ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 585 (1999) 83–92

Journal of Organo metallic Chemistry

Preparation of new acetylide and vinylidene complexes of ruthenium

Gabriele Albertin *, Stefano Antoniutti, Emilio Bordignon, Manuel Granzotto

Dipartimento di Chimica, Università Ca'Foscari di Venezia, Dorsoduro 2137, I-30123 Venice, Italy

Received 20 February 1999

Abstract

Monoacetylide $\mathrm{RuCl(C{\equiv}CR)P_4}$ complexes ($\mathrm{R = Ph}$, $\mathrm{4\text{-}MeC_6H_4}$, $\mathrm{1,4\text{-}C_6H_4C{\equiv}CH}$, $\mathrm{SiMe_3}$, Bu^t or COOMe; $\mathrm{P = P(OEt)_3}$ or $\mathrm{P(OMe)_3}$) were prepared by allowing $\mathrm{RuCl_2P_4}$ to react with terminal alkynes $\mathrm{RC{\equiv}CH}$ in the presence of an excess of $\mathrm{NEt_3}$. Dinuclear compounds $\mathrm{[\{Ru[P(OEt)_3]_5\}_2(\mu\text{-}1,4\text{-}C{\equiv}CC_6H_4C{\equiv}C)]Y_2}$ ($\mathrm{Y = PF_6}$ or $\mathrm{BPh_4}$) were also prepared from the reaction of $\mathrm{RuCl_2P_4}$ with $\mathrm{1,4\text{-}HC{\equiv}CC_6H_4C{\equiv}CH}$. Treatment of $\mathrm{RuCl_2P_4}$ with $\mathrm{Li^+[1,4\text{-}HC{\equiv}CC_6H_4C{\equiv}C]^-}$ afforded bis(alkynyl) $\mathrm{Ru(1,4\text{-}C{\equiv}CC_6H_4C{\equiv}CH)_2P_4}$ [$\mathrm{P = P(OEt)_3}$, $\mathrm{P(OMe)_3}$ or $\mathrm{PPh(OEt)_2}$] derivatives. Protonation reactions of monoacetylides $\mathrm{RuCl(C{\equiv}CR)P_4}$ with $\mathrm{CF_3SO_3H}$ led to vinylidene $\mathrm{[RuCl\{{=}C{=}C(H)R\}P_4]CF_3SO_3}$ [$\mathrm{R = Ph}$, $\mathrm{4\text{-}MeC_6H_4}$ or $\mathrm{1,4\text{-}C_6H_4C{\equiv}CH}$; $\mathrm{P = P(OEt)_3}$ or $\mathrm{P(OMe)_3}$] complexes, which were fully characterised by IR and ^{1}H-, ^{31}P- and ^{13}C-NMR spectra. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Alkynyl; Vinylidene; Dinuclear compounds

1. Introduction

The chemistry of acetylide and vinylidene organometallic complexes continues to attract interest, due to their potential use in several stoichiometric or catalytic transformations, such as dimerisation of alkynes to enynes or butatrienes [1], formation of unsaturated carbene complexes [2] and metallocumulenes [3], and other C–C coupling reactions [4]. In addition, carbon-rich organometallic compounds are also attractive, due to their potential for granting non-linear optical [5], liquid crystal [6], mixed-valence or conducting [7] properties.

These properties motivate constant studies on the synthesis of mono- and dinuclear σ-acetylide derivatives and their chemical reactivity [1–4,8]. Important in this context is the influence of the ancillary ligands, generally mono-, bi- and polydentate phosphine, cyclopentadienyl or arene rings. In contrast, very few reports refer to phosphite $\mathrm{P(OEt)_3}$, substituted-phosphite $\mathrm{PR(OR')_2}$ or $\mathrm{PR_2(OR')}$ ligands, and only recently some studies [9] on acetylide, vinylidene and enynyl derivatives of iron(II), ruthenium(II) and osmium(II) with these ligands have been reported by our research group. Following this initial work, we now report the synthesis and characterisation of new mono- and dinuclear acetylide complexes of ruthenium, together with their reactivity studies, which yielded new vinylidene derivatives.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out in an inert atmosphere (argon, N_2) using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes turned out to be quite air-stable and were stored at −20°C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon [10]; trimethyl- and triethylphosphite were Aldrich products purified by distillation under nitrogen. Alkynes were Aldrich products, used without any further purification. Lithium

---

* Corresponding author.

PII: S0022-328X(99)00193-X

acetylides $Li^+RC\equiv C^-$ (R = phenyl or *p*-tolyl) were prepared by reacting a slight excess of the appropriate acetylene (40 mmol) with lithium (35 mmol, 0.24 g) in 10 cm^3 of THF. 1,4-Diethynylbenzene was prepared following the method previously reported [11]. The related lithium acetylide $Li^+[1,4\text{-}HC\equiv CC_6H_4C\equiv C]^-$ was prepared by reacting 1,4-diethynylbenzene (16 mmol, 2 g) with lithium (15 mmol, 0.104 g) in 30 cm^3 of THF. The reaction mixture was refluxed until all the lithium had dissolved (about 8 h), and was kept under argon. Other reagents were purchased from commercial sources in the highest available purity and used as received. IR spectra were recorded on Digilab Bio-Rad FTS-40 or Nicolet Magna 750 FT-IR spectrophotometers. NMR spectra (^1H-, ^{13}C-, ^{31}P-) were obtained on a Bruker AC200 spectrometer at temperatures varying from − 90 to + 30°C, unless otherwise stated. ^1H and ^{13}C spectra are referred to internal TMS; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SWAN-MR software package [12] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25°C was measured with a Radiometer CDM 83 instrument.

2.2. Preparation of the complexes

Dichloro-compounds $RuCl_2[P(OEt)]_4$ and $RuCl_2P_4$ [$P = P(OMe)_3$ or $PPh(OEt)_2$] were prepared following the method previously reported [9b,13].

*2.2.1. $RuCl(C\equiv CR)P_4$ (**1–2**) [$P = P(OEt)_3$ (**1**) or $P(OMe)_3$ (**2**); R = Ph (**a**), 4-MeC_6H_4 (**b**) or 1,4-$C_6H_4C\equiv CH$ (**c**)]*

To a solution of $RuCl_2P_4$ (0.6 mmol) in 10 cm^3 of THF were sequentially added first an excess of the appropriate alkyne $RC\equiv CH$ (6 mmol) and then an excess of NEt_3 (6 mmol, 0.83 cm^3), and the reaction mixture was refluxed for about 50 min. The solvent was removed under reduced pressure, giving an oil which was triturated with 3 cm^3 of ethanol. After cooling the resulting solution to − 25°C, a pale-yellow solid separated out, which was crystallised from diethyl ether (5 cm^3) and ethanol (5 cm^3); yield from 30 to 40%.

Anal. Calc. for $C_{32}H_{65}ClO_{12}P_4Ru$ (**1a**): C, 42.6; H, 7.3; Cl, 3.9. Found: C, 42.5; H, 7.3; Cl, 3.8%.

Anal. Calc. for $C_{33}H_{67}ClO_{12}P_4Ru$ (**1b**): C, 43.3; H, 7.4; Cl, 3.9. Found: C, 43.2; H, 7.5; Cl, 3.8%.

