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Nucleophilic addition reactions to the allenylidene complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)]^+$: X-ray crystal structures of $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$, $[Cp^*Ru\{C(NHCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$, $[Cp^*Ru\{C(PMe^iPr_2)C{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ and $[Cp^*Ru\{C(S^n\,Pr)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$

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In memoriam of Dr. Juan Carlos del Amo Agua do, 28 years old, researcher of the Universidad Complutense, who was killed in 11 March bombing in Madrid

Abstract

The allenylidene complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ (**1**) reacts with benzophenoneimine yielding the azaallenyl derivative $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**2**).The addition of primary or secondary amines to **1** yields vinylaminocarbenes, which are better formulated as azoniabutadienyl complexes $[Cp^*Ru\{C(NRR')CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (R = H, R′ = $CH_2C{\equiv}CH$ (**3**), R = H, R′ = Me (**4**), R = R′ = ^{i}Pr (**5**)).Tertiary phosphines add to the C_α atom of the allenylidene chain furnishing allenylphosphonio species $[Cp^*Ru\{C(PR_3)C{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (PR_3 = PMe_3 (**6**), PMe^iPr_2 (**7**)). The reaction of **1** with propanethiol afforded the thiocarbene $[Cp^*Ru\{C(S^n\,Pr)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**8**), which can be treated as a η^1-thiabutadienyl.

Keywords: Allenylidene; Azaallenyl; Azoniabutadienyl; Thiocarbene

1. Introduction

The involvement of transition metal allenylidene complexes in the stoichiometric and catalytic transformations of alkynes is well established [1–4]. The reactivity of allenylidene ligands attached to different cationic ruthenium fragments such as $\{[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2]^+\}$ [5–7], $\{[(\eta^5\text{-}C_9H_7)Ru(CO)(PPh_3)]^+\}$ [5–7], $\{[CpRu(CO)(P^iPr_3)]^+\}$ [8–17] or $\{[(\eta^6\text{-arene})RuCl(PR_3)]^+\}$ [18–21] has been studied by several research groups. Although the reactivity of cationic allenylidene complexes is governed by the electron deficiency of both the C_α and C_γ atoms of the unsaturated chain, its is known that regioselective nucleophilic additions at C_γ take place when bulky, electron-rich metallic fragments are used, leading to σ-alkynyl complexes [2,5]. The

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substituents of the allenylidene ligand also play an important role in determining the final product of the nucleophilic addition. Thus, some alkynyl complexes resulting from the addition to the C_γ undergo an isomerization reaction leading to more stable allenyl derivatives [11,13,16,17]. The addition of electrophiles to the C_β of the allenylidene chain is less frequent. Following the report by Werner and co-workers [22] of the preparation of carbyne complexes of ruthenium by protonation of vinylidene complexes, we have recently described the dicationic vinylcarbyne derivatives $[Cp^*Ru{\equiv}CCH{=}CRR'(dippe)]^{2+}$ (R = R′ = Ph; R = H, R′ = Ph; dippe = 1,2-bis(diisopropylphosphino)ethane) [23] by protonation of the respective allenylidene complexes $[Cp^*Ru{=}C{=}C{=}CRR'(dippe)]^+$. The reactions of addition of nucleophiles to these complexes were also studied. In all cases addition to the C_γ was observed. The introduction of a strong π-acceptor ligand such as CO modifies both the electronic and the steric properties of the metallic fragment, modifying the reactivity of the allenylidene ligand accordingly. In the context of our studies in the chemistry of pentamethylcyclopentadienylruthenium complexes, we have recently reported the preparation and characterization of the electron-deficient allenylidene complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) [24]. In this work, we focus on the study of the reactivity of this complex towards a variety of nucleophiles containing N-, P- or S-donor atoms. In all cases, and at variance with the systems containing two phosphine ligands, products derived from the regioselective addition to the C_α of the allenylidene ligand have been isolated and characterized.

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 maximum). All solvents were deoxygenated immediately before use. The complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ (**1**) was prepared according to a recently reported procedure [24]. IR spectra were recorder 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 $SiMe_4$ (^1H and $^{13}C\{^1H\}$), or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalysis were performed by the Serveis Científico-Tècnics, Universitat de Barcelona.

2.2. Synthesis of $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**2**)

A dark purple solution of **1** (500 mg, 0.35 mmol) in 8 ml of dichloromethane was treated with benzophenoneimine (0.1 ml, 0.55 mmol, 80% excess). The mixture was stirred for 30 min. The solution became orange-brown and the volume was then reduced to 1 ml. The solution was layered with petroleum ether, yielding orange crystals which were filtered off, washed with petroleum ether and dried. Recrystallization from diethyl ether/petroleum ether afforded crystals suitable for single-crystal X-ray diffraction. Yield: 450 mg, 60%. Anal. Calc. for $C_{78}H_{65}NBF_{24}OPRu$: C, 57.4; H, 4.02. Found: C, 57.2; H, 4.10%. IR (Nujol): ν(CO) 1948 (s) cm^{-1}, ν(C=N=C) 1796 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.96 and 1.19 (m, 12H, $PCH(CH_3)_2$), 1.24 (d, 3H, $^2J_{HP} = 7.1$ Hz, PCH_3), 2.01 and 2.15 (m, 2H, $PCH(CH_3)_2$), 1.85 (d, 15H, $^4J_{HP} = 1.3$ Hz, $C_5(CH_3)_5$), 6.75 (s, 1H, CH=), 6.76–7.59 (m, 20H, Ph); $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 42.50 (s); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K) δ: 8.10 (d, $^1J_{CP} = 29.1$ Hz, PCH_3), 10.44 (s, $C_5(CH_3)_5$,), 17.12 (d, $^2J_{CP} = 3.6$ Hz, $PCH(CH_3)_2$), 18.46 (d, $^2J_{CP} = 3.6$ Hz, $PCH(CH_3)_2$), 27.04 (d, $^1J_{CP} = 27.4$ Hz, $PCH(CH_3)_2$), 28.24 (d, $^1J_{CP} = 24.6$ Hz, $PCH(CH_3)_2$), 99.64 (s, $C_5(CH_3)_5$), 127–133 (s, Ph + C_β), 148.67 (s, C=N=CPh_2), 140 (s, C_γ), 195.35 (d, $^2J_{CP} = 11.8$ Hz, C=N=CPh_2), 204.9 (d, CO, $^2J_{CP} = 17.6$ Hz).

