

Reactivity of $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ cations with alkynes: preparation of vinylidene and propadienyldiene complexes

Gabriele Albertin *, Stefano Antoniutti, Emilio Bordignon, Davide Bresolin

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

Received 22 November 1999; received in revised form 29 December 1999

Abstract

Treatment of $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ cations with phenylacetylene leads to the displacement of H_2 and the formation of vinylidene $[\text{Re}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{CO})_2\text{P}_3]^+$ (**1–3**) [$\text{P} = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$ or PPh_2OEt] derivatives. Infrared and NMR data support equilibrium in solution $[\text{Re}(\text{CO})_2\text{P}_3]^+ + \text{PhC}\equiv\text{CH} \rightleftharpoons [\text{Re}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{CO})_2\text{P}_3]^+$ involving the unsaturated complex, free alkyne and vinylidene derivative. 1,4-Diethynylbenzene also tautomerises to the Re(I) centre, affording the $[\text{Re}\{\text{C}=\text{C}(\text{H})(1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{CH})\}(\text{CO})_2\text{P}_3]\text{BF}_4$ [$\text{P} = \text{P}(\text{OEt})_3$ or $\text{PPh}(\text{OEt})_2$] vinylidene derivatives. Vinylidene complexes **1–3** are deprotonated easily by NEt_3 to give acetylides $\text{Re}(\text{C}\equiv\text{CR})(\text{CO})_2\text{P}_3$ (**4–6**) ($\text{R} = \text{Ph}$ or $1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$), which may in turn be reprotonated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ to reform vinylidenes **1–3**. Acetylide complexes **4–6** were also prepared by reacting unsaturated cations $[\text{Re}(\text{CO})_2\text{P}_3]^+$ with lithium acetylide. Binuclear complexes $\{\text{Re}(\text{CO})_2\text{P}_3\}_2(\mu\text{-}1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})$ (**7, 8**) [$\text{P} = \text{PPh}(\text{OEt})_2$ or PPh_2OEt] were obtained by sequential treatment of $[\text{Re}(\text{CO})_2\text{P}_3]^+$ cations, first with $1,4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$ and then with an excess of NEt_3 . Propadienyldiene complexes $[\text{Re}(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})_2\text{P}_3]\text{BF}_4$ (**9, 10**) [$\text{P} = \text{PPh}(\text{OEt})_2$ or PPh_2OEt] were prepared by allowing $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ cations or unsaturated species $[\text{Re}(\text{CO})_2\text{P}_3]^+$ to react with $\text{HC}\equiv\text{CC}(\text{Ph}_2)\text{OH}$ at room temperature. The characterisation of all new complexes by IR and ^1H -, $^{31}\text{P}\{^1\text{H}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra is also discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium; Hydride; Vinylidene; Acetylide; Propadienyldiene

1. Introduction

Transition metal complexes containing a Π -conjugated unsaturated chain continue to attract interest from both fundamental and applied viewpoints. Some of these complexes have potentially useful material properties [1], while others are probably intermediate in the coupling of alkynes to give enynes or butatrienes [2], in synthesis of unsaturated carbene complexes [3] and in other C–C coupling reactions [4]. Several studies have been reported on vinylidene complexes [5,6] $\text{M}=\text{C}=\text{CR}_2$, which constitute the simplest of these systems, but the next highest member, propadienyldiene, is also receiving increased attention, and numerous metal complexes have been prepared recently [7]. These complexes, however, do not include rhenium as the central metal, although its organometallic chemistry has in-

creased greatly in the past few years [8]. Acetylides and binuclear complexes with linear carbon chains C_n ($n = 2\text{--}5$) as bridging ligands are among the most interesting results [9] in the organometallic chemistry of rhenium, as well as the use of Re complexes in metal-assisted catalytic reactions such as alkyne metathesis [10], epoxydation of olefins [11] and alkane dehydrogenation [12]. However, the chemistry of metal–carbon single and multiple bonds of rhenium is mainly based on the cyclopentadienyl ligand [5a,8,9,13], and only recently [3a,14] have vinylidene and other carbene complexes bonded to a Re fragment not containing the Cp ligand been reported.

In a previous paper [15] we described the synthesis of $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_{5-n}\text{P}_n]^+$ ($n = 2, 3$ or 4 ; $\text{P} = \text{phosphites}$) and of the related unsaturated complexes $[\text{Re}(\text{CO})_{5-n}\text{P}_n]^+$, which turned out to be good precursors for some reactions. As an extension of our studies on the chemistry of acetylide and vinylidene complexes [16], we have now begun systematic investigation of the

* Corresponding author. Tel.: +39-041-2578555.

E-mail address: albertin@unive.it (G. Albertin).

reactivity of these $\eta^2\text{-H}_2$ rhenium complexes with terminal alkynes, which allowed new vinylidene and the first example of propadienyldiene complexes of rhenium to be prepared. Results are reported here.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an appropriate atmosphere (argon or H_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. Phosphines $\text{PPh}(\text{OEt})_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon [17]; triethylphosphite was an Aldrich product, purified by distillation under nitrogen. Alkynes $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}$, Bu' , $4\text{-MeC}_6\text{H}_4$, COOMe or COOEt) and $\text{HC}\equiv\text{CC}(\text{OH})\text{RR}'$ ($\text{R} = \text{Ph}$; $\text{R}' = \text{Ph}$, H or CH_3) were Aldrich products, used without further purification. Lithium phenylacetylide $\text{Li}^+\text{PhC}\equiv\text{C}^-$ was prepared by reacting a slight excess of phenylacetylene (40 mmol, 4.4 cm^3) with lithium (35 mmol, 0.24 g) in 10 cm^3 of tetrahydrofuran (THF). 1,4-Diethynylbenzene was prepared following the method reported previously [18]. The related lithium acetylide $\text{Li}^+[1,4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}]^-$ 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 then kept under argon. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared 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 between -90 and $+30^\circ\text{C}$, unless otherwise stated. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are referred to internal tetramethylsilane; $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive. The SWAN-MR software package [19] was used to treat NMR data. The conductivity of $10^{-3}\text{ mol dm}^{-3}$ solutions of the complexes in MeNO_2 at 25°C was measured with a radiometer CDM 83 instrument.

2.2. Synthesis of complexes

Hydrides $\text{ReH}(\text{CO})_2\text{P}_3$ and unsaturated complexes $[\text{Re}(\text{CO})_2\text{P}_3]\text{BPh}_4$ [$\text{P} = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$ or PPh_2OEt] were prepared according to the reported method [15].

2.2.1. $[\text{Re}\{\text{C}\equiv\text{C}(\text{H})\text{Ph}\}(\text{CO})_2\text{P}_3]\text{BF}_4$ (**1a–3a**)

$[\text{P} = \text{P}(\text{OEt})_3$ (**1a**), $\text{PPh}(\text{OEt})_2$ (**2a**) or PPh_2OEt (**3a**)]

To a solution of the acetylide complex $\text{Re}(\text{C}\equiv\text{CPh})\text{-(CO)}_2\text{P}_3$ (0.1 mmol) in 5 cm^3 of diethylether cooled to -80°C was added a slight excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.11 mmol, 16 μl) and the reaction mixture, brought to room temperature (r.t.), was stirred for 3 h. A red–orange solid separated out slowly, which was filtered and dried under vacuum; yield $\geq 80\%$.

Anal. Calc. for $\text{C}_{28}\text{H}_{51}\text{BF}_4\text{O}_{11}\text{P}_3\text{Re}$ (**1a**): C, 36.18; H, 5.53. Found: C, 36.02; H, 5.58%. $\Lambda_{\text{M}} = 84.8\text{ S cm}^2\text{ mol}^{-1}$.

Anal. Calc. for $\text{C}_{40}\text{H}_{51}\text{BF}_4\text{O}_8\text{P}_3\text{Re}$ (**2a**): C, 46.84; H, 5.01. Found: C, 46.63; H, 5.08%. $\Lambda_{\text{M}} = 85.5\text{ S cm}^2\text{ mol}^{-1}$.