Anal. Calc. for $C_{34}H_{65}ClO_{12}P_4Ru$ (**1c**): C, 44.1; H, 7.1; Cl, 3.8.Found: C, 44.2; H, 7.1; Cl, 3.7%.

Anal. Calc. for $C_{20}H_{41}ClO_{12}P_4Ru$ (**2a**): C, 32.7; H, 5.6; Cl, 4.8. Found: C, 32.5; H, 5.7; Cl, 4.6%.

Anal. Calc. for $C_{21}H_{43}ClO_{12}P_4Ru$ (**2b**): C, 33.7; H, 5.8; Cl, 4.7. Found: C, 33.6; H, 5.8; Cl, 4.6%.

Anal. Calc. for $C_{22}H_{41}ClO_{12}P_4Ru$ (**2c**): C, 34.9; H, 5.5; Cl, 4.7. Found: C, 34.7; H, 5.5; Cl, 4.6%.

*2.2.2. $RuCl(C\equiv CR)[P(OEt)_3]_4$ (**1**) [R = $SiMe_3$ (**d**), Bu^t (**e**) or COOMe (**f**)]*

These complexes were prepared like the related **1a**–**1c** by treating $RuCl_2[P(OEt)_3]_4$ (0.6 mmol, 0.5 g) with an excess of the appropriate alkyne (6 mmol) and an excess of NEt_3 (6 mmol, 0.83 cm^3) and then refluxing the resulting solution in THF (10 cm^3) for 3 h. After evaporation of the solvent at reduced pressure, the oil obtained was chromatographed through a silica gel column (20 × 2 cm) using a mixture of diethyl ether and benzene (ratio 2:1) as eluent. The first eluate (50 cm^3) was evaporated to dryness, leaving an oily product that could not be obtained as a solid. The spectroscopic data, however, confirm the purity and formulation of the products.

2.2.3. $Ru(C\equiv CPh)_2[PPh(OEt)_2]_4$

This complex [9b] was obtained in an attempt to prepare the chloroacetylide $RuCl(C\equiv CPh)P_4$ derivative, as follows: an excess of $PhC\equiv CH$ (6 mmol, 0.67 cm^3) and then an excess of NEt_3 (6 mmol, 0.83 cm^3) were added to a solution of $RuCl_2[PPh(OEt)_2]_4$ (0.6 mmol, 0.58 g) in 10 cm^3 of THF, and the reaction mixture refluxed for about 3 h. The solvent was removed under reduced pressure, giving an oil which was triturated with 5 cm^3 of ethanol. After slow cooling of the resulting solution to − 25°C, yellow microcrystals of the compound were obtained; yield 83%.

Anal. Calc. for $C_{56}H_{70}O_8P_4Ru$: C, 61.4; H, 6.4. Found: C, 61.3; H, 6.4%.

*2.2.4. $[\{Ru[P(OEt)_3]_5\}_2(\mu\text{-}1,4\text{-}C\equiv CC_6H_4C\equiv C)]Y_2$ (**3**) (Y = PF_6 or BPh_4)*

A 25 cm^3 three-necked round-bottomed flask was charged with $RuCl_2[P(OEt)_3]_4$ (0.6 mmol, 0.5 g), 1,4-$HC\equiv CC_6H_4C\equiv CH$ (0.3 mmol, 37.8 mg), $NaPF_6$ (1.8 mmol, 0.3 g), 10 cm^3 of THF and NEt_3 (6 mmol, 0.83 cm^3). The resulting mixture was refluxed for 2 h 30 min, and the solvent evaporated to dryness. The brown oil obtained was treated with ethanol (5 cm^3) and the resulting solution stirred until a solid separated out, which was crystallised from ethanol; yield ≥ 30% of **3**-PF_6. To the mother liquid an excess of $NaBPh_4$ (2.4 mmol, 0.82 g) in 3 cm^3 of ethanol was added and the orange solid obtained was filtered and crystallised from ethanol; yield ≥ 35% of **3**-BPh_4.

Anal. Calc. for $C_{70}H_{154}F_{12}O_{30}P_{12}Ru_2$ (**3**-PF_6): C, 36.9; H, 6.8. Found: C, 37.0; H, 6.9%. Anal. Calc. for $C_{118}H_{194}B_2O_{30}P_{10}Ru_2$ (**3**-BPh_4): C, 54.0; H, 7.5. Found: C, 53.8; H, 7.5%.

*2.2.5. $Ru(1,4\text{-}C\equiv CC_6H_4C\equiv CH)_2P_4$ (**4–6**) [$P = P(OEt)_3$ (**4**), $P(OMe)_3$ (**5**) or $PPh(OEt)_2$ (**6**)]*

An excess of $Li^+[1,4\text{-}HC\equiv CC_6H_4C\equiv C]^-$ (3.6 mmol, 6.8 cm^3 of a 0.53 mol dm^{-3} solution in THF) was added to a solution of the appropriate complex

$RuCl_2P_4$ (0.6 mmol) in 10 cm^3 of THF, and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure, giving an oil which was treated with 5 cm^3 of ethanol. The resulting solution was vigorously stirred until a red–brown solid separated out, which was crystallised from diethyl ether (5 cm^3) and ethanol (5 cm^3); yield 15–40%.

Anal. Calc. for $C_{44}H_{70}O_{12}P_4Ru$ (**4**): C, 52.0; H, 6.9. Found: C, 51.8; H, 7.0%. Anal. Calc. for $C_{32}H_{46}O_{12}P_4Ru$ (**5**): C, 45.3; H, 5.5. Found: C, 45.1; H, 5.5%. Anal. Calc. for $C_{60}H_{70}O_8P_4Ru$ (**6**): C, 63.0; H, 6.2. Found: C, 63.1; H, 6.2%.

2.2.6. $[RuCl\{=C=C(H)R\}P_4]CF_3SO_3$ (*7*–***8***) [$P = P(OEt)_3$ (*7*) or $P(OMe)_3$ (***8***); R = Ph (***a***), 4-MeC_6H_4 (***b***) or 1,4-$C_6H_4C\equiv CH$ (***c***)]

To a solution of the appropriate acetylide $RuCl(C\equiv CR)P_4$ (0.15 mmol) in 10 cm^3 of diethyl ether cooled to −80°C was added a slight excess of CF_3SO_3H (0.16 mmol, 14.2 μl) and the reaction mixture, brought to room temperature, was stirred for 1 h. A pink solid slowly separated out, which was filtered and dried in vacuo; yield ≥ 80%.

Anal. Calc. for $C_{33}H_{66}ClF_3O_{15}P_4SRu$ (**7a**): C, 37.7; H, 6.3; Cl, 3.4. Found: C, 37.6; H, 6.4; Cl, 3.4%.

Anal. Calc. for $C_{34}H_{68}ClF_3O_{15}P_4SRu$ (**7b**): C, 38.3; H, 6.4; Cl, 3.3. Found: C, 38.1; H, 6.5; Cl, 3.2%.

Anal. Calc. for $C_{35}H_{66}ClF_3O_{15}P_4SRu$ (**7c**): C, 39.1; H, 6.2; Cl, 3.3. Found: C, 39.0; H, 6.3; Cl, 3.2%.