2.3. Synthesis of $[Cp^*Ru\{C(NHCH_cH_dC{\equiv}CH_b)CH_a{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**3**)

Propargylamine (0.017 ml, 0.38 mmol) was added to a solution of the allenylidene compound **1** (500 mg, 0.35 mmol) in 8 ml of dichloromethane. The mixture was stirred for 5 h. The volume was reduced to 1 ml. The solution was layered with petroleum ether, yielding orange crystals which were recrystallized from dichloromethane/petroleum ether. Yield: 310 mg, 60%. Anal. Calc. for $C_{68}H_{59}NBF_{24}OPRu$: C, 54.3; H, 3.95. Found: C, 54.4; H, 4.08%. IR (Nujol): ν(CO) 1967 (s) cm^{-1}, ν(NH) 3304 cm^{-1}, ν(C≡C) 3406 cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 343 K): δ 0.86 and 1.08 (m, 12H, $PCH(CH_3)_2$), 1.40 (d, 3H, $^2J_{HP} = 7.9$ Hz, PCH_3), 1.97 (m, 1H, $PCH(CH_3)_2$), 2.11 (m, 1H, $PCH(CH_3)_2$), 1.64 (br, 15H, $C_5(CH_3)_5$), 2.56 (t, $^4J_{HbHc} = 2.6$ Hz, $^4J_{HbHd} = 2.6$ Hz, 1H, H_b), 4.20 and 4.25 (dd, $^2J_{HcHd} = 5.9$ Hz, $^4J_{HbHc} = 2.6$ Hz, $^4J_{HbHd} = 2.6$ Hz, 2H, H_c and H_d), 6.38 (s, 1H, H_a), 7.03 (m, 2H, Ph), 7.16 (m, 2H, Ph), 7.38 (m, 6H, Ph), 7.63 (br, 1H, NH); $^{31}P\{^1H\}$ NMR (161.89 MHz, $C_2D_2Cl_4$, 343 K): δ 37.99 (s); $^{13}C\{^1H\}$ NMR (75.4 MHz, $C_2D_2Cl_4$, 343 K) δ: 9.76 (d, $^1J_{CP} = 24.1$ Hz, PCH_3), 9.64 (s, $C_5(CH_3)_5$), 18.88 (d, $^2J_{CP} = 12.6$ Hz, $PCH(CH_3)_2$), 17.32 (d, $^2J_{CP} = 12.6$ Hz, $PCH(CH_3)_2$), 26.91 (d, $^1J_{CP} = 29.9$ Hz, $PCH(CH_3)_2$),

28.55 (d, $^1J_{CP}$ = 26.84 Hz, P*C*H(CH$_3$)$_2$), 40.99 (s, HN*C*H$_2$), 74.47 (s, C≡*C*H), 76.73 (s, *C*≡CH), 100.0 (s, *C*$_5$(CH$_3$)$_5$), 120–142 (*C*$_\beta$, *C*$_\gamma$ Ph), 205.22 (d, $^2J_{CP}$ = 17.7 Hz, *C*O), 248.5 (d, $^2J_{CP}$ = 11.5 Hz, *C*$_\alpha$).

2.4. Synthesis of [Cp*Ru{C(NRR′)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (R = H, R′ = CH$_3$ (4); R = R′ = CH(CH$_3$)$_2$ (5))

A procedure similar to that for **3** was followed for the preparation of these complexes, using 0.35 mmol of methylamine (**4**) or diisopropylamine (**5**), respectively. These compounds were also recrystallized from dichloromethane/petroleum ether.

Compound **4**. Yield: 280 mg, 55%. Anal. Calc. for $C_{66}H_{59}NBF_{24}OPRu$: C, 53.5; H, 4.02. Found: C, 53.4; H, 4.08%. IR (Nujol): *ν*(CO) 1958 (s) cm^{-1}, *ν*(NH) 3387 cm^{-1}. ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 343 K): *δ* 0.95 (m, 12H, PCH(C*H*$_3$)$_2$), 1.45 (d, 3H, $^2J_{HP}$ = 8.0 Hz, PCH$_3$), 2.05 (m, 1H, PC*H*(CH$_3$)$_2$), 2.14 (m, 1H, PC*H*(CH$_3$)$_2$), 1.72 (br, 15H, C$_5$(C*H*$_3$)$_5$), 2.62 (s, 3H, NHC*H*$_3$), 6.12–7.50 (m, 10H, Ph), 8.04 (br, 1H, N*H*); ^{31}P{^{1}H} NMR (161.89 MHz, C$_2$D$_2$Cl$_4$, 343 K): *δ* 40.36 (s); ^{13}C{^{1}H} NMR (75.4 MHz, C$_2$D$_2$Cl$_4$, 343 K) *δ* : 8.96 (d, $^1J_{CP}$ = 23.6 Hz, P*C*H$_3$), 10.02 (s, C$_5$(*C*H$_3$)$_5$), 17.74 (d, $^2J_{CP}$ = 13.6 Hz, PCH(*C*H$_3$)$_2$), 17.96 (d, $^2J_{CP}$ = 14.0 Hz, PCH(*C*H$_3$)$_2$), 25.96 (d, $^1J_{CP}$ = 28.6 Hz, P*C*H(CH$_3$)$_2$), 27.39 (d, $^1J_{CP}$ = 26.2 Hz, P*C*H(CH$_3$)$_2$), 35.65 (s, HN*C*H$_3$), 102.1 (s, *C*$_5$(CH$_3$)$_5$), 121–146 (*C*$_\beta$, *C*$_\gamma$, Ph), 203.75 (d, $^2J_{CP}$ = 18.26 Hz, *C*O), 255.32 (d, $^2J_{CP}$ = 10.7 Hz, *C*$_\alpha$).

Compound **5**. Yield: 320 mg, 60%. Anal. Calc. for $C_{71}H_{69}NBF_{24}OPRu$: C, 54.9; H, 4.48. Found: C, 54.7; H, 4.38%. IR (Nujol): *ν*(CO) 1968 (s) cm^{-1}. ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 343 K): *δ* 0.87 (m, 12H, PCH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{HH}$ = 3.7 Hz, 12H, NCH(C*H*$_3$)$_2$), 1.39 (d, 3H, $^2J_{HP}$ = 8.0 Hz, PC*H*$_3$), 1.98 (m, 1H, PC*H*(CH$_3$)$_2$), 2.06 (m, 1H, PC*H*(CH$_3$)$_2$), 1.72 (br, 15H, C$_5$(C*H*$_3$)$_5$), 3.05 (m, 2H, NC*H*(CH$_3$)$_2$), 6.20–7.40 (m, 10H, Ph); ^{31}P{^{1}H} NMR (161.89 MHz, C$_2$D$_2$Cl$_4$, 343 K): *δ* 39.65 (s); ^{13}C{^{1}H} NMR (75.4 MHz, C$_2$D$_2$Cl$_4$, 343 K) *δ*: 8.74 (d, $^1J_{CP}$ = 25.6 Hz, P*C*H$_3$), 10.15 (s, C$_5$(*C*H$_3$)$_5$), 18.23 (d, $^2J_{CP}$ = 13.0 Hz, PCH(*C*H$_3$)$_2$), 18.67 (d, $^2J_{CP}$ = 15.0 Hz, PCH(CH$_3$)$_2$), 25.32 (d, $^1J_{CP}$ = 27.9 Hz, PCH(CH$_3$)$_2$), 27.86 (d, $^1J_{CP}$ = 26.0 Hz, P*C*H(CH$_3$)$_2$), 28.94 (s, NCH(*C*H$_3$)$_2$), 47.56 (s, N*C*H(CH$_3$)$_2$), 100.36 (s, *C*$_5$(CH$_3$)$_5$), 125–148 (*C*$_\beta$, *C*$_\gamma$, Ph), 201.59 (d, $^2J_{CP}$ = 17.9 Hz, *C*O), 246.37, (d, $^2J_{CP}$ = 11.1 Hz, *C*$_\alpha$).