Anal. Calc. for $\text{C}_{52}\text{H}_{51}\text{BF}_4\text{O}_5\text{P}_3\text{Re}$ (**3a**): C, 55.67; H, 4.58. Found: C, 55.81; H, 4.64%. $\Lambda_{\text{M}} = 85.9\text{ S cm}^2\text{ mol}^{-1}$.

The complexes may also be prepared by treating $\text{ReH}(\text{CO})_2\text{P}_3$ (0.1 mmol) with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.11 mmol, 16 μl) in CH_2Cl_2 (5 cm^3) and then with an excess of $\text{PhC}\equiv\text{CH}$ (0.3 mmol, 26 μl). Removal of the solvent under reduced pressure and treatment with ethanol (2 cm^3) gives a red solid or a red oil which, however, turns out to be a mixture also containing the unsaturated $[\text{Re}(\text{CO})_2\text{P}_3]\text{BF}_4$ compound.

2.2.2. $[\text{Re}\{\text{C}\equiv\text{C}(\text{H})(1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{CH})\}(\text{CO})_2\text{P}_3]\text{BF}_4$ (**1c–2c**) [$\text{P} = \text{P}(\text{OEt})_3$ (**1c**) or $\text{PPh}(\text{OEt})_2$ (**2c**)]

A slight excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.11 mmol, 16 μl) was added to a solution of the acetylide complex $\text{Re}(1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})(\text{CO})_2\text{P}_3$ in 5 cm^3 of diethylether cooled to -80°C . The reaction mixture was brought to r.t. and stirred vigorously until a dark-green solid separated out, which was filtered and dried under vacuum; yield $\geq 40\%$.

Anal. Calc. for $\text{C}_{30}\text{H}_{51}\text{BF}_4\text{O}_{11}\text{P}_3\text{Re}$ (**1c**): C, 37.78; H, 5.39. Found: C, 37.62; H, 5.47%. $\Lambda_{\text{M}} = 85.3\text{ S cm}^2\text{ mol}^{-1}$.

Anal. Calc. for $\text{C}_{42}\text{H}_{51}\text{BF}_4\text{O}_8\text{P}_3\text{Re}$ (**2c**): C, 48.05; H, 4.90. Found: C, 48.19; H, 4.95%. $\Lambda_{\text{M}} = 84.5\text{ S cm}^2\text{ mol}^{-1}$.

2.2.3. $\text{Re}(\text{C}\equiv\text{CPh})(\text{CO})_2\text{P}_3$ (**4a–6a**) [$\text{P} = \text{P}(\text{OEt})_3$ (**4a**), $\text{PPh}(\text{OEt})_2$ (**5a**) or PPh_2OEt (**6a**)]

The complexes may be prepared following two different methods.

1. A slight excess of $\text{CF}_3\text{SO}_3\text{H}$ (0.66 mmol, 58 μl) was added to a solution of $\text{ReH}(\text{CO})_3\text{P}_2$ (0.6 mmol) in 10 cm^3 of CH_2Cl_2 cooled to -80°C . The reaction mixture was brought to r.t., stirred for 1 h, and an excess of $\text{Li}[\text{PhC}\equiv\text{C}]$ added (0.75 mmol, 0.31 cm^3 of a 2.44 mol dm^{-3} solution in THF). After 3 h of stirring, the solvent was removed under reduced pressure, giving an oil which was treated with ethanol (2 cm^3). The resulting solution was stirred vigor-

ously until a pale-yellow solid separated out, which was filtered and dried under vacuum. In the case of **4a**, an oil was obtained, which was chromatographed onto a silica gel column (length 50 cm, diameter 4 cm) using a mixture of light petroleum (b.p. 40–60°C), benzene and diethylether (ratio 10:1:1) as eluent. The first fraction eluted (60 cm³) was evaporated to dryness, giving an oily product which was pure by NMR and elemental analysis.

2. A slight excess of HBF₄·Et₂O (0.11 mmol, 16 µl of a 54% solution in diethylether) was added to a solution of ReH(CO)₃P₂ (0.1 mmol) in 3 cm³ of CH₂Cl₂ cooled to –80°C. The reaction mixture was brought to r.t., stirred for 1 h, and an excess of PhC≡CH (0.3 mmol, 26 µl) added. After 3–4 h of stirring, an excess of NEt₃ (0.3 mmol, 42 µl) was added and stirring was continued for 3 h. The solvent was removed under reduced pressure, giving an oil from which the acetylide complex was extracted with three 2 cm³-portions of benzene. The solvent was evaporated to dryness and the resulting oil triturated with 2 cm³ of ethanol until a pale-yellow solid separated out, which was filtered and dried under vacuum. This method also provided compound **4a** as an oil, which was purified by chromatography. The yield with each of the two methods was about 80%.

Anal. Calc. for C₂₈H₅₀O₁₁P₃Re (**4a**): C, 39.95; H, 5.99. Found: C, 40.11; H, 5.85%.

Anal. Calc. for C₄₀H₅₀O₈P₃Re (**5a**): C, 51.22; H, 5.37. Found: C, 51.08; H, 5.40%.

Anal. Calc. for C₅₂H₅₀O₅P₃Re (**6a**): C, 60.40; H, 4.87. Found: C, 60.22; H, 4.95%.

2.2.4. *Re(C≡CBu')(CO)₂[PPh(OEt)₂]₃* (**5b**)

This complex was prepared like the related phenylacetylide **5a** following method (2) and obtaining the compound as an oil; yield ≥ 70%.

Anal. Calc. for C₃₈H₅₄O₈P₃Re: C, 49.72; H, 5.93. Found: C, 49.88; H, 5.99%.

2.2.5. *Re(1,4-C≡CC₆H₄C≡CH)(CO)₂P₃* (**4c–6c**)

[*P* = *P*(OEt)₃ (**4c**), *P*Ph(OEt)₂ (**5c**) or *P*Ph₂OEt (**6c**)]

A solution of ReH(CO)₂P₃ (0.1 mmol) in 3 cm³ of CH₂Cl₂ cooled to –80°C was treated with a slight excess of HBF₄·Et₂O (0.11 mmol, 16 µl of a 54% solution) and the reaction mixture, brought to r.t., was stirred for 1 h. An excess of 1,4-diethynylbenzene (0.3 mmol, 37.8 mg) in 2 cm³ of CH₂Cl₂ was added and, after 3 h of stirring, an excess of NEt₃ (0.3 mmol, 42 µl) was further added. After 1 h the solvent was removed under reduced pressure, giving a red–brown solid which was chromatographed onto a silica gel column (50 × 4 cm) using a mixture of light petroleum, diethylether and benzene (ratio 8:1:1) as eluent. The first fraction eluted (100 cm³) was evaporated to dryness,

giving an oil which was triturated with ethanol (3 cm³) until an orange solid separated out, which was filtered and dried under vacuum; yield ≥ 65%. Compound **4c** did not solidify, but was found to be pure by NMR and analysis.

Anal. Calc. for C₃₀H₅₀O₁₁P₃Re (**4c**): C, 41.62; H, 5.82. Found: C, 41.48; H, 5.90%.

Anal. Calc. for C₄₂H₅₀O₈P₃Re (**5c**): C, 52.44; H, 5.24. Found: C, 52.58; H, 5.19%.

Anal. Calc. for C₅₄H₅₀O₅P₃Re (**6c**): C, 61.30; H, 4.76. Found: C, 61.18; H, 4.69%.