Anal. Calc. for $C_{21}H_{42}ClF_3O_{15}P_4SRu$ (**8a**): C, 28.5; H, 4.8; Cl, 4.0. Found: C, 28.3; H, 4.6; Cl, 3.9%.

Anal. Calc. for $C_{22}H_{44}ClF_3O_{15}P_4SRu$ (**8b**): C, 29.4; H, 4.9; Cl, 4.0. Found: C, 29.5; H, 5.0; Cl, 3.9%.

Anal. Calc. for $C_{23}H_{42}ClF_3O_{15}P_4SRu$ (**8c**): C, 30.4; H, 4.7; Cl, 3.9. Found: C, 29.9; H, 4.9; Cl, 3.9%.

2.2.7. $[RuCl\{=C=C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ (*7a-BF₄*)

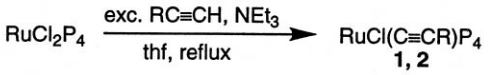
This compound was prepared exactly like the related triflate complex **7a** using $HBF_4\cdot Et_2O$ instead of CF_3SO_3H as the protonating agent; yield ≥ 80%

Anal. Calc. for $C_{32}H_{66}BClF_4O_{12}P_4Ru$: C, 38.8; H, 6.7; Cl, 3.6. Found: C, 38.9; H, 6.8; Cl, 3.5%.

3. Results and discussion

3.1. Preparation of acetylide derivatives

Dichloro complexes $RuCl_2P_4$ react with terminal alkynes in the presence of an excess of NEt_3 to give the mono-acetylide complexes $RuCl(C\equiv CR)P_4$, which were isolated in good yield and characterised (Scheme 1). The reaction also proceeds with 1,4-diethynylbenzene to afford the corresponding mono-acetylide containing the acetylenic end-group.



Scheme 1. $P = P(OEt)_3$ (**1**) or $P(OMe)_3$ (**2**); R = Ph (**a**), 4-MeC_6H_4 (**b**), 1,4-$C_6H_4C\equiv CH$ (**c**), $SiMe_3$ (**d**), Bu^t (**e**) or COOMe (**f**).

Studies on the reaction course in the absence of NEt_3 indicate (by NMR, see below) the formation of vinylidene intermediates $[RuCl\{=C=C(H)R\}P_4]^+$ which, by deprotonation, give the final acetylide derivatives **1**, **2**.

The activation of a terminal alkyne into a vinylidene by dichloro complexes is not unexpected, and probably takes place by the initial formation of a η^2-alkyne complex of the type $[RuCl(\eta^2\text{-}HC\equiv CR)P_4]^+$, followed by an intramolecular 1,2-[H] shift [14] to give the vinylidene complex. This intermediate may also be formed by a different pathway involving oxidative addition of the alkyne to a Ru(II) species to generate a Ru(IV) moiety, with subsequent migration of the Ru–H hydride to the β-carbon of the RuC≡CR, as previously observed [15]. In every case, the chloro-vinylidene $[RuCl\{=C=C(H)R\}P_4]^+$ species is always formed (detected by NMR), but in small amounts which do not allow its isolation in pure form.

Good analytical data were obtained for acetylide complexes **1a**–**c**, **2a**–**c**, which are air-stable white or pale yellow solids (the related **1d**–**f** are oils), diamagnetic and non-electrolytic. Their spectroscopic properties (IR and NMR) are reported in Table 1. The IR spectra show only one band in the ν(C≡C) region, at 2098–2013 cm^{-1} for all the acetylides except for $RuCl(1,4\text{-}C\equiv CC_6H_4C\equiv CH)P_4$ **1c** and **2c** complexes, which exhibit two ν(C≡C) absorptions at 2085, 2040 (**1c**) and 2084, 2039 cm^{-1} (**2c**), and the ν(CH) band of the terminal acetylene end C≡CH at 3250–3227 cm^{-1}.

The ^{13}C-NMR spectra confirm the presence of the acetylide ligand, showing the signals of the C_α and C_β carbon atoms as quintets, respectively at 119–107 ppm, with a $^2J_{CP}$ value of 20 Hz, and 109–110 ppm, with a $^3J_{CP}$ of about 2 Hz. In the case of 1,4-diethynylbenzene derivative (**1c**), the ^{13}C spectra also show the signals of the C_γ and C_δ carbon atoms of the acetylide ligand as singlets at 84.9 and 77.0 ppm, respectively. In the temperature range from +30 to −90°C, the $^{31}P\{^1H\}$-NMR spectra appear as sharp singlets, indicating the magnetic equivalence of the four phosphorus atoms of the phosphite ligands.

On this basis, a geometry with the chloride and acetylide ligands in a mutually *trans* position may reasonably be proposed for all the complexes (Scheme 2).

