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Synthesis and characterisation of saturated and unsaturated triruthenium clusters containing electronically symmetrical and asymmetrical alkynes

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Abstract

The synthesis and characterisation of μ_3-η^2-alkynyl triruthenium clusters, $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1**, saturated), $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(CO)_7]$ (**2**, unsaturated) and $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7]$ (**3**, saturated) containing symmetrical and asymmetrical alkynes in which R^1 and R^2 are electron donor or electron withdrawing groups in the *para* position of the aromatic ring(s) or R^2 is ferrocenyl, are reported. Clusters **1** were obtained from the reactions of $[PPN][Ru_3(\mu\text{-Cl})(CO)_{10}]$ with $R^1\text{-}4\text{-}C_6H_4CCR^2$ and dppm. Clusters **1** were successfully decarbonylated to give unsturated clusters **2**, with the exception of the $FcCCC_6H_4\text{-}4\text{-}NO_2$ containing cluster, which is stable. Novel adducts **3** were obtained in high yields by addition of PPh_3 to unsaturated clusters **2**. Clusters **1**–**3** were characterised by analytical and spectroscopic data, and structures were proposed on the basis of systematic ^{31}P NMR studies and correlations with X-ray structural data of related compounds available in the literature. Saturated compounds **1** contain a CO and a dppm ligands bridging the same edge, which is also parallel to the μ_3-η^2-alkyne, as opposed to the structure previously proposed for the PhCCPh and other derivatives, and established by X-ray crystallography for the PhC≡CCCPh cluster derivative, in which the dppm ligand bridges a different edge. Unsaturated compounds **2** exhibit the same structure established for the PhCCPh derivative in the solid state, with the alkyne bonded in the μ_3-η^2-mode perpendicular to the Ru_2 edge supported by the dppm ligand. Because the dppm phosphorus chemical shifts were sensitive to the alkyne electronic asymmetry, it was possible to show that clusters containing electronically asymmetrical alkynes exist in two inseparable isomeric forms, which differ with respect to the alkyne orientation. Similarly to their osmium analogues, saturated compounds **3** exist as inseparable mixtures of isomers that differ with respect to the position of the bridging CO and dppm ligands, and in the cases of asymmetrical alkyne derivatives, also with respect to the orientation of the alkyne. This work has established, therefore, that μ-CO and dppm ligand positions respective to the μ_3-η^2-alkyne in saturated clusters **1** and **3** are sensitive both to the nature of the coordinated alkyne and to the presence of a PPh_3 in place of a CO ligand on the metal frame.
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1. Introduction

In recent years there has been a great deal of interest in the structural, bonding, chemical and electrochemical aspects of metal cluster carbonyls containing coordinated alkynes or poly-ynes with different redox-active sites [1–3]. These clusters can exhibit electronic delocalisation (donor-π-acceptor systems) and show potential as molecular wires, sensors, electrochemical agents or non-linear optical materials, among others [4].

A number of saturated triruthenium-alkynyl clusters of general formula $[Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR')(CO)_{10}]$ have been obtained from the direct reactions of alkynes with $[Ru_3(CO)_{12}]$ [5], or by displacement, by the alkyne, of the labile ligands in activated precursors, $[Ru_3(CO)_{10}(NCMe)_2]$ [6] or $[PPN][Ru_3(\mu\text{-Cl})(CO)_{10}]$ [7,8], in the