2.2.6. [*Re*(CO)₂P₃]₂(μ-1,4-C≡CC₆H₄C≡C)] (**7c–8c**)

[*P* = *P*Ph(OEt)₂ (**7c**) or *P*Ph₂OEt (**8c**)]

A slight excess of HBF₄·Et₂O (0.22 mmol, 32 µl) was added to a solution of the appropriate hydride ReH(CO)₂P₃ (0.2 mmol) in 3 cm³ of CH₂Cl₂ cooled to –80°C and the reaction mixture was stirred for 1 h. A solution of 1,4-diethynylbenzene (0.1 mmol, 12.6 mg) in 2 cm³ of CH₂Cl₂ was added and, after 4 h of stirring, an excess of NEt₃ (0.6 mmol, 85 µl) was further added. Stirring of the reaction mixture was continued for about 3 h, and the solvent was then removed under reduced pressure, giving an oil which was chromatographed onto a silica gel column (50 × 4 cm) using a mixture of light petroleum, benzene and diethylether (ratio 8:1:1) as eluent. The first fraction eluted (100 cm³) was evaporated to dryness, giving a red–brown oil which was triturated with ethanol (3 cm³) until an orange solid separated out, which was filtered and dried under vacuum; yield ≥ 60%.

Anal. Calc. for C₇₄H₉₄O₁₆P₆Re₂ (**7c**): C, 49.44; H, 5.27. Found: C, 49.52; H, 5.35%.

Anal. Calc. for C₉₈H₉₄O₁₀P₆Re₂ (**8c**): C, 59.15; H, 4.76. Found: C, 59.32; H, 4.79%.

2.2.7. [*Re*(=C=C=CPh₂)(CO)₂P₃]₂BF₄ (**9–10**)

[*P* = *P*Ph(OEt)₂ (**9**) or *P*Ph₂OEt (**10**)]

To a solution of ReH(CO)₂P₃ (0.1 mmol) in 3 cm³ of CH₂Cl₂ cooled to –80°C was added a slight excess of HBF₄·Et₂O (0.11 mmol, 16 µl) and the reaction mixture, brought to r.t., was stirred for about 1 h. An excess of HC≡CC(Ph₂)OH (0.3 mmol, 62 mg) in 2 cm³ of CH₂Cl₂ was added, and stirring was continued for about 3 h. The solvent was removed under reduced pressure, giving a red–brown oil which was triturated with ethanol (3 cm³) until a purple solid separated out. Cooling of the mixture to 0°C favoured separation of the solid, which was filtered, washed three times with hexane (3 cm³), and crystallised from CH₂Cl₂ (1 cm³) and ethanol (3 cm³); yield ≥ 60%.

Anal. Calc. for C₄₇H₅₅BF₄O₈P₃Re (**9**): C, 50.68; H, 4.98. Found: C, 50.56; H, 5.07%. Λ_M = 86.2 S cm² mol^{–1}.

Anal. Calc. for C₅₉H₅₅BF₄O₅P₃Re (**10**): C, 58.57; H, 4.58. Found: C, 58.79; H, 4.46%. Λ_M = 85.1 S cm² mol^{–1}.

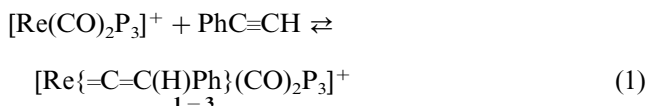
3. Results and discussion

3.1. Vinylidene complexes

The reactions of rhenium dicarbonyl complexes with phenylacetylene are summarised in Scheme 1.

Sequential treatment of hydride $\text{ReH}(\text{CO})_2\text{P}_3$, first with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and then with phenylacetylide, affords the vinylidene $[\text{Re}\{\text{=C=C(H)Ph}\}(\text{CO})_2\text{P}_3]^+$ (**1–3**) cations, as shown in Scheme 1. The reactions proceed via the intermediacy of the $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ cation, which undergoes displacement of the $\eta^2\text{-H}_2$ ligand by $\text{PhC}\equiv\text{CH}$. The latter molecule probably forms Π -adducts and tautomerises to the vinylidene ligand via a 1,2-hydrogen shift, which is the mechanism followed generally by d^6 metal systems [5,6,20,21]. Unfortunately, in our case, no Π -acetylide complex was detected by variable-temperature NMR studies, which showed the presence of the vinylidene complex and $\text{PhC}\equiv\text{CH}$ species only.

Alternatively, vinylidene derivatives **1–3** are also formed by treating the unsaturated complex cations [15] $[\text{Re}(\text{CO})_2\text{P}_3]^+$ with phenylacetylide according to Eq. (1):



Owing to equilibrium Eq. (1), attempts to isolate vinylidene complexes **1–3** in pure form failed, because a crude product also containing the $[\text{Re}(\text{CO})_2\text{P}_3]^+$ starting materials was always obtained. However, analytically pure samples of compounds $[\text{Re}\{\text{=C=C(H)Ph}\}(\text{CO})_2\text{P}_3]\text{BF}_4$ (**1–3**) may be yielded by the protonation with HBF_4 of the acetylide $\text{Re}(\text{C}\equiv\text{CPh})(\text{CO})_2\text{P}_3$ (vide infra). Dissolving these samples of **1–3** in CH_2Cl_2

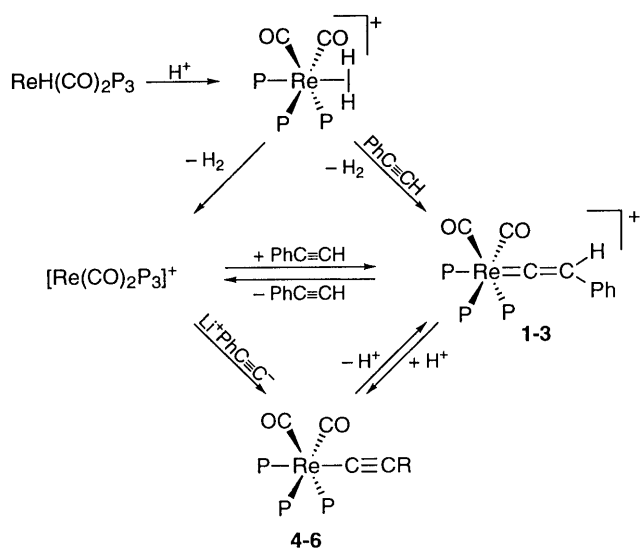
showed equilibrium Eq. (1), forming free alkyne and $[\text{Re}(\text{CO})_2\text{P}_3]^+$ cations. Only the addition of a large excess of $\text{PhC}\equiv\text{CH}$ made the concentration of $[\text{Re}(\text{CO})_2\text{P}_3]^+$ negligible.

Dissociation of a vinylidene complex to give free alkyne and an unsaturated complex, as observed in our case, is rather unexpected, since the previously reported vinylidene complexes **2–6** are very stable and the =C=C(H)R ligand may undergo several reactions but not displacement by other ligands. Only recently has the dissociation of a terminal alkyne from a monosubstituted vinylidene complex been reported [16a,b,c] for $[\text{M}(\text{C}\equiv\text{CR})\{\text{=C=C(H)R}\}\text{P}_4]^+$ ($\text{M} = \text{Fe}, \text{Ru}$), containing phosphite as ancillary ligands. It therefore seems that these phosphite molecules, acting as ancillary ligands, make vinylidene species =C=C(H)Ph rather labile in complexes **1–3**, the dissociation of which gives the free alkyne $\text{PhC}\equiv\text{CH}$, as in Eq. (1).

Diagnostic for the presence of the vinylidene ligand in complexes **1–3** and of the existence of equilibrium (Eq. (1)) in solution are the IR and NMR data reported in Table 1. The IR spectra of $[\text{Re}\{\text{=C=C(H)Ph}\}(\text{CO})_2\text{P}_3]\text{BF}_4$ (**1–3**) derivatives show two $\nu(\text{CO})$ bands at $2056\text{--}1958\text{ cm}^{-1}$, due to two carbonyl ligands in a mutually *cis* position. Furthermore, in the $1660\text{--}1630\text{ cm}^{-1}$ region, the characteristic couple of medium-intensity $\nu(\text{C}=\text{C})$ bands of the vinylidene ligand is present, in agreement with the proposed formulation.