Table 1
IR and NMR data for the ruthenium complexes

	Compound	IR [a]		^{1}H-NMR [b,c]		Spin system	^{31}P{^{1}H}-NMR [b,d]	^{13}C{^{1}H}-NMR [b,e]	
		$\bar{\nu}$ (cm^{-1})	Assignment	δ (J Hz)	Assignment		δ (J Hz)	δ (J Hz)	Assignment
1a	$\mathrm{RuCl(C{\equiv}CPh)[P(OEt)_3]_4}$	2093s	ν(C≡C)	4.26 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	132.3 (s)		
				1.22 (t)	$\mathrm{POCH_2C}H_3$				
1b	$\mathrm{RuCl(4\text{-}MeC_6H_4C{\equiv}C)[P(OEt)_3]_4}$	2098s	ν(C≡C)	4.26 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	132.4 (s)	109.5 (qnt, br) $^3J_{\mathrm{CP}} = 2$	$\mathrm{C_\beta}$ acetylide
				2.23 (s)	$\mathrm{4\text{-}C}H_3\mathrm{C_6H_4}$			108.0 (qnt) $^2J_{\mathrm{CP}} = 20$	$\mathrm{C_\alpha}$ acetylide
				1.21 (t)	$\mathrm{POCH_2C}H_3$			61.3 (s)	$\mathrm{PO}C\mathrm{H_2CH_3}$
								21.1 (s)	$\mathrm{4\text{-}}C\mathrm{H_3C_6H_4}$
								16.5 (s)	$\mathrm{POCH_2}C\mathrm{H_3}$
1c	$\mathrm{RuCl(1,4\text{-}C{\equiv}CC_6H_4C{\equiv}CH)[P(OEt)_3]_4}$	3227m	ν(CH)	4.25 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	131.9 (s)	119.0 (qnt) $^2J_{\mathrm{CP}} = 20$	$\mathrm{C_\alpha}$ acetylide
		2085s	ν(C≡C)	3.08 (s)	$\equiv\mathrm{C}H$			110.7 (qnt) $^3J_{\mathrm{CP}} = 2$	$\mathrm{C_\beta}$ acetylide
		2040w	ν(C≡CH)	1.21 (t)	$\mathrm{POCH_2C}H_3$			84.9 (s)	$\mathrm{C_\gamma}$ acetylide
								77.0 (s)	$\mathrm{C_\delta}$ acetylide
								61.4 (s)	$\mathrm{PO}C\mathrm{H_2CH_3}$
								16.5 (s)	$\mathrm{POCH_2}C\mathrm{H_3}$
1d	$\mathrm{RuCl[C{\equiv}CSi(CH_3)_3][P(OEt)_3]_4}$	2013s	ν(C≡C)	4.42 (m) [f]	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	129.4 (s) [f]		
				1.27 (t)	$\mathrm{POCH_2C}H_3$				
				0.25 (s)	$\mathrm{Si(C}H_3)_3$				
1e	$\mathrm{RuCl[C{\equiv}CC(CH_3)_3][P(OEt)_3]_4}$	2093s	ν(C≡C)	4.44 (m) [f]	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	133.8 (s) [f]		
				1.29 (t)	$\mathrm{POCH_2C}H_3$				
				0.26 (s)	$\mathrm{C(C}H_3)_3$				
1f	$\mathrm{RuCl[C{\equiv}C(CO)OMe][P(OEt)_3]_4}$	2076s	ν(C≡C)	4.23 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{A_4}$	130.7 (s)		
		1674s	ν(CO)	3.49 (s)	$\mathrm{OC}H_3$				
				1.23 (t)	$\mathrm{POCH_2C}H_3$				
2a	$\mathrm{RuCl(C{\equiv}CPh)[P(OMe)_3]_4}$	2089s	ν(C≡C)	3.82 (t)	$\mathrm{POC}H_3$	$\mathrm{A_4}$	134.5 (s)	110.9 (qnt) $^3J_{\mathrm{CP}} = 2$	$\mathrm{C_\beta}$ acetylide
								107.6 (qnt) $^2J_{\mathrm{CP}} = 20$	$\mathrm{C_\alpha}$ acetylide
								53.0 (t)	$\mathrm{PO}C\mathrm{H_3}$
2b	$\mathrm{RuCl(4\text{-}MeC_6H_4C{\equiv}C)[P(OMe_3]_4}$	2096s	ν(C≡C)	3.85 (t, br) [f]	$\mathrm{POC}H_3$	$\mathrm{A_4}$	136.1 (s) [f]		
				2.16 (s)	$\mathrm{4\text{-}C}H_3\mathrm{C_6H_4}$				
2c	$\mathrm{RuCl(1,4\text{-}C{\equiv}CC_6H_4C{\equiv}CH)[P(OMe)_3]_4}$	3250m	ν(CH)	3.82 (t) [g]	$\mathrm{POC}H_3$	$\mathrm{A_4}$	136.1 (s) [g]		
		2084s	ν(C≡C)	3.01 (s)	$\equiv\mathrm{C}H$				
		2039w	ν(C≡CH)						
3-PF$_6$	$\mathrm{[\{Ru[P(OEt)_3]_5\}_2(\mu\text{-}1,4\text{-}C{\equiv}CC_6H_4C{\equiv}C)](PF_6)_2}$	2103s	ν(C≡C)	4.18 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{AB_4}$	δ_A 129.7	126.3 (m, br)	$\mathrm{C_\beta}$ acetylide
				4.01 (m)			δ_B 126.1	113.5 (m)	$\mathrm{C_\alpha}$ acetylide
				1.29 (t)	$\mathrm{POCH_2C}H_3$		$J_{\mathrm{AB}} = 53.5$	62.6 (s, br)	$\mathrm{PO}C\mathrm{H_2CH_3}$
				1.26 (t)				61.6 (s, br)	
								16.3 (s)	$\mathrm{POCH_2}C\mathrm{H_3}$

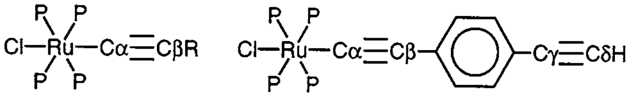
Table 1 (continued)

3-BPh$_4$	[{Ru[P(OEt)$_3$]$_5$}$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C)] (BPh$_4$)$_2$	2098s	ν(C≡C)	4.18 (m)	POCH_2CH$_3$	AB$_4$	δ_A 130.4		
				4.00 (m)			δ_B 126.5		
				1.29 (t)	POCH$_2$CH_3		$J_{AB} = 53.5$		
				1.26 (t)					
4	Ru(1,4-C≡CC$_6$H$_4$C≡CH)$_2$[P(OEt)$_3$]$_4$	3275m	ν(CH)	4.30 (m)	POCH_2CH$_3$	A$_4$	136.6 (s)	124.3 (qnt) $^2J_{CP} = 20$	C$_\alpha$ acetylide
		2070s	ν(C≡C)	3.08 (s)	≡CH			114.6 (qnt, br)	C$_\beta$ acetylide
		2034m	ν(C≡CH)	1.21 (t)	POCH$_2$CH_3			84.9 (s)	C$_\gamma$ acetylide
								76.9 (s)	C$_\delta$ acetylide
								61.3 (s)	POCH$_2$CH$_3$
								16.5 (s)	POCH$_2$$CH_3$
5	Ru(1,4-C≡CC$_6$H$_4$C≡CH)$_2$[P(OMe)$_3$]$_4$	3273m	ν(CH)	3.83 (t)	POCH_3	A$_4$	114.8 (s)		
		2073s	ν(C≡C)	3.14 (s)	≡CH				
		2030m	ν(C≡CH)						
6	Ru(1,4-C≡CC$_6$H$_4$C≡CH)$_2$[PPh(OEt)$_2$]$_4$	3289m	ν(CH)	4.15 (m)	POCH_2CH$_3$	A$_4$	152.8 (s)		
		2064m	ν(C≡C)	3.68 (m)					
		2030sh	ν(C≡CH)	3.16 (s)	≡CH				
				1.14 (m)	POCH$_2$CH_3				
7a	[RuCl{=C=C(H)Ph}{P(OEt)$_3$}$_4$]CF$_3$SO$_3$	1653m (br)	ν(C=C)	5.00 (qnt) $J_{PH} = 3$	=CH	A$_4$	112.0 (s)		
				4.25 (m)	POCH_2CH$_3$				
				1.32 (t)	POCH$_2$CH_3				
7a-BF$_4$	[RuCl{=C=C(H)Ph}{P(OEt)$_3$}$_4$]BF$_4$	1663m (br)	ν(C=C)	4.98 (qnt) $J_{PH} = 3$	=CH	A$_4$	112.0 (s)	364.5 (qnt) $^2J_{CP} = 18$	C$_\alpha$ vinylidene
				4.22 (m)	POCH_2CH$_3$			109.6 (qnt) $^3J_{CP} = 2$	C$_\beta$ vinylidene
				1.30 (t)	POCH$_2$CH_3			63.8 (s)	POCH$_2$CH$_3$
								16.2 (s)	POCH$_2$$CH_3$
7b	[RuCl{=C=C(H)4-MeC$_6$H$_4$}{P(OEt)$_3$}$_4$] CF$_3$SO$_3$	1663m	ν(C=C)	4.95 (qnt) $J_{PH} = 3$	=CH	A$_4$	112.2 (s)	366.1 (qnt) $^2J_{CP} = 18$	C$_\alpha$ vinylidene
				4.23 (m)	POCH_2CH$_3$			109.5 (qnt) $^3J_{CP} = 2$	C$_\beta$ vinylidene
				2.33 (s)	4-CH_3C$_6$H$_4$			63.8 (s)	POCH$_2$CH$_3$
				1.30 (t)	POCH$_2$CH_3			21.12 (s)	4-CH$_3$C$_6$H$_4$
								16.2 (s)	POCH$_2$$CH_3$
7c	[RuCl{=C=C(H)1,4-C$_6$H$_4$C≡CH}-{P(OEt)$_3$}$_4$] CF$_3$SO$_3$	3229m	ν(≡CH)	4.97 (qnt) $J_{PH} = 3$	=CH	A$_4$	111.3 (s)	363.5 (qnt) $^2J_{CP} = 18$	C$_\alpha$ vinylidene
		2085vw	ν(C≡C)	4.23 (m)	POCH_2CH$_3$			109.4 (qnt) $^3J_{CP} = 2$	C$_\beta$ vinylidene
		1653m	ν(C=C)	3.14 (s)	≡CH			83.7 (s)	C$_\gamma$ vinylidene
				1.31 (t)	POCH$_2$CH_3			77.6 (s)	C$_\delta$ vinylidene
								63.9 (s)	POCH$_2$CH$_3$
								16.2 (s)	POCH$_2$$CH_3$
8a	[RuCl{=C=C(H)Ph}{P(OMe)$_3$}$_4$]CF$_3$SO$_3$	1670m	ν(C=C)	5.17 (qnt) $J_{PH} = 3$	=CH	A$_4$	116.0 (s)	366.2 (qnt) $^2J_{CP} = 18$	C$_\alpha$ vinylidene
				3.86 (t)	POCH_3			109.8 (qnt) $^3J_{CP} = 2$	C$_\beta$ vinylidene
								54.7 (t)	POCH$_3$