2.5. Synthesis of [Cp*Ru{C(PMe$_3$)=C=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (6)

PMe$_3$ (0.043 ml, 0.50 mmol) was added to a solution of the allenylidene complex **1** (500 mg, 0.35 mmol). The mixture was stirred at 60 °C for 3 h and it was filtered through celite. The solvent was almost completely removed in vacuo. Addition of petroleum ether gave an orange crystalline solid which was filtered, washed with petroleum ether and dried. Yield: 310 mg, 60%. Anal. Calc. for $C_{68}H_{63}BF_{24}OP_2Ru$: C, 53.5; H, 4.16. Found: C, 53.4; H, 4.05%. IR (Nujol): *ν*(CO) 1888 (s) cm^{-1}, *ν*(C=C=C) 1856 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): *δ* 0.84, 0.97 and 1.13 (m, 12H, PCH(C*H*$_3$)$_2$), 1.18 (d, $^2J_{HP}$ = 8.5 Hz, 3H, PC*H*$_3$), 1.84 (m, 2H, PC*H*(CH$_3$)$_2$), 1.59 (d, $^4J_{HP}$ = 1.6 Hz, 15H, C$_5$(C*H*$_3$)$_5$), 1.73 (d, $^2J_{HP}$ = 12.3 Hz, 9H, P(C*H*$_3$)$_3$), 7.04–7.36 (m, 10H, Ph); ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): *δ* 22.6 (s, *P*Me$_3$), 43.8 (s, *P*Me^{i}Pr$_2$); ^{13}C{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): *δ* 10.82 (m, P(*C*H$_3$)$_3$), 10.50 (s, C$_5$(*C*H$_3$)$_5$), 18.68, 19.11 (m, PCH(*C*H$_3$)$_2$), 29.00 (d, $^1J_{CP}$ = 23.6 Hz, P*C*H(CH$_3$)$_2$), 29.94 (d, $^1J_{CP}$ = 25.7 Hz, P*C*H(CH$_3$)$_2$), 97.94 (d, $^3J_{CP}$ = 1.6 Hz, *C*$_5$(CH$_3$)$_5$), 102.28 (d, $^1J_{CP}$ = 23.2 Hz, *C*$_\alpha$), 115.50 (d, $^3J_{CP}$ = 21.0 Hz, *C*$_\gamma$), 120–130 (all s, Ph), 209.17 (d, $^2J_{CP}$ = 6.2 Hz, *C*$_\beta$), 210.39 (dd, $^2J_{CP}$ = 17.9 Hz, $^3J_{CP}$ = 8.2 Hz, *C*O).

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

This compound was obtained following a similar procedure to that for **6**. It was also isolated as secondary product in the nucleophilic addition of propanethiol to **1**. Yield: 400 mg, 60%. Anal. Calc. for $C_{72}H_{71}BF_{24}OP_2Ru$: C, 54.6; H, 4.52. Found: C, 54.4; H, 4.55%. IR (Nujol): *ν*(CO) 1897 (s) cm^{-1}, *ν*(C=C=C) 1850 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): *δ* 0.71, 1.16 and 1.35 (m, 27H, PCH(C*H*$_3$)$_2$, P′CH(C*H*$_3$)$_2$, P′C*H*$_3$), 1.63 (d, $^2J_{HP}$ = 11.1 Hz, 3H, PC*H*$_3$), 1.85 (m, 2H, PC*H*(CH$_3$)$_2$), 1.77 (d, $^4J_{HP}$ = 1.3 Hz, 15H, C$_5$(C*H*$_3$)$_5$), 2.57 (m, 1H, P′C*H*(CH$_3$)$_2$), 2.79 (m, 1H, P′C*H*(CH$_3$)$_2$), 7.16–7.40 (m, 10H, Ph); ^{31}P{^{1}H} NMR (161.89 MHz, CDCl$_3$, 298 K): *δ* 43.76 (s), 41.52 (s); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 298 K) *δ*: 4.64 (d, $^1J_{CP}$ = 57.7 Hz, P′*C*H$_3$), 10.62 (s, C$_5$(*C* H$_3$)$_5$), 15.82, 16.95, 17.37, 17.74, 18.62 and 19.60 (m, PCH(*C*H$_3$)$_2$ and P′CH(*C*H$_3$)$_2$), 22.68 (d, $^1J_{CP}$ = 42.7 Hz, P′*C*H(CH$_3$)$_2$), 23.59 (d, $^1J_{CP}$ = 45.9 Hz, P′*C*H(CH$_3$)$_2$), 29.77 (d, $^1J_{CP}$ = 25.7 Hz, P*C*H(CH$_3$)$_2$), 30.26 (d, $^1J_{CP}$ = 24.4 Hz, P*C*H(CH$_3$)$_2$), 98.02 (d, $^3J_{CP}$ = 1.7 Hz, *C*$_5$(CH$_3$)$_5$), 101.01 (d, $^1J_{CP'}$ = 23.2 Hz, *C*$_\alpha$), 115.49 (d, $^3J_{CP'}$ = 21.0 Hz, *C*$_\gamma$), 120–130 (all s, Ph), 206.96 (d, $^2J_{CP'}$ = 4.2 Hz, *C*$_\beta$), 210.99 (dd, $^2J_{CP}$ = 19.9 Hz, $^3J_{CP'}$ = 6.7 Hz, CO).