Instead, the IR spectra of samples **1–3** prepared by reacting $[\text{Re}(\text{CO})_2\text{P}_3]^+$ with $\text{PhC}\equiv\text{CH}$ showed invariably not only the $\nu(\text{CO})$ and $\nu(\text{C}=\text{C})$ absorptions but also two other $\nu(\text{CO})$ bands, due to unsaturated $[\text{Re}(\text{CO})_2\text{P}_3]^+$ compounds present in the samples, in agreement with Eq. (1). The establishment of this equilibrium is supported strongly by the NMR data which, in the $^{31}\text{P}\{^1\text{H}\}$ spectra, show two sets of AB_2 multiplets, one due to the $[\text{Re}\{\text{=C=C(H)Ph}\}(\text{CO})_2\text{P}_3]^+$ vinylidene complex and the other to the $[\text{Re}(\text{CO})_2\text{P}_3]^+$ precursor. The addition of a free alkyne decreases the intensity of the $[\text{Re}(\text{CO})_2\text{P}_3]^+$ signals and increases that of the multiplet attributed to the vinylidene, which turns out to be predominant with a fivefold excess of $\text{PhC}\equiv\text{CH}$.

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra confirm this equilibrium and indicate unambiguously the presence of the vinylidene ligand in **1–3**, showing the characteristic highly deshielded $\text{Re}=\text{C}$ carbene carbon resonance at $345\text{--}317\text{ ppm}$, which appears as a doublet of triplets (or a triplet of doublets) due to coupling with AB_2 -type phosphorus nuclei. The spectra also show the signal of the vinyl =C(H)Ph carbon resonance at $119\text{--}116\text{ ppm}$. The resonances of the carbonyl carbon atoms appear at $200\text{--}187\text{ ppm}$ as only one triplet of doublets, in agreement with the equivalence of the two CO ligands. On the basis of the spectroscopic data, we therefore propose a *fac-cis* geometry in solution, as shown in Scheme 1 for our vinylidene complexes **1–3**.



Scheme 1.

Table 1

Infrared and NMR spectroscopic data for rhenium compounds

	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)	Assign	δ	Assign		δ (J Hz)	δ (J Hz)	Assign
1a	[Re{=C=C(H)Ph} (CO) ₂ {P(OEt) ₃ } ₃]BF ₄	2056 m	ν CO	4.56 m	=C(H)	AB ₂	$\delta_A = 106.8$	317.8 td	C $_{\alpha}$
		1965 s		4.10 m	CH ₂		$\delta_B = 105.8$	$J_{CP} = J_{CP} = 13$	
		1660 m	ν C=C	1.37 m	CH ₃		$J_{AB} = 55.5$	193.8 td	CO
		1632 m						$J_{CP} = J_{CP} = 18$	
1c	[Re{=C=C(H) (1,4-C ₆ H ₄ C $\equiv$ CH)} (CO) ₂ {P(OEt) ₃ } ₃]BF ₄	3261 m	ν CH	4.55 m	=C(H)	A ₂ B	$\delta_A = 111.9$	317.0 m, br	C $_{\alpha}$
		2046 m	ν C $\equiv$ C	4.10 m	CH ₂		$\delta_B = 105.8$	187.4 m	CO
		1969 s	ν CO	1.38 m	CH ₃		$J_{AB} = 35$	117.8 m, br	C $_{\beta}$
		1643 m	ν C=C					77.9 s	C $_{\gamma}$
2a	[Re{=C=C(H)Ph} (CO) ₂ {PPh(OEt) ₂ } ₃]BF ₄	2040 s	ν CO	4.00–3.70 m	CH ₂	A ₂ B	$\delta_A = 121.4$	344.9 dt	C $_{\alpha}$
		1958 s		1.35 t	CH ₃		$\delta_B = 127.6$	$J_{CP} = 39$	
		1654 m	ν C=C	1.33 t			$J_{AB} = 27$	$J_{CP} = 11$	
		1630 m		1.31 t				189.8 td	CO
2c	[Re{=C=C(H) (1,4-C ₆ H ₄ C $\equiv$ CH)} (CO) ₂ {PPh(OEt) ₂ } ₃]BF ₄	2051 m	ν C $\equiv$ C	3.89 m	CH ₂	AB ₂	$\delta_A = 128.1$	343.4 m	C $_{\alpha}$
		1959 s	ν CO	2.59 s	$\equiv$ CH		$\delta_B = 122.2$	199.7 td	CO
		1640 m	ν C=C	1.34 t	CH ₃		$J_{AB} = 38$	$J_{CP} = 12$	
				1.30 t				$J_{CP} = 7$	
3a	[Re{=C=C(H)Ph} (CO) ₂ (PPh ₂ OEt) ₃]BF ₄			1.21 t				116.4 m, br	C $_{\beta}$
		2035 s	ν CO	4.22 m	=C(H)	AB ₂	$\delta_A = 104.6$	344.9 dt	C $_{\alpha}$
		1972 s		3.48 m	CH ₂		$\delta_B = 99.4$	$J_{CP} = 10$	
		1656 m	ν C=C	1.04 t	CH ₃		$J_{AB} = 33$	$J_{CP} = 35$	
1637 m		0.92 t			192.1 td		CO		
4a	Re(C $\equiv$ CPh)(CO) ₂ [P(OEt) ₃] ₃							$J_{CP} = J_{CP} = 10$	
								119.2 td	C $_{\beta}$
								$J_{CP} = 1$	
								65.0 t	CH ₂ CH ₃
4c	Re(1,4-C $\equiv$ CC ₆ H ₄ C $\equiv$ CH)(CO) ₂ [P(OEt) ₃] ₃							15.8 t	
		2088 m	ν C $\equiv$ C	4.15 m	CH ₂	A ₂ B	$\delta_A = 117.7$	194.0 dt	CO
		1966 s	ν CO	1.28 t	CH ₃		$\delta_B = 115.9$	$J_{CP} = 10$	
		1889 s					$J_{AB} = 46.1$	$J_{CP} = 80$	
					193.5 td				
4c	Re(1,4-C $\equiv$ CC ₆ H ₄ C $\equiv$ CH)(CO) ₂ [P(OEt) ₃] ₃							$J_{CP} = J_{CP} = 12$	
								114.76 td	C $_{\beta}$
								$J_{CP} = J_{CP} = 3.5$	
								105.9 td	C $_{\alpha}$
4c	Re(1,4-C $\equiv$ CC ₆ H ₄ C $\equiv$ CH)(CO) ₂ [P(OEt) ₃] ₃							$J_{CP} = J_{CP} = 20$	
								61.3 br	CH ₃ CH ₂
								16.5 m	

Table 1 (Continued)