Table 1 (continued)

8b	[RuCl{=C=C(H)4-MeC$_6$H$_4$}{P(OMe)$_3$}$_4$] CF$_3$SO$_3$	1672m	ν(C=C)	5.13 (qnt) $J_{PH}=3$	=C*H*	A$_4$	116.2 (s)	369.4 (qnt, br)	C$_\alpha$ vinylidene
				3.85 (m)	POC*H*$_3$			109.6 (qnt)	C$_\beta$ vinylidene
				2.13 (s)	4-C*H*$_3$C$_6$H$_4$			54.6 (t)	POCH$_3$
								15.2 (s)	4-CH$_3$C$_6$H$_4$
8c	[RuCl{=C=C(H)1,4-C$_6$H$_4$C≡CH} -{P(OMe)$_3$}$_4$]CF$_3$SO$_3$	3242m	ν(≡CH)	5.17 (qnt) $J_{PH}=3$	=C*H*	A$_4$	115.4 (s)		
		2062vw	ν(C≡C)	3.86 (t)	POC*H*$_3$				
		1657m	ν(C=C)	3.14 (s)	≡C*H*				

[a] In KBr pellets.
[b] In CD$_2$Cl$_2$ at 25°C.
[c] Phenyl proton resonances are omitted.
[d] Positive shift downfield from 85% H$_3$PO$_4$.
[e] Phenyl carbon resonances are omitted.
[f] In C$_6$D$_6$.
[g] In (CD$_3$)$_2$CO.



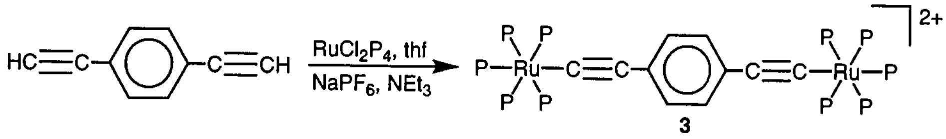
Scheme 2.

The easy synthesis of new mono-acetylides with P(OEt)$_3$ and P(OMe)$_3$ ligands prompted us to extend our study to include other phosphites such as PPh(OEt)$_2$, but in this case treatment of RuCl$_2$[PPh(OEt)$_2$]$_4$ with alkyne affords exclusively the bis(acetylide) [9b] Ru(C≡CR)$_2$P$_4$ derivative in every set of conditions. The influence of the phosphine ligand in determining the reaction course or the stability of the final acetylide complex seems to be crucial in the reaction of RuCl$_2$P$_4$ complexes with alkyne, as shown by our results and by others involving bidentate phosphine ligands [8b,c,16].

3.2. Preparation of dinuclear acetylide complexes

The synthesis of a RuC≡CC$_6$H$_4$C≡CRu unit was attempted by reacting the RuCl(1,4-C≡CC$_6$H$_4$C≡CH)P$_4$ **1c**, **2c** species with an equimolar amount of RuCl$_2$P$_4$ in the presence of NEt$_3$, according to the results obtained in the preparation of mono-acetylide complexes **1**, **2**. Unfortunately, this approach failed, and only an intractable mixture of products was obtained. We therefore reacted the 1,4-diethynylbenzene with two equivalents of RuCl$_2$[P(OEt)$_3$]$_4$ in the presence of NEt$_3$ and also NaPF$_6$ in THF, and obtained a red–orange solution from which, after work-up, an orange microcrystalline solid was separated in relatively low yield (≥ 30%) (Scheme 3).

Analytical, spectroscopic and conductivity data suggest a dinuclear complex of type **3**, containing two pentakis(phosphite)RuP$_5$ fragments bonded by a –C≡CC$_6$H$_4$C≡C– bridging unit. The formation of [{RuP$_5$}$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C)](PF$_6$)$_2$ (**3**-**PF$_6$**) complexes instead of the expected [RuClP$_4$]$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C) was surprising, and may be explained on the basis of the formation of free phosphite, due to some decomposition, which substitutes the Cl ligand and affords the final pentakis-complex. This dinuclear species **3** was also obtained as BPh$_4$ salt (**3**-BPh$_4$), and both PF$_6^-$ and BPh$_4^-$ compounds are air-stable solids soluble in polar organic solvents, in which they behave as 1:2 electrolytes [17]. The IR spectra show only one ν(C≡C) band at 2103 (**3**-**PF$_6$**) and at 2098 cm^{-1}(**3**-BPh$_4$) of the diacetylide ligand. Its presence is confirmed by the ^{13}C spectra, which show the C$_\alpha$ and C$_\beta$ carbon atom signals as multiplets at 113.5 and at 126.3 ppm, respectively (Table 1). In the spectra, the signals at 84.9 and 77.0 ppm (singlets) observed in the mononuclear complex **1c** and attributed to the C$_\gamma$ and C$_\delta$ carbon atoms of the diacetylide ligand are absent. The ^{31}P spectra show AB$_4$ multiplets, which may be



Scheme 3. P = P(OEt)$_3$.

simulated with the parameters reported in Table 1 and confirm the proposed formulation (see Fig. 1 for the ^{31}P spectrum of **3**-PF$_6$).