2.7. Synthesis of [Cp*Ru{C(S^{n}Pr)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (8)

A deep purple solution of **1** (500 mg, 0.35 mmol) in 10 ml of dichloromethane was treated with propanethiol

(0.05 ml, 0.70 mmol) and stirred for 6 h. The solvent was removed in vacuo. Petroleum ether was added, and the suspension was filtered off in order to remove the excess of propanethiol. The solution was concentrated and layered with petroleum ether. After two days an orange microcrystalline solid was obtained. It was filtered off, washed with petroleum ether and dried in vacuo. Recrystallization from diethyl ether/petroleum ether afforded crystals suitable for single-crystal X-ray diffraction. Yield: 240 mg, 45%. Anal. Calc. for $C_{68}H_{62}BF_{24}OPSRu$: C, 53.5; H, 4.09. Found: C, 53.4; H, 4.05%. IR (Nujol): ν(CO) 1898 (s) cm^{-1}, ν(C═C) 1590 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.98 (t, $^3J_{HH}=7.5$ Hz, 3H, $SCH_2CH_2CH_3$), 1.13 (m, 12H, $PCH(CH_3)_2$), 1.54 (d, $^2J_{HP}=8.7$ Hz, 3H, PCH_3), 1.70 (m, 2H, $SCH_2CH_2CH_3$), 1.99 (m, 1H, $PCH(CH_3)_2$), 2.20 (m, 1H, $PCH(CH_3)_2$), 1.59 (s, 15H, $C_5(CH_3)_5$), 3.11 (m, 2H, $SCH_2CH_2CH_3$), 6.62 (s, 1H, ═CH), 6.92, 7.16 and 7.34 (m, 10H, Ph); $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 36.37 (s); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K) δ: 7.56 (d, $^1J_{CP}=32.8$ Hz, PCH_3), 10.04 (s, $C_5(CH_3)_5$), 13.23 (s, $SCH_2CH_2C\ H_3$), 18.11 (d, $^2J_{CP}=8.7$ Hz, $PCH(CH_3)_2$), 17.68 (d, $^2J_{CP}=4.4$ Hz, $PCH(CH_3)_2$), 20.90 (s, $SCH_2CH_2CH_3$), 27.48 (d, $^1J_{CP}=26.3$ Hz, $PCH(CH_3)_2$), 29.34 (d, $^1J_{CP}=24.0$ Hz, $PCH(CH_3)_2$), 47.07 (s, $SCH_2CH_2CH_3$), 103.41 (s, $C_5(CH_3)_5$), 128.28, 128.51, 128.79 and 130.50 (all s, Ph), 138.08, 139.62, 141.39 (all s, C_γ, Ph), 142.46 (s, C_β), 203.72 (d, $^2J_{CP}=17.9$, Hz, CO), 309.70 (br, RuC_α).

2.8. X-ray structure determinations

Crystals of **2**, **7** and **8** were obtained by recrystallization from diethyl ether/petroleum ether, and **3** from dichloromethane/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°. Correction for absorption and crystal decay (insignificant) were applied by semi-empirical method from equivalents using program SADABS [25]. 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 SHELXTL [26]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. CF_3 groups of the $[BAr'_4]^-$ anion showed orientation disorder in all these compounds. 6 of 8 of the CF_3 groups were refined as pairs of CF_3 with complementary orientations for compounds **2**, **7** and **8**. In addition for compound **3**, one other CF_3 was partially splitted. All the remaining hydrogen atoms

Table 1
Crystal data and details of structure determination for compounds **2**, **3**, **7** and **8**

Compound	**2**	**3**	**7**	**8**
Formula	$C_{78}H_{65}BF_{24}NOPRu$	$C_{68}H_{59}BF_{24}NOPRu$	$C_{76}H_{81}BF_{24}O_2P_2Ru$	$C_{68}H_{62}BF_{24}OPRuS$
Formula weight	1631.16	1505.01	1656.23	1526.09
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Unit cell dimensions				
a (Å)	13.5058(8)	13.7633(5)	22.472(2)	12.6098(6)
b (Å)	15.6887(9)	15.0298(5)	22.123(2)	13.9079(7)
c (Å)	18.784(1)	18.0297(6)	17.030(2)	19.822(1)
α (°)	96.103(1)	79.344(1)	90	90.008(1)
β (°)	102.117(1)	82.689(1)	110.405(2)	91.813(1)
γ (°)	94.997(1)	82.125(1)	90	91.813(1)
V (Å^3)	3844.9(4)	3610.8(2)	7935(1)	3473.7(3)
Z	2	2	4	2
δ_{calc} (g/cm^3)	1.409	1.384	1.386	1.459
μ (Mo Kα) (mm^{-1})	0.327	0.341	0.337	0.384
F(000)	1656	1524	3392	1548
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
θ_{min}–θ_{max} (°)	1.7–25.0	2.0–25.1	2.4–24.1	1.0–25.0
Total, unique, R_{int}	25451, 13189, 0.023	33503, 12657, 0.049	62030, 12448, 0.044	26479, 10700, 0.050
Observed ($I>2\sigma(I)$)	12065	9915	11869	8728
Reflections, parameters	13189, 1114	12657,1071	12448, 1183	10700, 1055
R, wR_2 ($I>2\sigma(I)$)	0.0679, 0.1500	0.0699, 0.1534	0.0789, 0.1545	0.0868, 0.1603
R, wR_2 (all)	0.0748, 0.1549	0.0927, 0.1662	0.0841, 0.1575	0.1079, 0.1717
Goodness-of-fit	1.08	1.08	1.09	1.08
Residuals (e/Å^3)	−0.64, 0.73	−0.64, 0.71	−0.91, 0.69	−0.37, 0.69

in both compounds were refined using the SHELX riding model. The program ORTEP-3 [27] was used for plotting.

3. Results and discussion

We have previously studied the reactivity of the electron-rich allenylidene complex $[Cp^*Ru{=}C{=}C{=}CPh_2(dippe)]^+$ towards nucleophiles and electrophiles [23]. In that system, nucleophilic additions take place at the C_γ atom of the allenylidene chain, whereas electrophiles such as H^+ enter in the C_β position. At variance with this behaviour, the addition of nucleophiles to the electron-poor allenylidene complex **1** occur at the C_α. Scheme 1 summarizes the nucleophilic addition reactions studied in the present work.

Thus, the reaction of **1** with benzophenoneimine yields the azaallenyl derivative $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**2**). Although Cr or W azaallenyl complexes are known [28], ruthenium derivatives of this kind are rather scarce. The first isolated and characterized azaallenyl ruthenium complex was $[CpRu\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(P^iPr_3)][BF_4]$ [29], similarly prepared by addition of benzophenoneimine to the allenylidene complex $[CpRu{=}C{=}C{=}CPh_2(CO)(P^iPr_3)][BF_4]$. The X-ray crystal structure of **2** was determined. An ORTEP view of the cation $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ is shown in Fig. 1, together with a listing of selected bond lengths and angles.