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latter case resulting in selective formation of the desired products. In these clusters the alkyne is coordinated to the metal frame in the classic μ_3-η^2 perpendicular mode, and one of the aims of the above mentioned studies was the synthesis of the elusive unsaturated derivatives $[Ru_3(\mu_3\text{-}\eta^2\text{-RCCR}')(CO)_9]$ containing the alkyne coordinated in the μ_3-η^2- perpendicular mode, as in $[Fe_3(\mu_3\text{-}\eta^2\text{-RCCR})(CO)_9]$ [9]. Trapping of the alkyne in its unstable perpendicular coordination mode in the triruthenium and triosmium derivatives could only be achieved by incorporation of bis(dipheny1phosphino)methane (dppm) into the ligand shell of $[M_3(\mu_3\text{-}\eta^2\text{-RCCR}')(CO)_{10}]$ (M = Ru [10], Os [11]), and stabilization of the alkyne in this coordination mode in the unsaturated compounds $[M_3(\mu_3\text{-}\eta^2\text{-RCCR}')(CO)_9]$ was associated with the increased back-donating ability of the metal induced by the dppm ligand [12].

In this paper we report the synthesis and solution characterisation of three series of μ_3-η^2-alkynyl triruthenium clusters, $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1**, saturated), $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)(\mu\text{-dppm})(CO)_7]$ (**2**, unsaturated) and $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7]$ (**3**, saturated) containing symmetrical and asymmetrical alkynes in which R^1 and R^2 are electron donating or electron withdrawing groups in the *para* position of the aromatic ring(s), or R^2 = ferrocenyl. The interest in this type of compounds stems from the possibility of tuning the electronic properties, not only of the coordinated alkyne, but also of the metallic frame upon saturation/unsaturation and/or CO substitution with phosphines and diphosphines, and thus probing the communication between the metal frame and the alkyne in the cluster. Preliminary work on the electrochemistry of compounds **2** has been reported [1a], and work on their non-linear optical properties is in progress. It was also of interest to investigate the effect of R^1 and R^2 on the decarbonylation process of clusters **1** and stabilization of the unsaturated clusters **2**.

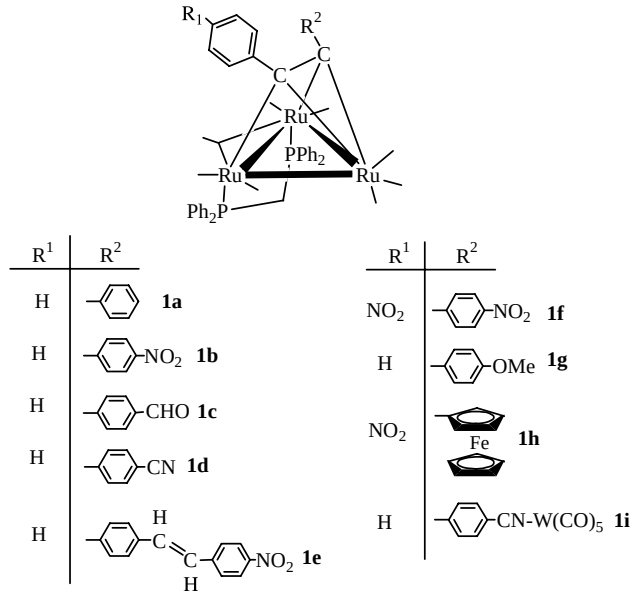
Clusters **1** were obtained from the reactions of $[PPN][Ru_3(\mu\text{-Cl})(CO)_{10}]$ with $R^1\text{-4-}C_6H_4CCR^2$, and with the exception of the cluster containing $R^1 = NO_2$ and R^2 = Fc, which was stable, were successfully decarbonylated to give clusters **2**, following Lavigne's methodologies [8,10]. Novel adducts **3** were obtained in high yields by addition of PPh_3 to unsaturated clusters **2**. The solution structures of clusters **1**–**3** were proposed on the basis of systematic ^{31}P NMR studies and correlations with X-ray structural data of related compounds available in the literature. The spectroscopic data provided definite proof for the existence of an isomeric form of compounds **1**, which is different from the one previously established by X-ray crystallography, thus highlighting the importance of solution structural investigation even in the cases where solid state structures are successfully determined.