These dinuclear complexes [{RuP$_5$}$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C)](BPh$_4$)$_2$ (**3**) containing the pentakis RuP$_5$ fragment cannot be used to obtain polynuclear complexes, owing to the reluctance of the phosphites to be substituted by other ligands (acetylide), making **3** practically unreactive towards 1,4-diethynylbenzene. We therefore prepared bis(acetylide) complexes *trans*-Ru(1,4-C≡CC$_6$H$_4$C≡CH)$_2$P$_4$ **4–6** with the aim of using them to prepare polynuclear complexes. The acetylide compounds were prepared by reacting dichloro complexes RuCl$_2$P$_4$ with lithium acetylide, as shown in Scheme 4.

The complexes are air-stable solids, characterised in the usual way by analytical and IR and NMR data (Table 1). The mutually *trans* position of the two acetylide ligands is confirmed by the ^{31}P spectra, which appear as sharp singlets for all derivatives **4–6**. The IR spectra show only one ν(C≡C) band at 2073–2064 cm^{-1} and one ν(C≡CH) band at 2034–2030 cm^{-1} of the C≡CC$_6$H$_4$C≡CH acetylide ligand. The medium intensity band of ν(CH) is also present at 3289–3273 cm^{-1}. In the ^{13}C-NMR spectra of **4**, the C$_\alpha$ and C$_\beta$ of the C≡CC$_6$H$_4$C≡CH group appear as quintets at 124.3 ($^2J_{CP}$ = 20 Hz) and 114.6, respectively, due to the coupling of four equivalent phosphorus *nuclei*, while the C$_\gamma$ and C$_\delta$ appear as singlets at 84.9 and 76.9 ppm.

Bis(acetylide) complexes **4–6** were reacted with RuCl$_2$P$_4$, in an attempt to obtain a trinuclear derivative of the type Cl–Ru–Ru–Ru–Cl or polynuclear ones containing the diacetylide C≡CC$_6$H$_4$C≡C as bridging unit. Unfortunately, although the reaction was carried out in various conditions, changing the experimental set-up and the ratio between the reagents, only untractable mixtures of products were obtained and the reaction was not investigated further.

3.3. Vinylidene derivatives

Arylacetylide RuCl(C≡CR)P$_4$ **1a–b**, **2a–b** complexes react with CF$_3$SO$_3$H or HBF$_4$·Et$_2$O to give vinylidene derivatives [RuCl{=C=C(H)R}P$_4$]$^+$ **7**, **8**, which were isolated as CF$_3$SO$_3^-$ or BF$_4^-$ salts and characterised (Scheme 5). The reaction also proceeds with 1,4-diethynylbenzene derivatives **1c**, **2c**, giving the corresponding complexes **7c**, **8c** containing an alkyne–vinylidene ligand. Instead, alkynyls RuCl(C≡CR)P$_4$ **1d–1f** containing an alkyl-substituent,

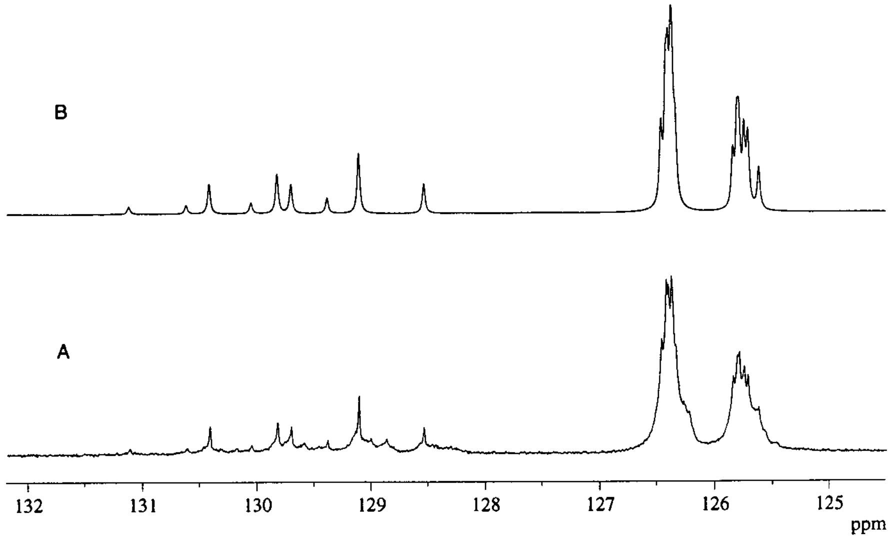
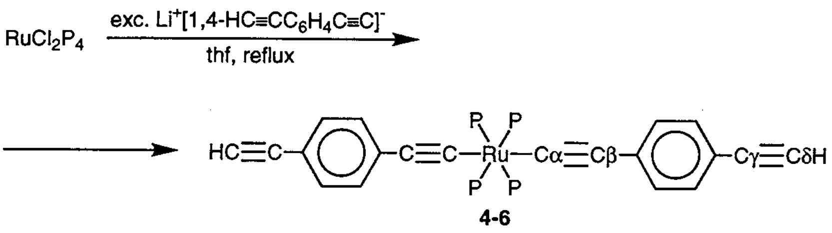
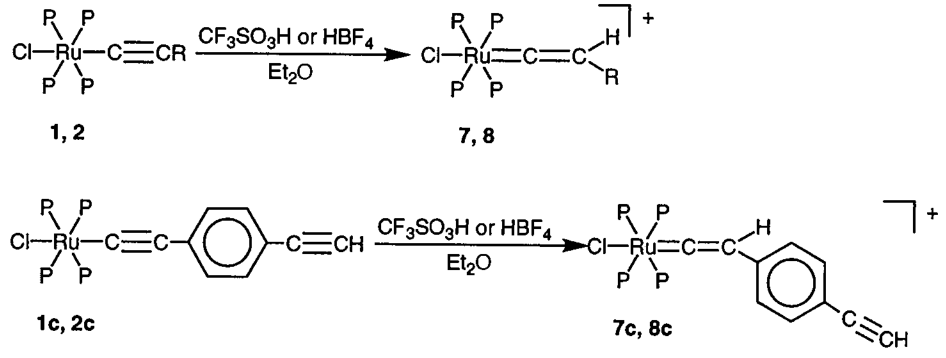


Fig. 1. Observed (A) and calculated (B) ^{31}P{^{1}H}-NMR spectra of the compound [{Ru[P(OEt)$_3$]$_5$}$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C)](PF$_6$)$_2$ (**3**-PF$_6$) in CD$_2$Cl$_2$ at 25°C. The simulated spectrum was obtained with the parameters reported in Table 1.



Scheme 4. P = P(OEt)$_3$ (**4**), P(OMe)$_3$ (**5**) or PPh(OEt)$_2$ (**6**).



Scheme 5. P = P(OEt)$_3$ (**7**) or P(OMe)$_3$ (**8**); R = Ph (**a**), 4-MeC$_6$H$_4$ (**b**) or 1,4-C$_6$H$_4$C≡CH (**c**).

react with HBF_4 or CF_3SO_3H at low temperature to give the corresponding vinylidene complexes which, however, are unstable over −10°C (by NMR) and cannot be isolated in the solid state.