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)	Assign			δ	Assign	δ (J Hz)
5a	Re(C≡CPh)(CO) ₂ [PPh(OEt) ₂] ₃	2086 m	ν C≡C	4.40–3.80 m	CH ₂	AB ₂	$\delta_A = 130.7$	195.6 td	CO
		1970 s	ν CO	1.36 t	CH ₃		$\delta_B = 130.4$	$J_{CP} = J_{CP} = 10$	
		1885 s		1.39 t			$J_{AB} = 34.0$	194.6 dt	
							$J_{CP} = 12$		
							$J_{CP} = 57$		
							115.13 td		C $_{\beta}$
							$J_{CP} = J_{CP} = 3$		
							111.3 td		C $_{\alpha}$
							$J_{CP} = J_{CP} = 18$		
							62.62 t		CH ₂
							62.26 t		
							16.5 m		CH ₃
5b	Re(Bu'C≡C)(CO) ₂ [PPh(OEt) ₂] ₃	2046 m	ν C≡C	4.30–3.60 m ^f	CH ₂	AB ₂	$\delta_A = 135.4$ ^f		
		1968 s	ν CO	1.20 s	CH ₃ Bu'		$\delta_B = 132.4$		
		1867 s		1.17 t	CH ₃ phos		$J_{AB} = 17$		
				1.14 t					
5c	Re(1,4-C≡CC ₆ H ₄ C≡CH)(CO) ₂ [PPh(OEt) ₂] ₃	3280 m	ν CH	4.20–3.60 m	CH ₂	AB ₂	$\delta_A = 134.8$	195.4 td	CO
		2078 s	ν C≡C	3.15 s	≡CH		$\delta_B = 131.9$	$J_{CP} = J_{CP} = 12$	
		2006 m	ν C≡CH	1.33 t	CH ₃		$J_{AB} = 19$	113.9 dt	C $_{\beta}$
		1903 s	ν CO	1.31 t				$J_{CP} = 17$	
								$J_{CP} = 2$	
							107.1 dt		C $_{\alpha}$
							$J_{CP} = 36$		
							$J_{CP} = 16$		C $_{\gamma}$
							84.8 s		C $_{\delta}$
							77.2 s		CH ₂
							62.24 t		
							61.37 d		
							16.4 m		CH ₃
6a	Re(C≡CPh)(CO) ₂ (PPh ₂ OEt) ₃	2083 m	ν C≡C	3.76 m	CH ₂	AB ₂	$\delta_A = 101.7$	197.6 dt	CO
		1944 s	ν CO	3.39 qi			$\delta_B = 99.0$	$J_{CP} = 9.5$	
		1873 s		1.17 t	CH ₃		$J_{AB} = 30$	$J_{CP} = 45$	
				0.99 t				197.0 dt	
								$J_{CP} = 8$	
							$J_{CP} = 20$		
							118.7 td		C $_{\beta}$
							$J_{CP} = J_{CP} = 2$		C $_{\alpha}$
							117.06 td		
							$J_{CP} = J_{CP} = 16$		
							63.1 d		CH ₂
							63.3 t		
							16.20 m		CH ₃
6c	Re(1,4-C≡CC ₆ H ₄ C≡CH)(CO) ₂ (PPh ₂ OEt) ₃	3269 w	ν CH	3.80–3.20 m	CH ₂	AB ₂	$\delta_A = 105.4$	197.3 m	CO
		2082 m	ν C≡C	3.18 s	≡CH		$\delta_B = 101.8$	123.3 td	C $_{\alpha}$
		1999 m	ν C≡CH	3.11 s			$J_{AB} = 18$	$J_{CP} = J_{CP} = 16$	
		1938 m	ν CO	1.14 t	CH ₃		$\delta_A = 101.8$	113.4 dt	
		1892 s		1.07 t			$\delta_B = 99.4$	$J_{CP} = 33$	
		1859 m		0.99 t		$J_{AB} = 30$	$J_{CP} = 16$		
				0.95 t			118.8 br		C $_{\beta}$
							118.5 br		C $_{\gamma}$
							84.80 s		
							84.68 s		C $_{\delta}$
							77.53 s		
							77.16 s		CH ₂
							63.3 t		
							62.8 t		
							62.9 t		CH ₃
							16.3 t		
							16.2 t		
							16.0 t		

Table 1 (Continued)

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)	Assign	δ	Assign		δ (J Hz)	δ (J Hz)	Assign
7c {Re(CO) ₂ [PPh(OEt) ₂] ₃ } ₂ (μ -1,4-C $\equiv$ CC ₆ H ₄ C $\equiv$ C)	2087 m	ν C $\equiv$ C	4.15 m	CH ₂	AB ₂	δ_A = 134.7	195.5 td	CO
	1964 s	ν CO	3.87 m			δ_B = 131.9	$J_{CP} = J_{CP} = 11$	
	1908 s		1.33 t	CH ₃	$J_{AB} = 18$	114.2 dt	C $_{\beta}$	
			1.31 t			$J_{CP} = 18$		
8c [Re(CO) ₂ (PPh ₂ OEt) ₃] ₂ (μ -1,4-C $\equiv$ CC ₆ H ₄ C $\equiv$ C)	2077 m	ν C $\equiv$ C	3.70–3.20 m	CH ₂	AB ₂	δ_A = 105.3	197.3 m	CH ₂
	1945 m	ν CO	1.10 t	CH ₃		δ_B = 102.5	118.9 br	CO
	1896 s		1.03 t		$J_{AB} = 18$	112.7 m	C $_{\beta}$	
	1875 m		0.95 t		AB ₂	δ_A = 102.1	63.3 m	C $_{\alpha}$
						δ_B = 99.6	62.9 m	CH ₂
						$J_{AB} = 30$	16.1 m	CH ₃
						δ_A = 129.3	298.0 dt	C $_{\alpha}$
	9 [Re(=C=C=CPh ₂)(CO) ₂] {PPh(OEt) ₂] ₃]BF ₄	2014 m	ν C=C=C	3.80 m	CH ₂	A ₂ B	δ_B = 125.2	$J_{CP} = 21$
1927 s		ν CO	1.26 t	CH ₃	$J_{AB} = 27$		$J_{CP} = 10$	
			1.22 t				204.3 td	CO
							$J_{CP} = J_{CP} = 10$	
							202.5 br	C $_{\beta}$
							163.2 s	C $_{\gamma}$
							63.6 t	CH ₂
10 [Re(=C=C=CPh ₂)(CO) ₂] (PPh ₂ OEt) ₃]BF ₄	2011 m	ν C=C=C	3.33 m	CH ₂	A ₂ B	δ_A = 103.6	16.1 m	CH ₃
	1922 s	ν CO	0.95 t	CH ₃		δ_B = 98.3	298.9 dt	C $_{\alpha}$
			0.92 t			$J_{CP} = 20$	$J_{CP} = 10$	
						$J_{AB} = 26$	199.2 br	C $_{\beta}$
							191.8 dt	CO
							$J_{CP} = 20$	
							$J_{CP} = 10$	
							160.2 s	C $_{\gamma}$
						65.1 m	CH ₂	
						15.9 t	CH ₃	

^a In KBr pellets.^b In CD₂Cl₂ at 25°C.^c Phenyl proton resonances are omitted.^d Positive shift downfield from 85% H₃PO₄.^e Phenyl carbon resonances are omitted.^f In C₆D₆.

The proton NMR spectra of **1–3** are also consistent with the presence of the vinylidene ligand, showing the characteristic =C(H)Ph signal as a multiplet at 4.56–4.22 ppm. In addition to the resonances of the phosphite and BPh₄⁻ anion, the spectra also show the signals of free PhC $\equiv$ CH, in agreement with the dissociation of the terminal alkyne from the vinylidene complexes, as in Eq. (1).

Unsaturated complexes or dihydrogen derivatives containing a carbonyl–phosphite ratio different from 2:3, i.e. of the type [Re(CO)₃P₂]⁺, [Re(CO)P₄]⁺, [Re(η^2 -

H₂)(CO)₃P₂]⁺, [Re(η^2 -H₂)(CO)P₄]⁺, etc., were also reacted with phenylacetylide, but no formation of vinylidene or Π -acetylide complexes was ever observed. This unreactivity led us to attempt to prepare vinylidene complexes by protonation of the related acetylide Re(PhC $\equiv$ C)(CO)₃P₂ and Re(PhC $\equiv$ C)(CO)P₄ derivatives, containing a carbonyl–phosphite ratio different from 2:3. Although the reaction with HBF₄·Et₂O proceeded easily at low temperature, no evidence of the formation of =C=C(H)Ph or Π -alkyne complexes was detected by NMR. The reaction mixture, in fact, only showed the

presence of unsaturated $[\text{Re}(\text{CO})_3\text{P}_2]^+$, $[\text{Re}(\text{CO})\text{P}_4]^+$ species and the free $\text{PhC}\equiv\text{CH}$. It seems, therefore, that the stoichiometry of rhenium precursors is important in determining the stability of vinylidene complexes; in particular, only the dicarbonyl $\text{Re}(\text{CO})_2\text{P}_3$ fragment allows vinylidene complexes **1–3** to be obtained.

Instead, varying the steric and electronic properties of the phosphite ligands in the series from $\text{P}(\text{OEt})_3$ to $\text{PPh}(\text{OEt})_2$ or PPh_2OEt does not seem to influence the stability of rhenium vinylidene derivatives, all the $[\text{Re}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{CO})_2\text{P}_3]^+$ (**1–3**) being insoluble in the solid state and giving Eq. (1) in solution.