2. Results and discussion

2.1. Synthesis of $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (1b–1h)

The alkyne substituted species **1b**–**1h** were prepared by the Lavigne methodology [10], starting from the "activated" anionic cluster $[PPN][Ru_3(\mu\text{-Cl})(CO)_{10}]$ (**PPN1**), generated in situ from $[Ru_3(CO)_{12}]$ by treatment with PPNCl in THF. Addition of the respective alkynes $R^1\text{-4-}C_6H_4CCR^2$ (Scheme 1) to burgundy **PPN1** at room temperature, under a stream of argon, generated the dark yellow anionic intermediate clusters $[PPN][Ru_3(\mu\text{-Cl})(CO)_9(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)]$ (**PPN 1b**–**h**) in spectroscopically quantitative yields which were isolated as crystalline powders for the next step of the preparation of clusters **1b**–**1h**. The speed of these reactions was sensitive to the electronic properties of the substituent on the alkyne. Good electron withdrawing groups (–NO_2, –CHO and –CN) accelerated the reactions, which were instantaneous, whereas in the case of the electron donor group –OMe the mixture had to be stirred for 1 h for reaction completion.

Clusters **PPN1b**–**h** were identified by their IR spectra in the ν_{CO} region (see experimental) which were all very similar to that of **PPN1a** previously reported [8c]. The analogous reactions of **PPN1** with the nitrogenated alkynes $R^1\text{-4-}C_6H_4CCPh$ ($R^1 = NH_2$ and $N = CHC_6H_4\text{-4-}NO_2$) did not yield the desired products according to IR spectroscopy, most probably due to nucleophilic attack of the nitrogen electron pair at the metal core, which thus competes with the alkyne, and on the thin-layer chromatography (TLC) plates the reaction mixtures



Scheme 1. Structures of clusters $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-4-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1a**–**1i**).

yielded several unidentified species which underwent decomposition.

Products **1b**–**1h** were obtained by slow addition of dppm in CH_2Cl_2 to clusters **PPN1b**–**h** in CH_2Cl_2, in the presence of MeOH, to help displace the Cl^- ligand, and under a slight pressure of CO to avoid CO dissociation (vide infra). Clusters **1b**–**h** were isolated as purple microcrystalline solids in yields varying from 77 (**1h**) to about 50% (**1g**) (see Table 1), depending on the alkyne, the CO pressure and the mode of addition of the dppm. Best yields were obtained from the reactions of **PPN1b**, **PPN1f** and **PPN1h** containing alkynes bearing the electron withdrawing $–NO_2$ group, which suggests that the metal frames of these clusters were most electron deficient and prone to nucleophilic attack of the dppm. When the solution was saturated with CO, formation of the starting material $[Ru_3(CO)_{12}]$ was noted, whereas fast addition of the dppm to solutions of **PPN1a**–**h** led to the formation of $[Ru_3(CO)_{10}(dppm)]$ [13] and $[Ru_3(R^1\text{-}4\text{-}C_6H_4CCR^2)(dppm)_2(CO)_6]$ [10a] which were identified by their IR spectra.

Cluster **1j**, previously obtained from the reaction of $[Ru_3(CO)_{10}(dppm)]$ with PhC≡CC≡CPh in the presence of Me_3NO in 36% yield [14], was also prepared by the Lavigne methodology and obtained in 60% yield (see Table 1).

The cluster adduct $[Ru_3(\mu_3\text{-}\eta^2\text{-}\{(CO)_5W\}NC\text{-}4\text{-}C_6H_4CCPh)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1i**) could only be synthesised from $[Ru_3(\mu_3\text{-}\eta^2\text{-}NC\text{-}4\text{-}C_6H_4CCPh)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1d**) by reaction with $[W(CO)_5$ THF], formed in situ from the hexacarbonyl, in THF, under photolytic conditions [15]. Attempts at isolating cluster **PPN1i** from the reaction of **PPN1** and $\{(CO)_5W\}NC\text{-}4\text{-}C_6H_4CCPh$ also led to the formation of $[Ru_3(CO)_{12}]$, presumably due to the facile dissociation and decomposition of the "$W(CO)_5$" fragment from the alkyne in the presence of MeOH, thus generating free CO, which was scavenged by **PPN1** [8].