The complex has a three-legged piano stool structure. The Ru1–C12 separation of 2.057(4) Å is consistent with a single bond, whereas the C12–N1 and N1–C14 bond lengths, 1.272(5) and 1.262(6) Å indicate double C=N bonds. The angle C12–N1–C14 has a value of 168.7(5)°, which indicates an essentially linear C=N=C C assembly. In the related complex $[CpRu\{C(N{=}CPh_2)CH{=}CPh_2\}(CO)(P^iPr_3)]^+$ [29], this angle has a value of 149.9(6)°, being therefore more deviated from linearity. The IR spectrum of **2** displays one strong band at 1796 cm^{-1} ascribed to the C=N=C group. The resonance for the ruthenium-bound C_α atom of the azaallenyl ligand appears as one doublet at 195.35 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

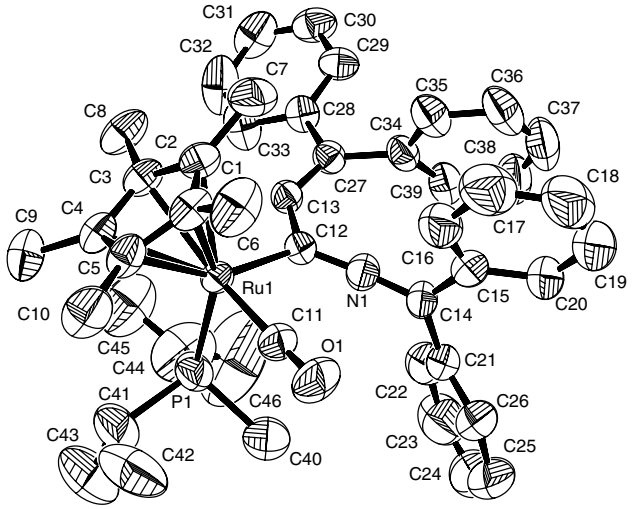
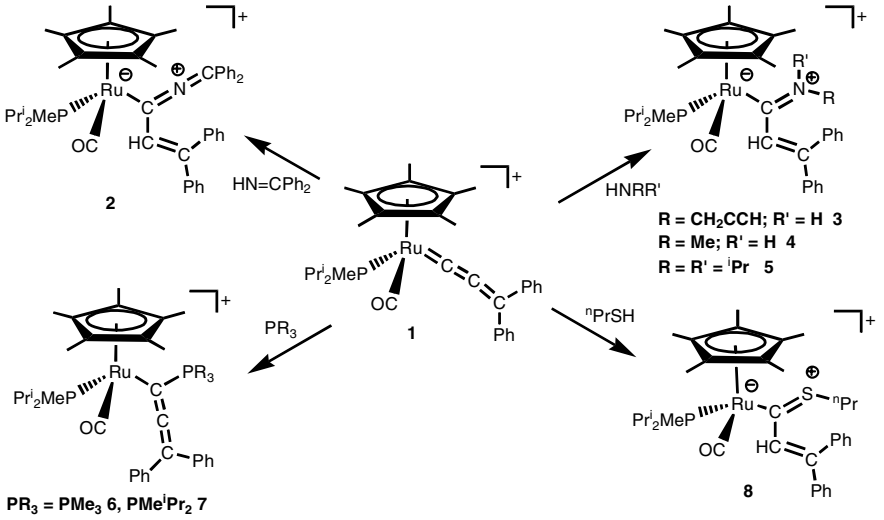
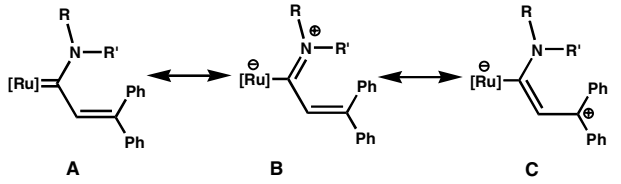


Fig. 1. ORTEP diagram of the cation $[Cp^*Ru\{C(N{=}CPh_2)\text{-}CH{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ in compound **2**. Selected bond distances (Å) and angles (°): Ru1–2.338(1); Ru1–C11 1.850(5); Ru1–C12 2.057(4); C12–C13 1.467(6); C13–C27 1.345(6); C12–N1 1.272(5); C14–N1 1.262(6); C11–O1 1.1.47(5); Ru1–C12–N1 122.8(3); N1–C14–C15 120.7(5); N1–C14–C21 1117.4(5); N1–C12–Ru1 122.8(3); N1–C12–C13 118.8(4); C14–N1–C12 168.7(5); C12–Ru1–P1 89.9(1); C11–Ru1–P1 87.0(1); Ru1–C12–C13 118.4(3).



Scheme 1. Summary of nucleophilic addition reactions to the allenylidene complex **1**.

Primary and secondary amines such as HC≡CCH$_2$NH$_2$, MeNH$_2$ or ^{i}Pr$_2$NH also react with the allenylidene complex **1** adding to the C_α–C_β bond furnishing the corresponding derivatives [Cp*Ru{C(NRR′)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][BAr$'_4$] (R = H, R′ = CH$_2$C≡CH **3**; R = H, R′ = Me **4**; R = R′ = ^{i}Pr **5**). In general, the addition of amines to the C_α–C_β of allenylidenes yields vinylaminocarbenes, for which the following main resonance structures must be considered [11]:



Structure A corresponds to a vinylaminocarbene, whereas B corresponds to an η^1-azoniabutadienyl complex. The X-ray crystal structure of compound **3** was determined. An ORTEP view of the cation [Cp*Ru{C(NHCH$_2$C≡CH)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)]$^+$ is shown in Fig. 2, together with a listing of selected bond lengths and angles.