The new vinylidene complexes **7**, **8** are pink solids stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes [17]. Their characterisation is supported by analytical and spectroscopic data, reported in Table 1. In particular, the IR spectra show the characteristic one or two medium-intensity bands ν(C=C) of the vinylidene ligand at 1672–1653 cm^{-1}. In the spectra of alkyne–vinylidene complexes **7c**, **8c**, ν(C≡C) absorptions at 2085–2062 and ν(≡CH) bands at 3242–3229 cm^{-1} are also present. The ^{1}H-NMR spectra show the vinyl proton of the =C=C(H)R ligand in **7**, **8** as a quintet at 5.17–4.95 ppm, due to the coupling to four equivalent P nuclei of the phosphite ligands. In the spectra of **7c** and **8c**, containing the =C=C(H)1,4-C$_6$H$_4$C≡CH group, the signal of the ≡CH proton is also present as a singlet at 3.14 ppm. However, strong support for the formulation of complexes **7**, **8** as vinylidene comes from the ^{13}C{^{1}H}-NMR spectra, which show the characteristic Ru=C=carbene carbon resonances as quintets at 369–363 ppm, with a $^2J_{CP}$ value of 18.0 Hz, and the vinylic carbon resonances =C(H)R as quintets near 109 ppm, with $^3J_{CP}$ of 2–3 Hz. Furthermore, in the ^{13}C spectra of the [RuCl{=C=C(H)1,4-C$_6$H$_4$C≡CH}P$_4$]$^+$ cation **7c** (Fig. 2), the signals of C$_\gamma$ and C$_\delta$ acetylide carbon atoms are also observed as singlets at 83.7 and 77.6 ppm, in agreement with the formulation proposed. Lastly, a *trans* geometry for all the vinylidene complexes in solution may be proposed, on the basis of the sharp singlet appearing in the ^{31}P{^{1}H}-NMR spectra.

Acetylide complexes RuCl(C≡CR)P$_4$ also react with other electrophilies reagents such as $CF_3SO_3CH_3$, I_2, ArN_2^+, but in this case no stable vinylidene complexes were obtained. The reactivity of dinuclear [{RuP$_5$}$_2$(μ-1,4-C≡CC$_6$H$_4$C≡C)]$^{2+}$ **3** cations and bis(acetylide) Ru(1,4-C≡CC$_6$H$_4$C≡CH)$_2$P$_4$ **4**–**6** was also tested with electrophilies (H$^+$, CH_3^+, etc.), but whereas dinuclear **3** is unreactive towards protonation reactions, the bis(acetylide) afforded an oily mixture of products which were not characterised.

Vinylidene complexes **7**, **8** may easily be deprotonated with base (NEt$_3$) to give the starting acetylide RuCl(C≡CR)P$_4$ derivatives (Eq. (1)).

$$[\mathrm{RuCl\{{=}C{=}C(H)R\}P_4}]^+ + \mathrm{NEt_3}$$
$$\rightarrow [\mathrm{RuCl(C{\equiv}CR)P_4}] + \mathrm{NHEt_3^+} \qquad (1)$$

Instead, the substitution reactions of the vinylidene ligands are very slow in **7**, **8**, and the complexes turn out to be quite robust in solution. This contrasts with the properties shown by the comparable [Ru(C≡CR){=C=C(H)R}P$_4$]$^+$ derivatives, previously reported by us [9b], which showed the vinylidene to be a labile ligand, easily replaceable by CO, phosphite, nitrile and isocyanide. Instead, similar behaviour of our vinylidenes **7**, **8** and of the known

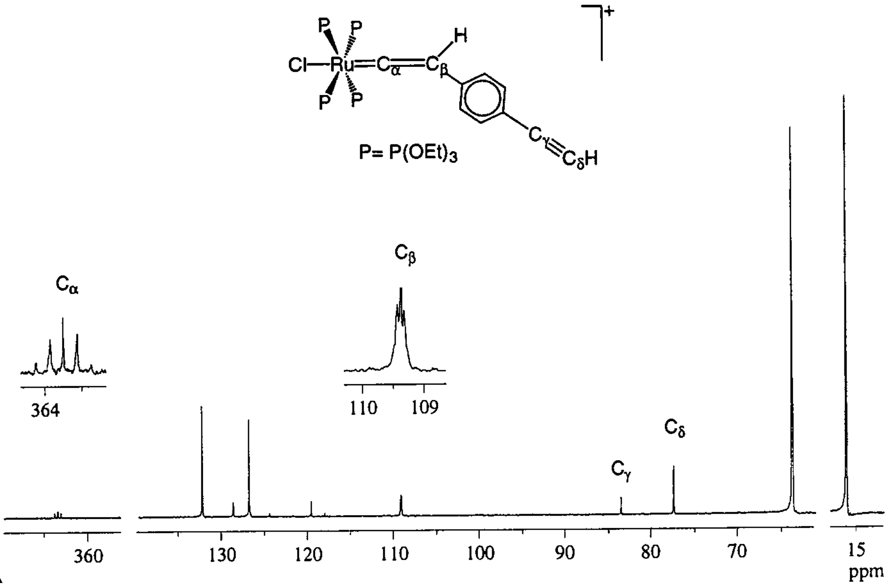


Fig. 2. $^{13}C\{^1H\}$-NMR spectrum of the compound [RuCl{=C=C(H)(1,4-$C_6H_4C{\equiv}CH$)}{$P(OEt)_3$}$_4$]CF_3SO_3 (**7c**) in CD_2Cl_2 at 25°C.

[Ru(C≡CR){=C=C(H)R}P_4]$^+$ derivatives was observed in the reaction towards amines or alcohols to give carbene complexes. In both cases, the same unreactivity was observed, and only decomposition took place over a long reaction time in both types of vinylidene derivatives.

4. Conclusions

The present investigations show that the use of monodentate phosphite as ancillary ligand allows the preparation of new monoacetylide RuCl(C≡CR)P_4 derivatives, including 1,4-diethynylbenzene as an alkyne. Dinuclear complexes [{RuP_5}$_2$(μ-1,4-C≡CC_6H_4-C≡C)]$(PF_6)_2$ and bis(alkynyl) Ru(1,4-C≡CC_6H_4C≡CH)$_2P_4$ derivatives were also synthesised. Among the properties shown by the monoacetylides, we emphasise the fact that protonation reactions are easy, yielding new stable vinylidene [RuCl{=C=C(H)R}P_4]CF_3SO_3 complexes.

Acknowledgements

This work was supported by the Ministero della Ricerca Scientifica e Tecnologica (MURST), Rome. We thank Dr Giuseppe Balacco (Menarini Ricerche S.p.A.) for permission to use his SwaN-MR software. We also thank Daniela Baldan for technical assistance.

References

[1] (a) C.S. Yi, N. Liu, A.L. Rheingold, L.M. Liable-Sands, Organometallics 16 (1997) 3910. (b) C.S. Yi, N.H. Liu, Organometallics 15 (1996) 3968. (c) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, P. Frediani, Organometallics 15 (1996) 272. (d) H. Matsuzaka, Y. Takagi, Y. Ishii, M. Nishio, M. Hidai, Organometallics 14 (1995) 2153. (e) J.F. Corrigan, N.J. Taylor, A.J. Carty, Organometallics 13 (1994) 3778. (f) Y. Kishimoto, P. Eckerle, T. Miyatake, R. Noyori, J. Am. Chem. Soc. 116 (1994) 12131. (g) M. Schäfer, N. Mahr, J. Wolf, H. Werner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1315. (h) D.L. Hughes, M. Jiménez-Tenorio, G.J. Leigh, A.T. Rowley, J. Chem. Soc. Dalton Trans. (1993) 3151. (i) L.D. Field, A.V. George, G.R. Purches, I.H.M. Slip, Organometallics 11 (1992) 3019. (j) A.K. McMullen, J.P. Selegue, J.-G. Wang, Organometallics 10 (1991) 3421.