2.2. Characterisation of $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1b**–**1i**)

Clusters **1b**–**1i** were formulated on the basis of analytical and spectroscopic data (see Tables 1 and 2) and by comparison with the data reported for **1a** and other analogous clusters [10]. They are all relatively stable in air in the solid state, and only **1g** undergoes decomposition when manipulated in the presence of air and light. The IR spectra of **1b**–**1h** are very similar to that of **1a**, with respect to both band frequencies and intensities, which were mostly insensitive to the substituents on the alkyne; all exhibit a bridging CO band besides bands due to the terminal CO ligands. The ^1H NMR spectra of all compounds exhibit multiplets in the δ 6.5 and 7.9 region due to the phenyl protons and two multiplets in the δ 3–4 region attributed to the dppm methylene hydrogens as previously observed for **1a** and other analogous systems [14,16,17]. The ^1H NMR spectra of clusters **1c**, **1g**, and **1h** also exhibit the expected peaks due to the –CHO, –OMe and ferrocenyl hydrogens, respectively (see Table 2).

Table 1
Analytical and spectroscopic data for the $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7]$ (**1a**–**1j**) derivatives

Cluster (% yield)	Elemental analyses Found (Calc.) %	IR[a] (ν_{CO})/cm^{-1}
$R^1 = H$, $R^2 = Ph$ (**1a**) (50%)	$C_{47}H_{32}O_8P_2Ru_3$ C: 51.79(51.65); H: 2.96(2.95).	2052s, 2001vs, 1972m, 1830w
$R^1 = NO_2$, $R^2 = Ph$ (**1b**) (65%)	$C_{47}H_{31}NO_{10}P_2Ru_3$ C: 49.74(49.61); H: 2.87(2.75); N: 1.17(1.23)	2059s, 2005vs, 1974w, 1834w
$R^1 = CHO$, $R^2 = Ph$ (**1c**) (58%)	$C_{48}H_{32}O_9P_2Ru_3$ C: 51.57(51.43); H: 2.75(2.88)	2057s, 2004vs, 1976sh, 1940wbr
$R^1 = CN$, $R^2 = Ph$ (**1d**) (56%)	$C_{48}H_{31}NO_8P_2Ru_3$ C: 51.71(51.57); H: 2.74(2.80); N: 1.22(1.25)	2225w (CN), 2057s, 2003vs, 1976m, 1835wbr
$R^1 = CHCHC_6H_4\text{–}4\text{–}NO_2$, $R^2 = Ph$ (**1e**) (52%)	$C_{55}H_{37}NO_{10}P_2Ru_3$ C: 53.40(53.27); H: 2.93(3.01); N: 1.06(1.13)	2056s, 2002vs, 1974m, 1833w
$R^1 = NO_2$, $R^2 = C_6H_4\text{–}4\text{–}NO_2$ (**1f**) (68%)	$C_{47}H_{30}N_2O_{12}P_2Ru_3$ C: 47.84(47.72); H: 2.48(2.56); N: 2.31(2.37)	2058s, 2000vs, 1974m, 1835w
$R^1 = OCH_3$, $R^2 = Ph$ (**1g**) (51%)	$C_{48}H_{34}O_9P_2Ru_3$ C: 51.43(51.34); H: 2.92(3.05)	2053s, 2001vs, 1973m, 1830vw
$R^1 = NO_2$, $R^2 = Fc$ (**1h**) (77%)	$C_{51}H_{35}NO_{10}P_2Ru_3Fe$ C: 49.29(49.16); H: 2.84(2.83); N: 1.27(1.12)	2055s, 2000vs, 1973m, 1826vw
$R^1 = CNWCO_5$, $R^2 = Ph$ (**1i**) (56%)	$C_{53}H_{31}NO_{13}P_2Ru_3W$ C: 43.91(44.24); H: 2.11(2.17); N: 1.01(0.97)	2073w, 2058s, 2005vs, 1977sh, 1939vs, 1900m
$R^1 = CCPh$ $R^2 = Ph$ (**1j**) (60%)	$C_{49}H_{32}O_8P_2Ru_3$ C: 52.60(52.83); H: 2.84(2.90)	2107vw, 2061s, 2013m, 2001vs, 1972sh, 1839w