The results obtained with phenyl acetylide prompted us to extend investigations to other terminal alkynes $\text{RC}\equiv\text{CH}$ ($\text{R} = 4\text{-MeC}_6\text{H}_4$, Bu' , COOMe or COOEt), including bis(alkyne) 1,4-diethynylbenzene 1,4- $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$. In these cases too, treatment of dihydrogen cations $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ with an excess of terminal alkynes afforded vinylidene complexes according to Scheme 2.

However, equilibrium (2) is shifted substantially to the left side, and only in the presence of a large excess of alkyne was the vinylidene $[\text{Re}\{\text{C}=\text{C}(\text{H})\text{R}\}(\text{CO})_2\text{P}_3]^+$ species detected by NMR spectroscopy. This result prevented the preparation of solid samples of vinylidene complexes with a substituent different from phenyl (i.e. $\text{R} = 4\text{-MeC}_6\text{H}_4$, Bu' , etc.). Instead, in the case of the bis(alkyne), equilibrium (3) is shifted far enough to the right to allow vinylidene $[\text{Re}\{\text{C}=\text{C}(\text{H})(1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{CH})\}(\text{CO})_2\text{P}_3]^+$ (**1c**, **2c**) to be isolated as BF_4 salts in the solid state. The IR and NMR data (Table 1) support the proposed formulation for **1c** and **2c**, but also show that the unsaturated complex $[\text{Re}(\text{CO})_2\text{P}_3]^+$ is always present in the resulting solid. In fact, analytically pure samples of **1c** and **2c** were prepared, like the related **1–3**, by treatment of acetylide $\text{Re}(1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})(\text{CO})_2\text{P}_3$ with HBF_4 . The spectroscopic data of vinylidene **1c** and **2c** also suggest a *mer-trans* geometry of the type shown in Scheme 2, revealing only

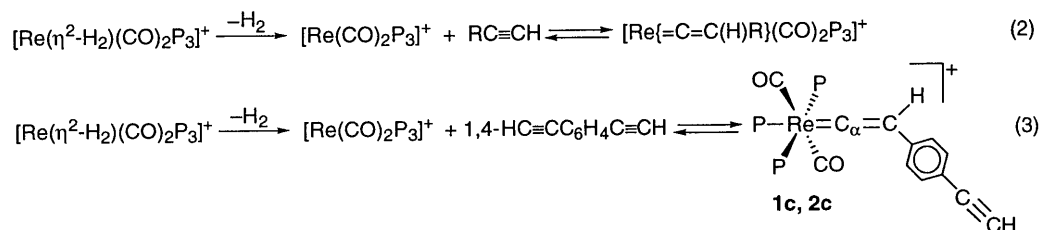
one $\nu(\text{CO})$ band in the IR and an AB_2 -type multiplet in the $^{31}\text{P}\{\text{H}\}$ -NMR.

3.2. Acetylide complexes

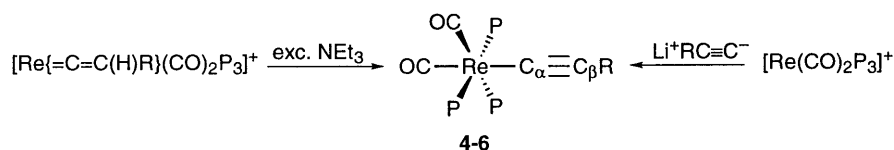
Vinylidene complexes $[\text{Re}\{\text{C}=\text{C}(\text{H})\text{R}\}(\text{CO})_2\text{P}_3]^+$ (**1–3**) react with base (NEt_3) to give acetylide derivatives $\text{Re}(\text{C}\equiv\text{CR})(\text{CO})_2\text{P}_3$ (**4–6**), which were isolated in good yield and characterised. Alternatively, acetylides **4–6** may be prepared by reacting unsaturated $[\text{Re}(\text{CO})_2\text{P}_3]^+$ complexes with lithium acetylide in THF, as shown in Scheme 3.

The new rhenium acetylide complexes are pale-yellow solids stable in air and in solution of polar and non-polar organic solvents, in which they behave as non-electrolytes [22]. The analytical and spectroscopic data (Table 1) support their formulation. In particular, the IR spectra show a medium-intensity band at $2082\text{--}2050\text{ cm}^{-1}$ due to $\nu(\text{C}\equiv\text{C})$ of the acetylide ligand, and two strong absorptions between 1970 and 1859 cm^{-1} attributed to the two carbonyl ligands in a mutually *cis* position. The $^{13}\text{C}\{\text{H}\}$ -NMR spectra are consistent with the presence of the acetylide ligand, showing the C_α and C_β carbon signals as doublets of triplets, or triplets of doublets, the former with $^2J_{\text{CP}}$ of $16\text{--}36\text{ Hz}$ at $123\text{--}106\text{ ppm}$, and the latter with $^3J_{\text{CP}}$ of $3\text{--}4\text{ Hz}$ at $119\text{--}113\text{ ppm}$, due to coupling with two equivalent phosphorus nuclei, unlike the third. The spectra also show two doublets of triplets at $198\text{--}194\text{ ppm}$ attributed to the carbonyl carbon atoms of two inequivalent CO ligands. On the basis of these data and of the $^{31}\text{P}\{\text{H}\}$ -NMR spectra, which appear as AB_2 or A_2B multiplets, a *mer-cis* geometry of the type shown in Scheme 3 is proposed for the acetylide derivatives.

Complexes $\text{Re}(1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})(\text{CO})_2\text{P}_3$ (**4c**, **5c**, **6c**) show some differences in their IR and NMR spectra (Table 1) and deserve brief discussion. The IR spectrum of $\text{PPh}(\text{OEt})_2$ derivative **5c** shows the characteristic bands of the $\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$ ligand, including $\nu(\text{C}\equiv\text{C})$



Scheme 2. $\text{R} = 4\text{-MeC}_6\text{H}_4$, Bu' , COOMe or COOEt ; $\text{P} = \text{P}(\text{OEt})_3$ (**1**) or $\text{PPh}(\text{OEt})_2$ (**2**).



Scheme 3. $\text{R} = \text{Ph}$ (**a**), Bu' (**b**) or $1,4\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$ (**c**); $\text{P} = \text{P}(\text{OEt})_3$ (**4**), $\text{PPh}(\text{OEt})_2$ (**5**) or PPh_2OEt (**6**).

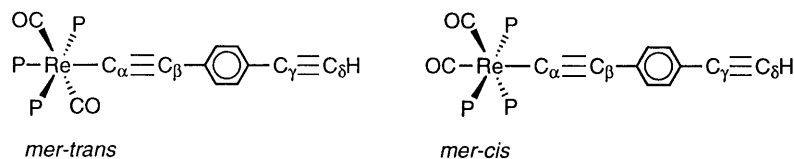
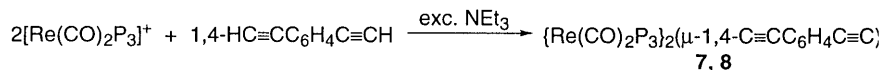


Fig. 1.

Scheme 4. P = PPh(OEt)₂ (**7**) or PPh₂OEt (**8**).

at 2078, $\nu(\text{CH})$ at 3288 and $\nu(\text{C}\equiv\text{CH})$ at 2006 cm^{-1} , but only one $\nu(\text{CO})$ band, suggesting the presence of two *trans* carbonyl ligands. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum is an AB₂ multiplet, whereas the $^{13}\text{C}\{^1\text{H}\}$ spectrum unambiguously shows the C_α and C_β acetylide carbon atoms as doublets of triplets at 113.9 and 107.1 ppm. On the basis of these data, a *mer-trans* geometry of the type shown in Fig. 1 is proposed for acetylide complex **5c**.

