $^2J_{HP} = 8.9$ Hz, PCH_3), 2.04 (m, 2 H, PCH(CH$_3$)$_2$), 1.95 (d, 15 H, $^4J_{HP} = 1.1$ Hz, C$_5$(CH_3)$_5$), 7.42 and 7.71 (m, 10 H, Ph); ^{31}P$\{^1$H$\}$ NMR (161.89 MHz, CDCl$_3$, 298 K): δ 53.11 (s); ^{13}C$\{^1$H$\}$ NMR (75.4 MHz, CDCl$_3$, 298 K) δ: 7.8 (d, $^1J_{CP} = 25.9$ Hz, PCH$_3$), 10.51 (s, C$_5$(CH$_3$)$_5$,), 17.89 (d, $^2J_{CP} = 19.9$ Hz, PCH(CH$_3$)$_2$), 17.16 (d, $^2J_{CP} = 23.6$ Hz, PCH(CH$_3$)$_2$), 27.4 (d, $^1J_{CP} = 27.4$ Hz, PCH(CH$_3$)$_2$), 27.7 (d, $^1J_{CP} = 27.4$ Hz, PCH(CH$_3$)$_2$), 104.5 (s, C_5(CH$_3$)$_5$), 129.3, 131.6 and 133.5 (s, Ph), 141.8 (s, C_γ), 186.8 (d, $^3J_{CP} = 2.4$ Hz, C_β), 201.5 (d, $^2J_{CP} = 17.6$ Hz, CO), 289 (d, $^2J_{CP} = 15.8$ Hz, C_α).

2.7. X-ray structure determinations

Crystals of **4b** and **5** were obtained by recrystallization from ethyl ether/petroleum ether. Crystal data and experimental details are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX 3-circle diffractometer with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with $\delta(\omega)$ 0.30°.

Table 1
Crystal data and details of structure determination for compounds **4b** and **5**

| Compound	4b	5
Formula	$C_{56}H_{54}BF_{24}OPRu$	$C_{51}H_{44}BF_{24}O_2PRu$
Formula weight	1341.84	1287.71
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions		
a (Å)	12.8742(7)	12.5835(9)
b (Å)	12.9394(7)	12.731(1)
c (Å)	19.396(1)	18.854(1)
α (°)	79.822(1)	81.842(2)
β (°)	74.193(1)	74.481(2)
γ (°)	88.168(1)	80.988(2)
V (Å^3)	3059.5(3)	2858.4(4)
Z	2	2
δ (calc) (g/cm^3)	1.457	1.496
μ(Mo Kα) (mm^{-1})	0.392	0.418
$F(000)$	1356	1292
λ (Å)	Mo Kα 0.71073	Mo Kα 0.71073
$\theta_{min}-\theta_{max}$ (°)	1.6, 25.1	1.6, 24.0
Total, unique, R_{int}	23,893, 10,692, 0.030	22,471, 8932, 0.047
Observed ($I>2\sigma I$)	9302	6637
Reflections, parameters	10,692, 994	8932, 897
R, wR_2 ($I>2\sigma I$)	0.0877, 0.1945	0.0898, 0.1876
R, wR_2 (all)	0.1000, 0.2031	0.1203, 0.2047
Goodness-of-fit	1.12	1.04
Residuals (e/Å^3)	−0.78, 1.93	−0.52, 0.79

Correction for absorption and crystal decay (insignificant) were applied by semi-empirical method from equivalents using program SADABS [14]. The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined on F^2 by full matrix least-squares procedures using the program SHEL-XTL [15]. All non hydrogen atoms were refined with anisotropic displacement coefficients. CF$_3$ groups of the $[BAr'_4]^-$ anion showed orientation disorder in these compounds. All CF$_3$ groups were refined as pairs of CF$_3$ with complementary orientations for compound **4b**, and 7 of 8 groups for compound **5**. One methyl group (corresponding to C46) in the phosphine ligand of **5** also showed disorder which was not modelled. All the remaining hydrogen atoms in both compounds were refined using the SHELX riding model. The program OR-TEP-3 [16] was used for plotting.