The Ru1–C11 bond length of 2.020(4) Å is longer than the value expected for a Ru=C bond, i.e. 1.86(2) Å in the alkoxycarbene [TpRu=C(OMe)CH$_2$COOMe(dippe)]$^+$ (Tp = hidro*tris*(pyrazolyl)borate) [30], but very similar to the value of 2.063(6) Å reported for the azoniabutadienyl complex [CpRu{C(NEt$_2$)CH=CPh$_2$}(CO)(P^{i}Pr$_3$)]$^+$ [11]. The C11–N1 separation of 1.329(5) Å is intermediate between a single and a double carbon–nitrogen bond. These data suggest that for compound **3** there is a contribution of the azoniabutadienyl resonance structure B which seems more important than the vinylaminocarbene structure A. The Ru–C_α (2.063(6) Å) and C_α–N (1.306(7) Å) bond distances in [CpRu{C(NEt$_2$)CH=CPh$_2$}(CO)(P^{i}Pr$_3$)]$^+$ indicate that for this compound the contribution of the azoniabutadienyl resonance structure is even more important than for **3**. One possible explanation for this comes from the fact that Cp* is a better π-donor than Cp, and hence the metal centre results more electron-rich in Cp* complexes when compared to their Cp counterparts. As a result, the resonance structure with one negative charge at the ruthenium is more favoured in the complex containing Cp than in the Cp* case. Thus, complexes **3**–**5** are more properly referred to as azoniabutadienyl deriv-

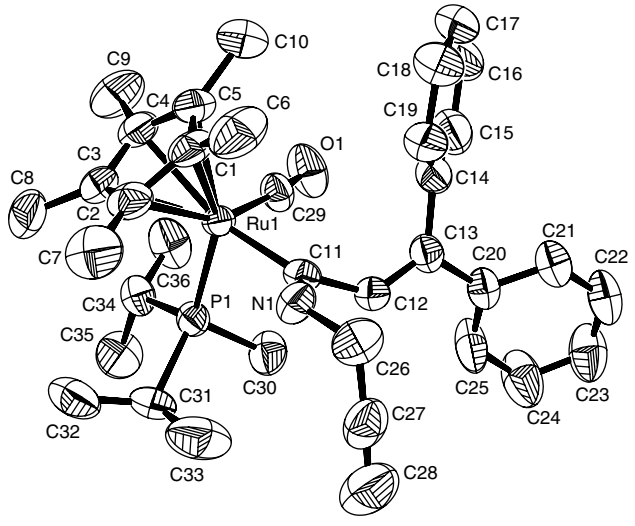


Fig. 2. ORTEP diagram of the cation [Cp*Ru{C(NHCH$_2$C≡CH)-CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)]$^+$ in compound **3**. Selected bond distances (Å) and angles (°): Ru1–P1 2.346(1); Ru1–C29 1.853(5); Ru1–C11 2.020(4); C11–C12 1.472(6); C12–C13 1.345(6); N1–C11 1.329(5); N1–C26 1.469(6); C13–C14 1.481(7); C13–C20 1.484(6); Ru1–C11–N1 120.1(3); N1–C11–C12 112.5(4); C11–C12–C13 132.9(4); Ru1–C11–C12 127.3(3); C12–C13–C14 122.9(4); C12–C13–C20 199.5(4); C11–N1–C26 127.5(4); C11–Ru1–P1 97.7(1).

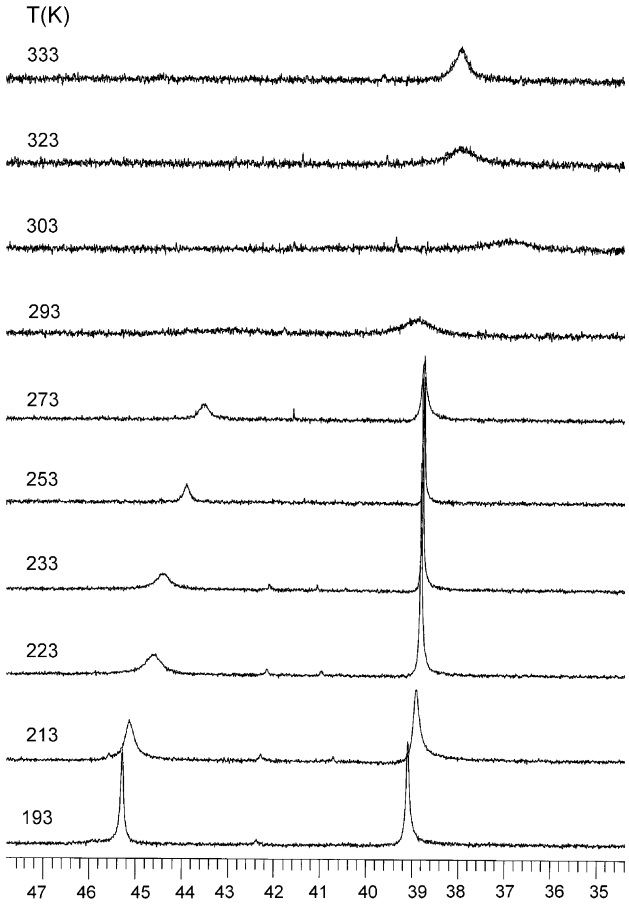
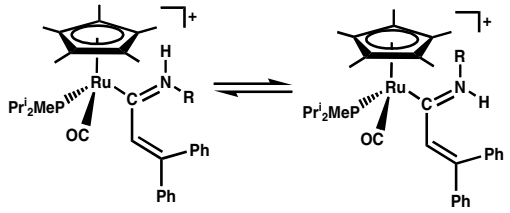


Fig. 3. VT ^{31}P{^{1}H} NMR spectra of compound **3** in CD_2Cl_2 (temperature range 193–293 K) and in $C_2D_2Cl_4$ (temperature range 303–333 K).

atives than vinylaminocarbenes. The $^{31}P\{^{1}H\}$ NMR spectra of these compounds display broad resonances at 25 °C (Fig. 3).

As the temperature is lowered, the broad resonances decoalesce to two peaks, which get progressively sharper. If the temperature is raised, the original spectra are restored, and at higher temperatures the broad features give rise to one single resonance. A similar behaviour is observed in the ^{1}H NMR spectra of these compounds (Fig. 4), which clearly indicate the occurrence of an equilibrium between two rapidly interconverting species.

We have interpreted this behaviour in terms of the restricted rotation around the C–N bond which originates two possible diastereoisomers for complexes **3** and **4**.



This also holds in case of **5**, since the two ^{i}Pr groups attached to the nitrogen atom are not equivalent and undergo rapid exchange in the NMR timescale. By integration of the ^{1}H NMR resonances corresponding to the protons of each of the species in equilibrium at each temperature it was possible to determine the values of the equilibrium constant for compound **3**. Fig. 5 shows a plot of $\ln K_{eq}$ versus $1/T$ for this equilibrium.