[a] Measured in CH_2Cl_2.

Table 2
^{1}H and ^{31}P{^{1}H} NMR data for clusters **1a**–**1j**, **2a**–**2f** and **3a**–**3f**

Cluster	δ^1H (ppm)[a,b]	δ^{31}P {^{1}H}, J_{P-P} (Hz)[a,b]
1a	6.80–7.42(m, 30H, C_6H_5), 3.64(m, 1H, CH_2), 3.10(m br, 1H, CH_2)	35.5 (s)
1b	7.20–8.18(m, 29 H, C_6H_5 and C_6H_4), 3.84(m br, 1H, CH_2), 3.36(m br, 1H, CH_2)	36.15 (d, 135), 35.42 (d)
1c	10.0(s, 1H, CHO), 7.20–7.82(m, 29H, C_6H_5 and C_6H_4), 3.84(m, 1H, CH_2), 3.36(m br, 1H, CH_2)	36.47 (d, 130), 36.06 (d)
1d	6.90–7.50(m, 29H, C_6H_5 and C_6H_4), 3.62(m, 1H, CH_2), 3.10(m, 1H, CH_2)	35.85 (d, 132), 35.35 (d)
1e	7.00–8.20(m, 35H, C_6H_5, C_6H_4 and CH=CH), 3.62(m, 1H, CH_2), 3.12(m, 1H, CH_2)	35.5 (s)
1f	6.82–7.46(m, 28H, C_6H_4), 3.69(m, 1H, CH_2), 3.22(m br, 1H, CH_2)	36.0 (s)
1g	6.60–7.50(m, 29H, C_6H_5 and C_6H_4), 3.80(s, 3H, OCH_3), 3.65(m, 1H, CH_2), 3.12(m, 1H, CH_2)	35.5 (s)
1h	7.10–8.40(m, 24H, C_6H_5 and C_6H_4), 4.30(s, 5H, Cp), 4.20–4.27(m, 4H, C_5H_4), 3.75(m, 1H, CH_2), 3.07(m, 1H, CH_2)	35.47 (d, 136), 33.91 (d)
1i	6.80–7.40(m, 29H, C_6H_5 and C_6H_4), 3.10(m, 1H, CH_2), 3.55–3.65(m, 1H, CH_2)	36.06 (d, 134), 35.19 (d)
1j	7.10–7.70(m, 30H, C_6H_5), 5.97(m, 1H, CH_2), 4.65(m, 1H, CH_2)	33.5 (d, 40), 12.6 (d), 12.3 (s) [2:2:3][c]
2a	6.83–7.51(m, 30H, C_6H_5), 3.71(m, 1H, CH_2), 3.12(m, 1H, CH_2)	40.6 (s)
2b	7.25–8.21(m, 29 H, C_6H_5 and C_6H_4), 3.84(m, 1H, CH_2), 3.46(m, 1H, CH_2)	43.1 (s), 41.3 (s) [1:3][c]
2c	10.02(s, 1H, CHO), 9.90(s, 1H, CHO), 6.8–7.6(m, 58H, C_6H_5 and C_6H_4), 3.95(m, 2H, CH_2), 3.25(m, 2H, CH_2)	42.5 (s), 41.3 (s) [1:3][c]
2d	6.70–7.80(m, 29H, C_6H_5 and C_6H_4), 4.00(m, 1H, CH_2), 3.20(m, 1H, CH_2)	42.4 (s), 41.3 (s) [1:3][c]
2e	6.80–8.40(m, 35H, C_6H_5, C_6H_4 and CH=CH), 4.20(m, 1H, CH_2), 3.30(m, 1H, CH_2)	41.2 (s), 41.1 (s) [1:1][c]
2f	6.80–8.00(m, 28H, C_6H_4), 3.90(m, 1H, CH_2), 3.25(m, 1H, CH_2)	42.2 (s)
3a	6.72–8.32(m, 45H, C_6H_5), 4.82(m, 1H, CH_2), 3.43(m, 1H, CH_2)	42.5 (br s), 15.0 (br s)
3b	6.80–7.70(m, 44H, C_6H_5 and C_6H_4), 3.82(m br, 1H, CH_2), 3.40(m, 1H, CH_2)	42.5 (br s), 13 (br s)
3c	9.82(s, 1H, CHO), 6.80–7.60(m, 44H, C_6H_5 and C_6H_4), 4.40(m, 1H, CH_2), 3.80(m, 1H, CH_2)	41.0 (br s), 12.0 (br s)
3d	6.66–8.12(m, 44H, C_6H_5 and C_6H_4),4.00 (m, 1H, CH_2), 3.21(m, 1H, CH_2)	42.0 (br s), 12.5 (br s)
3e	7,04–8.12(m, 50H, C_6H_5, C_6H_4, CH=CH), 4.21(m,1H, CH_2), 3.33(m, 1H, CH_2)	42.5 (br s), 15.5 (br s)
3f	7.20–7.60(m, 43H, C_6H_5 and C_6H_4), 3.90(m, CH_2), 3.35(m, CH_2)	42.5 (br s), 12.5 (br s)