CCDC reference numbers 232973 and 232974.

3. Results and discussion

Scheme 1 summarizes the alkyne activation reactions discussed here. The acetone adduct $[Cp^*Ru\{OCMe_2\}(CO)(PMe^iPr_2)][BAr'_4]^{31}$ **2** reacts with phenylacetylene in CD$_2$Cl$_2$ at −40 °C furnishing the π-alkyne complex $[Cp^*Ru(\eta^2\text{-}HC\equiv CPh)(CO)(PMe^iPr_2)][BAr'_4]$ **(3)**, which was characterized in solution by ^{1}H and ^{31}P{^{1}H}

NMR spectroscopy. The proton of the π-alkyne ligand appears as one doublet at 4.65 ppm in the ^{1}H NMR spectrum, whereas the ^{31}P{^{1}H} consists of one singlet at 42.13 ppm. When temperature is raised up to 25 °C, these resonances disappear, being replaced by new signals, respectively, at 6.04 ppm in the ^{1}H NMR spectrum and at 51.56 ppm in the ^{31}P{^{1}H} NMR spectrum. This indicates transformation of the π-alkyne into the vinylidene complex $[Cp^*Ru=C=CHPh(CO)(PMe^iPr_2)][BAr'_4]$ **(4a)**.
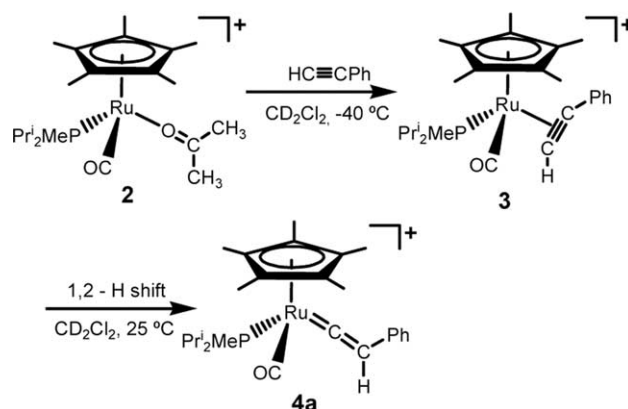
At variance with the related systems containing two phosphine ligands [5–9], in this case there is no evidence for the formation of a Ru^{IV} hydrido-alkynyl complex as intermediate in the alkyne to vinylidene tautomerization. This reflects the important change in the electron richness, and in hence, in the reactivity of the metal centre when replacing one bulky, strong electron-releasing phosphine ligand by the much smaller, π-acceptor CO ligand. Therefore, in this system the formation of vinylidene complexes occurs most likely through a direct 1,2-H shift [4].