The difference in energy ΔH^{0} between the two isomers, calculated from the slope of the least-square best fit line to these data, is of the order of only 1 ± 0.1 kcal mol^{-1}, whereas the activation energy barrier $\Delta G^{\neq}$ has been estimated to be ca. 13 kcal mol^{-1}. The latter value was derived from the separation δv of the exchanging resonances in the slow-exchanging NMR spectrum, and the observed coalescence temperature T_c for each set of resonances, using the following approximate equation [31]:

$$\Delta G^{\neq} = RT_c[22.96 + \ln(T_c/(2.2\delta v))].$$

Complex **1** reacts with tertiary phosphines such as PMe_3 or $PMe^{i}Pr$ yielding allenylphosphonio derivatives $[Cp^{*}Ru\{C(PR_3)=C=CPh_2\}(CO)(PMe^{i}Pr_2)][BAr'_4]$ ($PR_3 = PMe_3$ (**6**), $PMe^{i}Pr_2$ (**7**)). These compounds result apparently from the attack of the phosphine at the C_α atom of the allenylidene group [7,13]. However, its has been observed that the reaction of **1** with one equivalent of PMe_3 at room temperature affords one mixture containing the allenylphosphonio derivative **6** plus another species, identified as the alkynylphosphonio complex $[Cp^{*}Ru(C\equiv CC(PMe_3)Ph_2)(CO)(PMe^{i}Pr_2)][BAr'_4]$ [32]. The latter results from the addition of the PMe_3 at the C_γ of the allenylidene, as we have previously observed in the complex $[Cp^{*}Ru(C\equiv CC(PEt_3)Me_2)(PEt_3)_2][BPh_4]$ [33]. However, when the mixture is heated up to 60 °C for 6 h, the alkynylphosphonio disappears, and only the allenylphosphonio **6** remains. This suggests that the product resulting from the attack of the phosphine at C_γ is kinetic, and that the thermodynamically stable final product is always the allenylphosphonio derivative. Furthermore, it has been reported that the complex $[(\eta^{5}\text{-Indenyl})Ru\{C\equiv CC(PMe_3)Ph_2\}(dppm)][PF_6]$ (dppm = 1,1-bis(diphenylphosphino)methane) undergoes an isomerization process to yield the thermodynamically more stable allenylphosphonio complex $[(\eta^{5}\text{-Indenyl})Ru\{C(PMe_3)=C=CPh_2\}(dppm)][PF_6]$ [34].

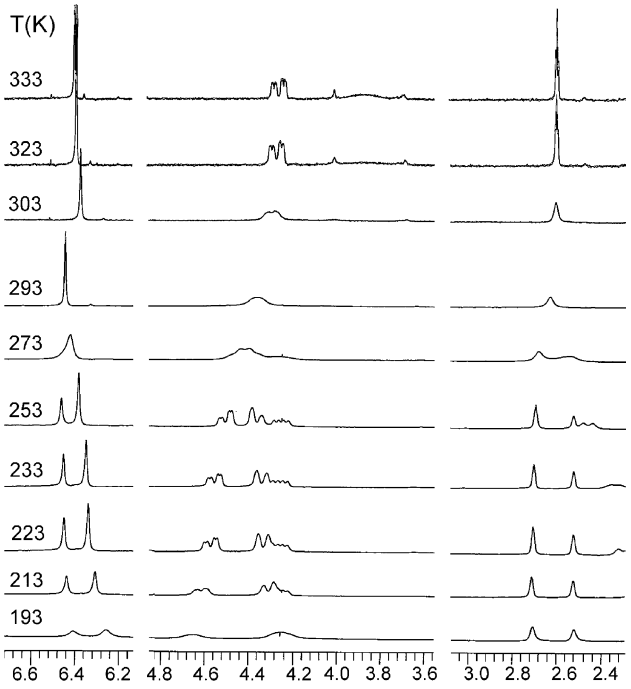


Fig. 4. VT ^{1}H NMR spectra of compound **3** in CD_2Cl_2 (temperature range 193–293 K) and in $C_2D_2Cl_4$ (temperature range 303–333 K).

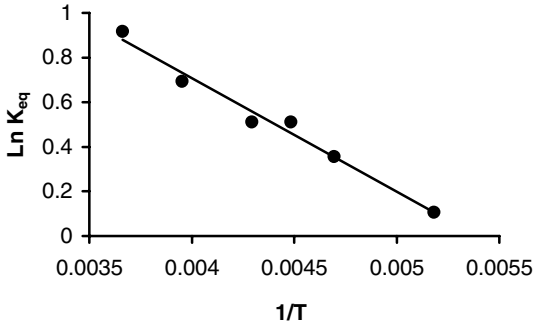
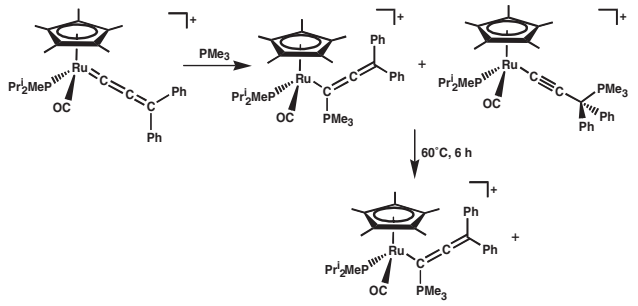


Fig. 5. Plot of $\ln K_{eq}$ vs. $1/T$ (K^{-1}) for the equilibrium in solution between the two isomers of compound **3**.

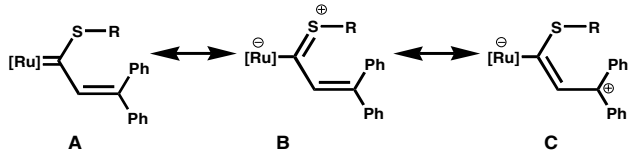


As it has been previously observed for the alkynylphosphonio complex $[Cp^*Ru(C{\equiv}CC(PEt_3)Me_2)(PEt_3)][BPh_4]$ [33], complex **7** is also formed as by-product in many reactions involving the allenylidene complex **1**, as a degradation product. The $^{31}P\{^1H\}$ NMR spectra of **6** and **7** display two singlet resonances, one for the PMe^iPr_3 attached to ruthenium and another one for the phosphine at the C_α. The fact that no resolved coupling $^3J_{PP}$ is observed for these compounds is consistent with the NMR spectral properties reported for related compounds such as $[CpRu\{C(PR_3){=}C{=}CPh_2\}(CO)(P^iPr_3)][BF_4]$ ($PR_3 = PHPh_2$, $PMePh_2$, PPh_3) [13]. The resonances for the C_α atoms appear as doublets in the $^{13}C\{^1H\}$NMR spectra of these complexes at 102.28 and 101.01 ppm for **6** and **7**, respectively, whereas the resonances of the C_β and C_γ atoms of the allenyl chain appear at lower fields. The crystal structure of compound **7** was determined. An ORTEP view of the cation $[Cp^*Ru\{C(PMe^iPr_2)CH{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ is shown in Fig. 6, together with a listing of selected bond lengths and angles.

The structure is comparable to that of the allenylphosphonio derivative $[CpRu\{C(PHPh_2)CH{=}CPh_2\}(CO)(P^iPr_3)]^+$ [13]. The Ru1–C12 separation of 2.168(5) Å suggests a single Ru–C bond, as expected, whereas the C12–C13–C14 angle of 176.9(5)° indicates the linearity of the allenyl moiety.