[a] In $CDCl_3$.
[b] Room temperature.
[c] Relative intensities.

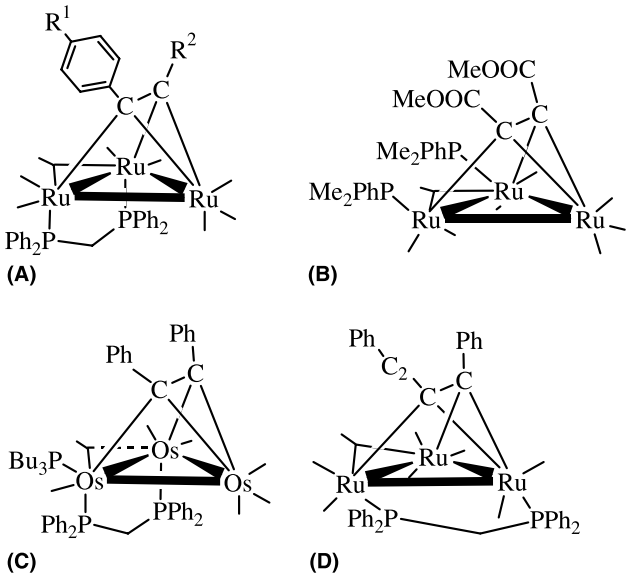
In the ^{31}P{^{1}H} NMR spectra of clusters **1a**–**1i**, the phosphorus nuclei of the dppm ligand appear around δ 35 as a singlet or two second-order AB type doublets, depending on the nature of the alkyne ligand. In the second case, the spectra were simulated to determine the exact chemical shifts of the P nuclei [18].

The ^{31}P{^{1}H} NMR spectra of clusters **1a** and **1f**, which contain symmetrical alkynes PhCCPh and NO_2-4-$C_6H_4CCC_6H_4$-4-NO_2, exhibit a broad singlet at δ 35.5 [10] and 36.0, respectively, which sharpens upon lowering the temperature down to −90 °C (in CD_2Cl_2/CS_2), thus indicating that the two phosphorus atoms are equivalent.