The vinylidene complexes $[Cp^*Ru=C=CHR(CO)(PMe^iPr_2)][BAr'_4]$ (R = Ph **4a**, ^tBu **4b**, H **4c**) were isolated as crystalline solids by reaction of $[Cp^*RuCl(CO)(PMe^iPr_2)]$ **2** with NaBAr$'_4$ in fluorobenzene in the presence of alkyne. As it has been observed in other instances, the primary vinylidene complex **4c** was most likely generated by desilylation of the trimethylsilylvinylidene derivative $[Cp^*Ru=C=CHSiMe_3(CO)(PMe^iPr_2)]^+$, which was not isolated. Attempts to generate **4c** by direct reaction of **2** with NaBAr$'_4$ in fluorobenzene under acetylene failed. The binuclear complex $[\{Cp^*Ru(CO)(PMe^iPr_2)\}_2(\mu\text{-Cl})][BAr'_4]$ [12], which competes with the formation of the vinylidene species, was isolated from this reaction. The most characteristic spectral features of these complexes are the resonances for the proton attached to C$_\beta$ in their ^{1}H NMR spectra, and the resonances for the carbon atom bound to ruthenium C$_\alpha$ in their ^{13}C{^{1}H} NMR spectra. These signals appear in the range expected for vinylidene complexes. However, compared to similar complexes containing two phosphine ligands, their positions
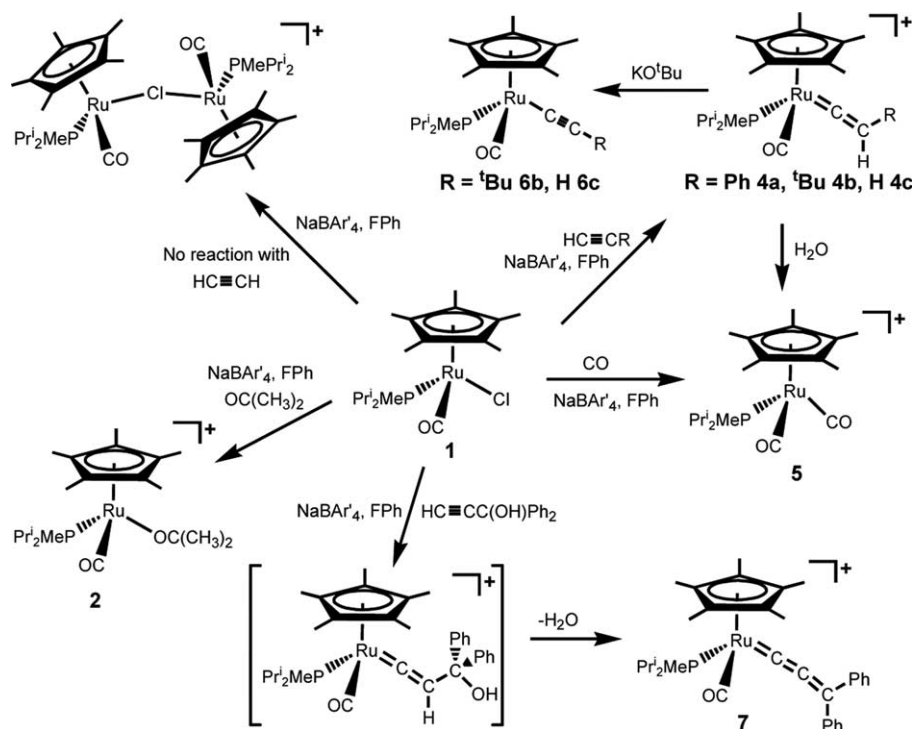
Scheme 1. Summary of alkyne activation reactions by compound **1**.

appear shifted to lower fields, as a result of the decreased electron density at the metal centre. The crystal structure of **4b** was determined. An ORTEP view of the complex cation [Cp*Ru=C=CH'Bu(CO)(PMe^{i}Pr$_2$)]$^+$ is shown in Fig. 1, together with a listing of selected bond lengths and angles.

The complex has a pseudo-octahedral three-legged piano stool structure, similar to that observed for other half-sandwich vinylidene complexes. The Ru1–C11 bond distance of 1.880(6) Å corresponds to a Ru=C double bond, but it appears slightly longer than [Cp*Ru=C=CHCOOMe(dippe)][BPh$_4$] (1.807(9) Å) [5] and in other half-sandwich bis(phosphine) vinylidene complexes, which have Ru=C bond lengths in the range 1.76–1.85 Å [4]. The value of 178.8(6)° for the Ru1–C11–C12 angle is consistent with the linearity of the vinylidene ligand. Interestingly, very few vinylidene ruthenium half-sandwich compounds containing CO have been actually isolated, i.e., [Cp*Ru=C=CHPh(CO)(PCy$_2$CH$_2$CH$_2$OMe)][BPh$_4$] [17]. The protonation of the alkynyl complex [CpRu(C≡CPh)(CO)(PPh$_3$)] with HBF$_4$ at −80 °C in CD$_2$Cl$_2$ yields quantitatively the cationic vinylidene complex [CpRu=C=CHPh(CO)(PPh$_3$)]$^+$, but it converts into an equilibrium mixture of the vinylidene (9%) plus the π-alkyne adduct [CpRu(η^2-HC≡CPh)(CO)(PPh$_3$)]$^+$ (91%) when the temperature is raised to 25 °C [18]. On the other hand, Bruce and co-workers [19] have reported that the formation of the alkoxy-carbene derivatives [CpRu=C(OR)-
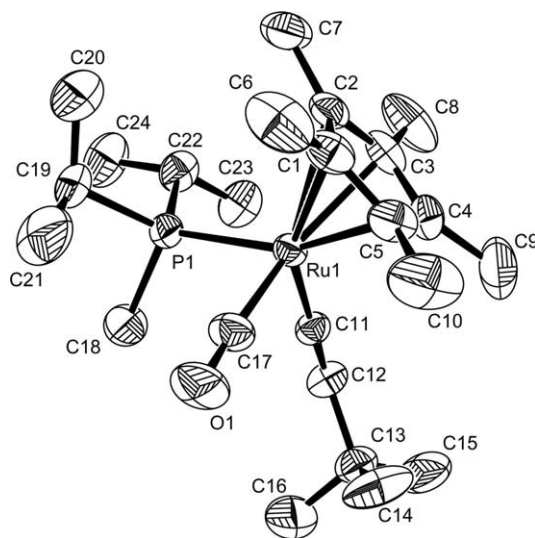