On the contrary, the IR spectra of related complexes $\text{Re}(1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})(\text{CO})_2\text{P}_3$ (**4c**, **6c**) show three bands in the $\nu(\text{CO})$ region, indicating the presence of more than one compound. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra support this hypothesis, showing two well-separated AB₂ or A₂B multiplets which may be simulated with the parameters reported in Table 1. These data are interpreted on the basis of two isomers, with the two CO ligands in a mutually *cis* position in one case, and *trans* in the other. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra confirm the presence of the two isomers of the type shown in Fig. 1, with two sets of signals for the C_α and C_β acetylide carbon atoms, consisting of one triplet of doublets and one doublet of triplets for the C_α and two broad signals for the C_β. Two singlets for the C_γ and two for the C_δ are also visible, together with two sets of partially overlapping carbonyl carbon atoms, in agreement with the proposed formulation. However, it may be noted that the IR spectra of compounds **4c**, **6c** only reveal one $\nu(\text{C}\equiv\text{C})$ band, probably due to the small difference in the values of $\nu(\text{C}\equiv\text{C})$ between the two isomers, which makes the bands practically coincide. Support for this hypothesis is given by comparison of the $\nu(\text{C}\equiv\text{C})$ values of our acetylides **4–6** (Table 1), which shows how these values are only very slightly influenced by the nature of the phosphite ligands, with changes within 3–6 cm^{-1} , in agreement with the presence of two $\nu(\text{C}\equiv\text{C})$ bands overlapping the two isomers.

The preparation of acetylide complexes **4c**, **5c**, **6c** with 1,4-diethynylbenzene prompted us to extend the study to the synthesis of binuclear complexes containing the $\text{ReC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRe}$ unit. Treatment of $[\text{Re}(\text{CO})_2\text{P}_3]^+$ cations first with the alkyne and then

with an excess of NEt₃ afforded binuclear $\{\text{Re}(\text{CO})_2\text{P}_3\}_2(\mu\text{-}1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})$ complexes (**7**, **8**) (Scheme 4), which were isolated as yellow–orange solids and characterised.

The complexes are air-stable and non-electrolytic, and their formulation is confirmed by analytical and spectroscopic data (Table 1). In particular, the appearance of only one $\nu(\text{C}\equiv\text{C})$ band in the IR spectra and the absence of any $\nu(\text{C}\equiv\text{CH})$ absorption indicate a binuclear species. This is further confirmed by comparison of their $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra with those of mononuclear **4c**, **5c**, **6c**, which only show the presence of only the signals of C_α and C_β acetylide carbon atoms for binuclear species **7**, **8**. However, comparison between these spectra shows some significant differences, suggesting here again the existence of several isomers.

Complex $[\text{Re}(\text{CO})_2\{\text{PPh}(\text{OEt})_2\}_3]_2(\mu\text{-}1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})$ (**7**) shows two strong $\nu(\text{CO})$ IR bands at 1964 and 1908 cm^{-1} , attributed to two carbonyl ligands in a mutually *cis* position and only one AB₂ multiplet in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum. Furthermore, besides the signals of the C_α and C_β acetylide ligands, only one triplet of doublets at 195.5 ppm is present in the $^{13}\text{C}\{^1\text{H}\}$ spectra, attributed to two magnetically equivalent carbonyl carbon atoms. On this basis, a *fac-cis* geometry of the type shown in Fig. 2 is proposed for the complex.

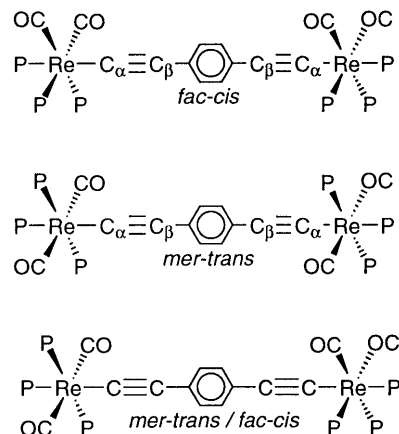
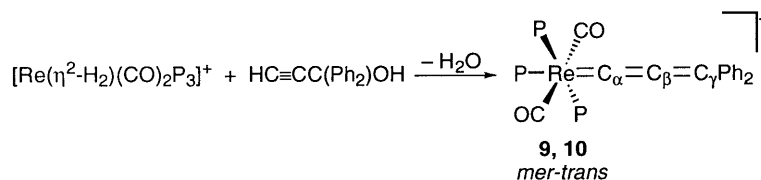


Fig. 2.

Scheme 5. P = PPh(OEt)₂ (9) or PPh₂OEt (10).

Instead, the IR spectrum of complex $\{\text{Re}(\text{CO})_2(\text{PPh}_2\text{OEt})_3\}_2(\mu\text{-}1,4\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})$ (8) shows three $\nu(\text{CO})$ bands at 1945, 1896 and 1875 cm^{-1} . In the temperature range between +30 and -90°C , the related $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum displays two AB₂ multiplets which may be interpreted, as in the case of mononuclear complexes 4c, 6c, as indicating two isomers with *fac-cis* and *mer-trans* arrangement of carbonyl and phosphite ligands around the rhenium atom. Since the complex is binuclear, four isomers should be expected of the type shown in Fig. 2, the two *mer-trans/fac-cis* isomers being equivalent. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra fit this hypothesis, showing two partly overlapping sets of both carbonyl carbon signals and acetylide carbon atoms (both C_α and C_β) resonances.

3.3. Propadienyldiene complexes

Dihydrogen derivatives $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$, prepared in situ by the protonation of $\text{ReH}(\text{CO})_2\text{P}_3$, reacted at r.t. with 1,1-diphenyl-2-propyn-1-ol to give propadienyldiene complexes $[\text{Re}(=\text{C}=\text{C}=\text{CPh}_2)(\text{CO})_2\text{P}_3]\text{BF}_4$ (9, 10), which were isolated as dark-blue solids and characterised (Scheme 5).

Propadienyldiene species 9, 10 may also be obtained by reacting the unsaturated $[\text{Re}(\text{CO})_2\text{P}_3]^+$ cations with 1,1-diphenyl-2-propyn-1-ol. The reaction probably proceeds through tautomerisation of the terminal alkyne $\text{HC}\equiv\text{CC}(\text{Ph}_2)\text{OH}$ on the rhenium centre to give the vinylidene intermediate $[\text{Re}\{\text{C}=\text{C}(\text{H})\text{C}(\text{Ph}_2)\text{OH}\}(\text{CO})_2\text{P}_3]^+$ which, by elimination of H_2O , affords final complexes 9, 10. Although in this case too equilibrium probably involves the formation of the vinylidene intermediate, the final propadienyldiene complex is stable with respect to dissociation of the ligands, and only after 24 h does its solution show decomposition.

As observed in the synthesis of monosubstituted vinylidene complexes 1–3, only the $\text{Re}(\text{CO})_2\text{P}_3$ fragment with a carbonyl:phosphite ratio of 2:3 allows propadienyldiene complexes to be prepared. The reactions of other $\eta^2\text{-H}_2$ derivatives such as $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_3\text{P}_2]^+$ and $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})\text{P}_4]^+$ with $\text{HC}\equiv\text{CC}(\text{Ph}_2)\text{OH}$ do not afford any propadienyldiene complexes, unsaturated cations $[\text{Re}(\text{CO})_3\text{P}_2]^+$ or $[\text{Re}(\text{CO})\text{P}_4]^+$ being the only isolated products. It may also be noted that other propargylic alcohols, such as $\text{HC}\equiv\text{CC}(\text{H}_2)\text{OH}$, $\text{HC}\equiv\text{CC}(\text{H})(\text{Ph})\text{OH}$ and $\text{HC}\equiv\text{C}(\text{CH}_3)(\text{Ph})\text{OH}$, were re-

acted with $[\text{Re}(\eta^2\text{-H}_2)(\text{CO})_2\text{P}_3]^+$ or $[\text{Re}(\text{CO})_2\text{P}_3]^+$ and, although the reaction proceeded with colour changes of the solution, no stable propadienyldiene complexes were isolated.