The addition of propanethiol to the C_α–C_β bond of the allenylidene ligand in **7** yields formally the thiocarbene complex $[Cp^*Ru\{C(S^nPr)CH{=}CPh_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**8**). This compound was structurally characterized by single-crystal X-ray diffraction. An ORTEP view of the cation $[Cp^*Ru\{C(S^nPr)CH{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ is shown in Fig. 7, together with a listing of selected bond lengths and angles.

The Ru1–C11 bond length has a value of 2.065(7) Å, much longer than the separations of 1.829(3) and 1.837(4) Å found, respectively, for $[Ru{=}CHSPhCl_2(PCy_3)_2]$ [a] and $[Ru{=}CHSPhCl_2(P^iPr_3)_2]$ [b], but of the same order than the Ru–C bond distances found in the azaallenyl and azoniabutadienyl complexes **2**–**5** reported in this work. The Ru1–S1 bond length of 1.657(6) Å is shorter than the analogous separation in $[Ru{=}CHSPhCl_2(P^iPr_3)_2]$ (1.706(4) Å) [b], and in general shorter than a standard C–S single bond (1.75–1.79 Å). As it happens with the vinylaminocarbenes, we can consider the following main resonance structures for a vinylthiocarbene:



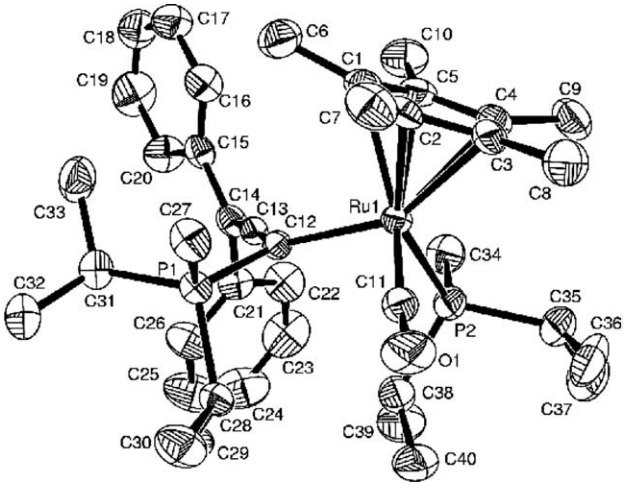


Fig. 6. ORTEP diagram of the cation $[Cp^*Ru\{C(PMe^iPr_2){=}C{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ in compound **7**. Selected bond distances (Å) and angles (°): Ru1–P2 2.227(1); Ru1–C11 1.844(6); Ru1–C12 2.168(5); C12–C13 1.306(7); C13–C14 1.333(7); C12–P1 1.803(5); Ru1–C12–P1 118.8(2); C12–Ru1–P2 89.7(1); C12–C13–C14 176.9(5); Ru1–C12–C13 128.5(4); C11–Ru1–C12 97.7(2); C11–Ru1–P2 91.9(2).

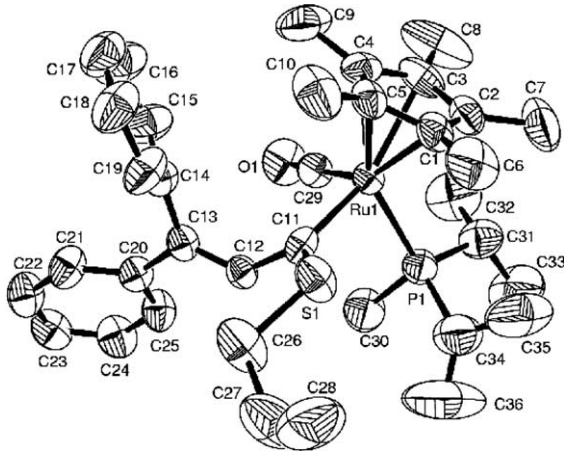


Fig. 7. ORTEP diagram of cation $[Cp^*Ru\{C(SCH_2CH_2CH_3){-}CH{=}CPh_2\}(CO)(PMe^iPr_2)]^+$ in compound **8**. Selected bond distances (Å) and angles (°): Ru1–P1 2.336(2); Ru1–C29 1.794(8); Ru1–C11 2.065(7); C11–S1 1.657(6); C11–C12 1.444(8); C12–C13 1.332(8); Ru1–C11–C12 126.1(4); Ru1–C11–S1 120.5(4); C11–C12–C13 129.1(6); C12–C11–S1 113.4(5); C11–Ru1–P1 90.4(2); C11–S1–C26 112.2(3).

The observed sequence of bond lengths suggests that the contribution of the structure B is more important, and hence complex **8** can be better considered as a η^1-thiabutadienyl rather than a thiocarbene. The resonance for the C_α atom appears as one broad signal at 309.70 ppm in the $^{13}C\{^1H\}$NMR spectrum, shifted to lower fields with respect to the position of the resonances for the C_α atoms in the azoniabutadienyl complexes **2**–**5**, which appear in the range 246–255 ppm.

4. Conclusion

The allenylidene complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ undergoes nucleophilic addition reactions which take place at the C_α atom of the allenylidene chain, at variance with other systems previously studied for which such reactions occur at the C_γ position. The reaction with benzophenoneimine yields the azaallenyl derivative $[Cp^*Ru\{C(N{=}CPh_2)CH{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$, whereas addition of primary or secondary amines yield aminocarbenes which are better formulated as azoniabutadienyl derivatives $[Cp^*Ru\{C(NRR')CH{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$. There is restricted rotation at the C_α–N bond of these complexes. The activation energy barrier has been estimated to be ca. 13 kcal mol^{-1} in the case R = H, R′ = $CH_2C{\equiv}CH$, the difference in energy between the stereoisomers being only 1 kcal mol^{-1}. The addition of tertiary phosphines leads to allenylphosphonio derivatives $[Cp^*Ru\{C(PR_3)C{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$, whereas the reaction with propanethiol yields the thiocarbene $[Cp^*Ru\{C(S^n Pr)CH{=}CPh_2(CO)(PMe^iPr_2)][BAr'_4]$ which is better considered as a thiabutadienyl complex as inferred from its X-ray crystal structure analysis. In summary, despite of the well-known differences between systems bearing Cp or Cp* ligands, in this particular case the reactivity of the complex $[Cp^*Ru{=}C{=}C{=}CPh_2(CO)(PMe^iPr_2)]^+$ towards nucleophiles parallels in general terms that of the related CpRu system $[CpRu{=}C{=}C{=}CPh_2(CO)(P^iPr_3)]^+$ [8–17,29].

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.06.002.

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