Fig. 1. ORTEP diagram of the cation [Cp*Ru=C=CH'Bu(CO)(PMe^{i}Pr$_2$)]$^+$ in compound **4b**. Selected bond distances (Å) and angles (°): Ru1–C11 1.880(6); Ru1–C17 1.875(7); Ru1–P1 2.349(2); C11–C12 1.273(9); C12–C13 1.52(1); Ru1–C11–C12 178.8(6); C11–C12–C13 128.1(7); C11–Ru1–P1 86.4(2); C17–Ru1–C11 91.1(3).

CH$_2$Ph(CO)(PPh$_3$)]$^+$ (R = Me, Et, ^{i}Pr) by protonation of [CpRu(C≡CPh)(CO)(PPh$_3$)] with HPF$_6$ in ROH is mediated by the vinylidene complex [CpRu=C=CHPh(CO)(PPh$_3$)]$^+$, but this was never isolated. Clearly, the ability of the moieties {[CpRu(CO)(P)]$^+$}

to stabilize vinylidene ligands is not as good as that of their bis(phosphine) counterparts {[CpRu(P)$_2$]$^+$}.

The transformation of vinylidene ligands into carbonyl groups by the effect of moisture has been reported [11,20,21]. The reactions of **2** with NaBAr$'_4$ and 1-hexyne or HC≡CCOOMe in fluorobenzene led to mixtures containing the corresponding vinylidene complexes and the dicarbonyl derivative [Cp*Ru(CO)$_2$(PMe^{i}Pr$_2$)][BAr$'_4$] (**5**). Upon stirring the reaction mixtures at room temperature for several hours all of the remaining vinylidene complexes have been converted into the dicarbonyl derivative **5**. This process also has been observed in the reactions with HCCPh, HC≡C^{t}Bu or HC≡CSiMe$_3$, but seems to take place much slower, allowing the isolation of the pure vinylidene complexes. The source of water is most likely that present in the halide scavenger NaBAr$'_4$. Thus, when this salt is thoroughly dried by prolonged pumping in vacuo at 80 °C, the moisture content is much lower and hence mixtures with higher content of vinylidene complex are obtained. In any case, and in comparison with the other vinylidene complexes described in the present work, the vinylidene complexes [Cp*Ru=C=CHR(CO)(PMe^{i}Pr$_2$)]$^+$ (R = ^{n}Bu, COOMe, not isolated due to the formation of the dicarbonyl complex **5**) display an enormous tendency to react with traces of water present in the reaction mixture. Compound **5** is easily accessible by reaction of **2** with NaBAr$'_4$ under CO in fluorobenzene. Its crystal structure was determined. An ORTEP of [Cp*Ru(CO)$_2$(PMe^{i}Pr$_2$)]$^+$ view is shown in Fig. 2.

The complex has a three-legged piano stool structure, with bond lengths and angles in the range observed for other ruthenium half-sandwich dicarbonyl derivatives reported in the literature [22], being unexceptional.