[2] (a) C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi, Organometallics 15 (1996) 3804. (b) D. Pilette, K. Ouzzine, H. Le Bozec, P.H. Dixneuf, C.E.F. Richard, W.R. Roper, Organometallics 11 (1992) 809.

[3] (a) D. Touchard, S. Guesmi, M. Bouchaib, P. Haquette, A. Daridor, P.H. Dixneuf, Organometallics 15 (1996) 2579. (b) V. Cadierno, M.P. Gamasa, J. Gimeno, M. Gonzalez-Cueva, E. Lastra, J. Borge, S. García-Granda, E. Pérez-Carreño, Organometallics 25 (1996) 2137. (c) G. Roth, H. Fischer, Organometallics 15 (1996) 1139. (d) M.I. Bruce, P. Hinterding, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1996) 1009. (e) M. Martín, O. Gevert, H. Werner, J. Chem. Soc. Dalton Trans. (1996) 2275. (f) D. Touchard, N. Pirio, P.H. Dixneuf, Organometallics 14 (1995) 4920. (g) R. Aumann, B. Jasper, R. Fröhlich, Organometallics 14 (1995) 3173.

[4] (a) M.A. Esteruelas, A.V. Gómez, A.M. López, J. Modrego, E. Oñate, Organometallics 16 (1997) 5826. (b) C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 16

(1997) 2768. (c) V. Cadierno, M.P. Gamasa, J. Gimeno, M.C. López-González, J. Borge, J. García-Granda, Organometallics 16 (1997) 4453. (d) B.M. Trost, J.A. Flygare, J. Am. Chem. Soc. 114 (1992) 5476. (e) A.K. McMullen, J.P. Selegue, J.G. Wang, Organometallics 10 (1991) 3421. (f) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J.Y. Satoh, J. Am. Chem. Soc. 113 (1991) 9604.

[5] (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 291. (b) C. Dhenaut, I. Ledoux, D.W. Samuel, J. Zyss, M. Bourgault, H. Le Bozec, Nature 374 (1995) 339. (c) N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21. (d) S.R. Marder, Inorganic Materials, in: D.W. Bruce, D. O'Hare (Eds.), Wiley, Chichester, UK, 1992, p. 115.

[6] (a) S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, J. Chem. Soc. Chem. Commun. (1984) 3. (b) A.A. Dembek, R.R. Burch, A.E. Feiring, J. Am. Chem. Soc. 115 (1993) 2087. (c) M. Altmann, U.H.F. Bunz, Angew. Chem. Int. Ed. Engl. 34 (1995) 569. (d) M. Altmann, V. Enkelmann, G. Lieser, U.H.F. Bunz, Adv. Mater. 7 (1995) 726. (e) L. Oriol, J.L. Serrano, Adv. Mater. 7 (1995) 248.

[7] (a) J.L. Seesler, B. Wang, A. Harriman, J. Am. Chem. Soc. 117 (1995) 704. (b) A. Harriman, F. Odobel, J.-P. Sauvage, J. Am. Chem. Soc. 117 (1995) 9461. (c) P. Belser, R. Dux, M. Baak, L. De Cola, V. Balzani, Angew. Chem. Int. Ed. Engl. 34 (1995) 595. (d) V. Grosshenny, A. Harriman, R. Ziessel, Angew. Chem. Int. Ed. Engl. 34 (1995) 1100. (e) E.C. Constable, Angew. Chem. Int. Ed. Engl. 30 (1991) 407.

[8] (a) D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, Organometallics 17 (1998) 3844. (b) I. de los Rios, M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 17 (1998) 3356. (c) M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, Organometallics 17 (1998) 3034. (d) M.A. Esteruelas, A.V. Gómez, A.M. López, E. Oñate, N. Ruiz, Organometallics 17 (1998) 2297. (e) K.J. Harlow, A.F. Hill, T. Welton, A.J.P. White, D.J. Williams, Organometallics 17 (1998) 1916. (f) L.-K. Liu, K.-Y. Chang, Y.-S. Wen, J. Chem. Soc. Dalton Trans. (1998) 741. (g) M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1998) 1793. (h) R. Wiedemann, R. Fleischer, D. Stalke, H. Werner, Organometallics 16 (1997) 866. (i) Y. Kawata, M. Sato, Organometallics 16 (1997) 1093. (j) T. Weyland, C. Lapinte, G. Frapper, M.J. Calhorda, J.-F. Halet, L. Toupet, Organometallics 16 (1997) 2024. (k) M. Tamm, T. Jentzsch, W. Werncke, Organometallics 16 (1997) 1418. (l) S.-M. Yang, M.C.-W. Chan, K.-K. Cheung, C.-M. Che, S.-M. Peng, Organometallics 16 (1997) 2819. (m) H.M. Lee, J. Yao, G. Jia, Organometallics 16 (1997) 3927.

[9] (a) G. Albertin, S. Antoniutti, E. Bordignon, J. Organomet. Chem. 513 (1996) 147. (b) G. Albertin, S. Antoniutti, E. Bordignon, F. Cazzaro, S. Ianelli, G. Pelizzi, Organometallics 14 (1995) 4114. (c) G. Albertin, S. Antoniutti, E. Bordignon, E. Del Ministro, S. Ianelli, G. Pelizzi, J. Chem. Soc. Dalton Trans. (1995) 1783. (d) G. Albertin, S. Antoniutti, E. Bordignon, J. Chem. Soc. Dalton Trans. (1995) 719. (e) G. Albertin, S. Antoniutti, E. Del Ministro, E. Bordignon, J. Chem. Soc. Dalton Trans. (1992) 3203. (f) G. Albertin, P. Amendola, S. Antoniutti, S. Ianelli, G. Pelizzi, E. Bordignon, Organometallics 10 (1991) 2876.

[10] R. Rabinowitz, J. Pellon, J. Org. Chem. 26 (1961) 4623.

[11] A.S. Hay, J. Org. Chem. 25 (1960) 637.

[12] G. Balacco, J. Chem. Inf. Comput. Sci. 34 (1994) 1235.

[13] W.G. Peet, D.H. Gerlach, Inorg. Synth. 15 (1974) 38.

[14] J. Silvestre, R. Hoffmann, Helv. Chim. Acta 68 (1985) 1461.

[15] (a) I. de los Rios, M. Jiménez-Tenorio, M. Carmen-Puerta, P. Valerga, J. Chem. Soc. Chem. Commun. (1995) 1757. (b) I. de los Rios, M. Jiménez-Tenorio, M. Carmen-Puerta, P. Valerga, J. Am. Chem. Soc. 119 (1997) 6529.

[16] (a) D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Organometallics 16 (1997) 3640. (b) O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.

[17] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.