Complexes 9, 10 are dark-blue solids and stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes [22]. Their analytical and spectroscopic data (Table 1) support their formulation and suggest a *mer-trans* geometry in solution (Scheme 5). In particular, the IR spectra show only one strong $\nu(\text{CO})$ band at 1927 (9) and 1922 cm^{-1} (10) due to two carbonyl ligands in a mutually *trans* position. The spectra also have one medium-intensity band at 2014 (9) and 2011 cm^{-1} (10), attributed to the $\nu(\text{C}=\text{C}=\text{C})$ of the propadienyldiene ligand. However, diagnostic for the presence of the $=\text{C}_\alpha=\text{C}_\beta=\text{C}_\gamma\text{Ph}_2$ ligand are the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra, which show one doublet of triplets at 298.0 (9) and 298.9 ppm (10), due to the C_α carbon atom of the propadienyldiene ligand. Furthermore, at 202.5–199.2 and 163.2–160.2 ppm there are also the signals of the C_β and C_γ carbon atoms, respectively, of the $\text{C}_\alpha=\text{C}_\beta=\text{C}_\gamma\text{Ph}_2$ ligand, whereas at 204.3–191.8 ppm the carbonyl carbon resonances appear as a triplet of doublets or a doublet of triplets, due to coupling with the phosphorus nuclei of the phosphite. Finally, in the temperature range +30 to -80°C , the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra show an AB₂ or A₂B multiplet, in agreement with a *mer-trans* geometry for the first propadienyldiene complexes of rhenium.

Acknowledgements

The financial support of MURST — Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 1998–1999 — is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

References

- [1] (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 291. (b) S.R. Marder, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, Wiley, Chichester, 1992. (c) M. Altmann, U.H.S. Bunz, Angew. Chem. Int. Ed. Engl. 34 (1995) 569. (d) N.J. Lang, Angew. Chem. Int. Ed. Engl. 33 (1994) 547. (e) V. Grosshenny, A. Harriman, R.

- Ziessel, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1100. (f) T. Marder, H. Fyfe, M. Mlekuz, G. Stringer, N. Taylor, in: R. Laine (Ed.), *Inorganic and Organometallic Polymers with Special Properties*, NATO ASI 206, Kluwer, Dordrecht, 1992. (g) N.J. Long, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 21.
- [2] (a) C.S. Yi, N. Liu, A.L. Rheingold, L.M. Liable-Sands, *Organometallics* 16 (1997) 3910. (b) C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa, F. Zanobini, P. Frediani, *Organometallics* 15 (1996) 272. (c) H. Matsuzaka, Y. Takagi, Y. Ishii, M. Nishio, M. Hidai, *Organometallics* 14 (1995) 2153. (d) J.F. Corrigan, N.J. Taylor, A.J. Carty, *Organometallics* 13 (1994) 3778. (e) M. Schäfer, N. Mahr, J. Wolf, H. Werner, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1315. (f) D.L. Hughes, M. Jiménez-Tenorio, G.J. Leigh, A.T. Rowley, *J. Chem. Soc. Dalton Trans.* (1993) 3151. (g) L.D. Field, A.V. George, G.R. Purches, I.H.M. Slip, *Organometallics* 11 (1992) 3019.
- [3] (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.
- [4] (a) C. Bruneau, P.H. Dixneuf, *Acc. Chem. Res.* 32 (1999) 311. (b) M.A. Esteruelas, A.V. Gómez, A.M. López, J. Modrego, E. Oñate, *Organometallics* 16 (1997) 5826. (c) C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* 16 (1997) 2768. (d) H.M. Lee, J. Yao, G. Jia, *Organometallics* 16 (1997) 3927. (e) V. Cadierno, M.P. Gamasa, J. Gimeno, M.C. López-González, J. Borge, J. García-Granda, *Organometallics* 16 (1997) 4453. (f) B.M. Trost, J.A. Flygare, *J. Am. Chem. Soc.* 114 (1992) 5476. (g) A.K. McMullen, J.P. Selegue, J.G. Wang, *Organometallics* 10 (1991) 3421. (h) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J.Y. Satoh, *J. Am. Chem. Soc.* 113 (1991) 9604.
- [5] (a) M.I. Bruce, *Chem. Rev.* 91 (1991) 197. (b) M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Chem. Soc. Dalton Trans.* (1998) 1793.
- [6] (a) D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, *Organometallics* 16 (1997) 3640. (b) I. de los Rios, M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, *J. Am. Chem. Soc.* 119 (1997) 6529. (c) Y. Kawata, M. Sato, *Organometallics* 16 (1997) 1093. (d) B. Buriez, I.D. Burns, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, *Organometallics* 18 (1999) 1504.
- [7] M.I. Bruce, *Chem. Rev.* 98 (1998) 2797.
- [8] (a) K.A. Conner, R.A. Walton, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, vol. 4, Pergamon, Oxford, 1987. (b) C.P. Casey, *Science* 259 (1993) 1552.
- [9] (a) D.R. Senn, A. Wong, A.T. Patton, M. Marsi, C.E. Strouse, J.A. Gladysz, *J. Am. Chem. Soc.* 110 (1988) 6096. (b) M.R. Terry, L.A. Mercando, C. Kelley, G.L. Geoffroy, P. Nombell, N. Lugan, R. Mathieu, R.L. Ostrander, B.E. Owens-Waltermire, A.L. Rheingold, *Organometallics* 13 (1994) 843. (c) C.P. Casey, Y. Ha, D.R. Powell, *J. Organomet. Chem.* 472 (1994) 185. (d) W. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 117 (1995) 11922. (e) T. Bartik, W. Weng, J.A. Ramsden, S. Szafert, S.B. Falloon, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 120 (1998) 11071. (f) N.E. Kolobova, A.B. Antonova, O.M. Khitrova, M.Y. Antipin, Y.T. Struchkov, *J. Organomet. Chem.* 137 (1977) 69.
- [10] (a) W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt, H. Komber, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1636. (b) R. Toreky, R.R. Schrock, W.M. Davis, *J. Am. Chem. Soc.* 114 (1992) 3367.
- [11] W.A. Herrmann, R.W. Fischer, D.W. Marz, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1638.
- [12] M.L. Loza, S.R. De Gala, R.H. Crabtree, *Inorg. Chem.* 33 (1994) 5073 and references therein.
- [13] (a) C.P. Casey, R.S. Cariño, R.K. Hayashi, K.D. Schladetzky, *J. Am. Chem. Soc.* 118 (1996) 1617. (b) M. Leeaphon, A.L. Ondracek, R.J. Thomas, P.E. Fanwick, R.A. Walton, *J. Am. Chem. Soc.* 117 (1995) 9715. (c) L.L. Padolik, J.C. Gallucci, A. Wojcicki, *J. Am. Chem. Soc.* 115 (1993) 9986.
- [14] A.J.L. Pombeiro, S.S.P.R. Almeida, M.F.C.G. Silva, J.C. Jeffrey, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1989) 2381.
- [15] G. Albertin, S. Antoniutti, S. Garcia-Fontán, R. Carballo, F. Padoan, *J. Chem. Soc. Dalton Trans.* (1998) 2071.
- [16] (a) G. Albertin, S. Antoniutti, E. Bordignon, M. Granzotto, *J. Organomet. Chem.* 585 (1999) 83. (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.
- [17] R. Rabinowitz, G. Pellon, *J. Org. Chem.* 26 (1961) 4623.
- [18] A.S. Hay, *J. Org. Chem.* 25 (1960) 637.
- [19] G. Balacco, *J. Chem. Inf. Comput. Sci.* 34 (1994) 1235.
- [20] (a) J. Silvestre, R. Hoffmann, *Helv. Chim. Acta* 68 (1985) 1461. (b) Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, *J. Am. Chem. Soc.* 116 (1994) 8105.
- [21] (a) M.D. Fryzuk, L. Huang, N.T. McManus, P. Paglia, S.J. Rettig, G.S. White, *Organometallics* 11 (1992) 2979. (b) J.R. Lumphrey, J.P. Selegue, *J. Am. Chem. Soc.* 114 (1992) 5518. (c) C. Bianchini, M. Peruzzini, A. Vacca, F. Zanobini, *Organometallics* 10 (1991) 3697.
- [22] W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.