As it is characteristic for cationic vinylidene complexes, the deprotonation of **4b**–**c** using KO^{t}Bu as base led to the neutral alkynyl derivatives [Cp*Ru(C≡CR)(CO)(PMe^{i}Pr$_2$)] (R = ^{t}Bu **6b**, H **6c**). As expected, these compounds display in their IR spectra one strong ν(C≡C) band at 2050 and 2070 cm^{-1}, respectively.

The allenylidene complex [Cp*Ru=C=C=CPh$_2$(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] (**7**) was obtained by activation of the hydroxyalkyne HC≡CC(OH)Ph$_2$ by **2** using NaBAr$'_4$ in fluorobenzene. As it occurs in other cases previously reported, the process involves most likely the formation of a hydroxyvinylidene intermediate [6–9,11] which undergoes spontaneous dehydration affording the dark purple allenylidene complex **7** (Scheme 1). The resonance for the ruthenium-bound C$_\alpha$ atom of the allenylidene ligand appears as one doublet at 289 ppm in the ^{13}C{^{1}H} NMR spectrum. This compound displays one strong ν(C=C=C) band at 2004 cm^{-1} in its IR spectrum. This absorption band appears shifted to higher wavenumbers than in the related bis(phosphine) complexes [Cp*Ru=C=C=CPh$_2$(P)$_2$]$^+$ (1890 cm^{-1} for (P)$_2$ = dippe [23]; 1907 cm^{-1} for (P)$_2$ = (PEt$_3$)$_2$ [7,8]; 1916 cm^{-1} for
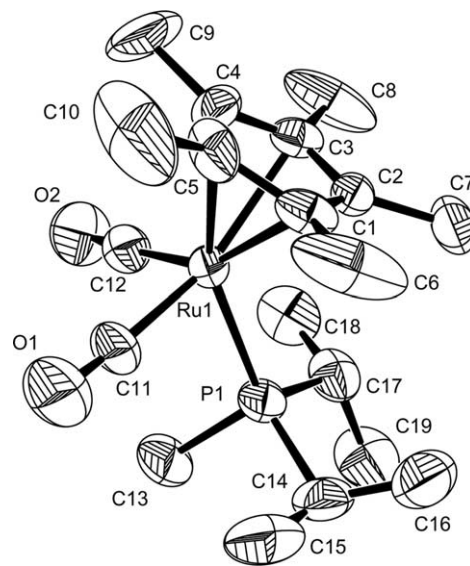
Fig. 2. ORTEP diagram of the cation [Cp*Ru(CO)$_2$(PMe^{i}Pr$_2$)]$^+$ in compound **5**. Selected bond distances (Å) and angles (°): Ru1–P1 2.363(2); Ru1–C11 1.921(8); Ru1–C12 1.87(1); C11–O1 1.11(1); C12–O2 1.14(1); Ru1–C11–O1 174(1); Ru1–C12–O2 176.1(9); C11–Ru1–P1 88.4(3); C12–Ru1–P1 88.5(3); C12–Ru1–C11 91.4(4).

(P)$_2$ = (PMe^{i}Pr$_2$)$_2$ [9]). In neutral ruthenium allenylidene complexes (i.e., [Cp*Ru=C=C=CPh$_2$(Cl)(PPh$_3$)] [2]) this band also appears below 1900 cm^{-1}, whereas the related derivative [CpRu=C=C=CPh$_2$(CO)(P^{i}Pr$_3$)][BF$_4$] [23] displays the band at 2002 cm^{-1}. This indicates that **7** contains an electron-poor ruthenium centre due to the presence of the carbonyl ligand in the coordination sphere. As a result, the reactivity patterns of the allenylidene complex **7** are expected to be remarkably different to those of the Cp*Ru bis(phosphine) allenylidene derivatives that we have studied in the past, but very close to the reactivity patterns displayed by the electron-poor system [CpRu=C=C=CPh$_2$(CO)(P^{i}Pr$_3$)]$^+$ [13]. The nucleophilic addition reactions to the allenylidene complex **7** will be reported in a forthcoming paper.

Acknowledgement

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.05.029.

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