In the ^{31}P{^{1}H} NMR spectra of the asymmetrical derivatives **1b**–**1d** and **1h**–**1i**, however, the phosphorus nuclei appear as two second order AB type doublets ($J_{P-P} \sim 130$Hz) whose chemical shift difference ($\delta\Delta = \delta_{P1} - \delta_{P2}$/Hz) decreases with the electronic asymmetry of the coordinated alkyne [**1h** (NO_2/Fc, 190) > **1i** (H/–CN–W(CO)$_5$, 106) > **1b** (H/–NO_2, 90) > **1d** (H/–CN, 60) ≈ **1c** (H/–CHO, 50)] (see Table 2). The spectrum of cluster **1b** stays unchanged upon lowering the temperature down to −90 °C.

In contrast, in the spectra of the asymmetric derivatives **1e** and **1g**, which contain alkynes R^1-4-C_6H_4CCPh (R^1 = CHCHC_6H_4-4-NO_2 and OMe), respectively, the two phosphorus nuclei appear as a singlet (see Table 2), which shows that R^1 does not alter significantly the electronic density on the ruthenium atom bonded to the carbon bearing the R^1-4-C_6H_4– group, as in compounds **1b**–**1d** and **1h**–**1i**, either because the electron withdrawing group (R^1 = –NO_2) is situated too far away from the metal on the organic chain (cluster **1e**), or because R^1 is an electron donating group (–OMe) that does not contribute significantly with electron density to the cluster (**1g**). Similar behaviour has been reported for the acetylide compounds [RuCp(PPh_3)$_2$(C≡CC_6H_4-4-R)] (R = H, –CHCHC_6H_4-4-NO_2 and –NCHC_6H_4-4-NO_2), whose phosphorus chemical shift (a singlet) is not affected by the nature of the R group either [19].

All these data suggest that compounds **1b**–**1e**, **1g**–**1h** and **1i** are isostructural with the symmetrical derivatives **1a** and **1f** whose dppm phosphorus atoms are equivalent and whose structure is proposed herein to contain a CO and a dppm ligands bridging the same edge which is also parallel to the μ_3-η^2-alkyne (see Scheme 2(A)). An alternative structure containing the bridging dppm ligand bonded to a different metal edge had been assumed previously for **1a**, in spite of the fact that the dppm phosphorus nuclei had been found to be equivalent in



Scheme 2. (A) Proposed structure for clusters **1a**–**1i** (see Scheme 1); (B) and (C) molecular structures of $[Ru_3\{\mu_3\text{-}\eta^2\text{-}C_2(CO_2Me)\}_2(PMe_2Ph)_2(\mu\text{-}CO)(CO)_7]$ [20] and $[Os_3(\mu_3\text{-}\eta^2\text{-}PhCCPh)(PBu)_3(\mu\text{-}CO)(CO)_6]$ [21], respectively; (D) structure of **1j** determined by X-ray diffraction studies [14].

the ^{31}P NMR spectrum [10]. This was done based on a supposed structure determined for the $C_2(CO_2Me)_2$ analogous derivative [16], which to our knowledge, has never been published, although the ^1H NMR data of this compound described later (no ^{31}P NMR data were reported) suggested indeed that the structure was asymmetrical. Nevertheless our proposal is supported in the first place by the fact that the X-ray molecular structure of the related compound $[Ru_3\{\mu_3\text{-}\eta^2\text{-}C_2(CO_2Me)_2\}(PMe_2Ph)_2(\mu\text{-}CO)(CO)_7]$ (Scheme 2(B)) [20] is symmetrical and similar to that proposed for clusters **1b**–**1i**, except that the PMe_2Ph ligands occupy equatorial positions in place of the dppm that we believe occupy axial positions, as a result of the presence of the bridging CO on the same edge. Furthermore, the ligand arrangement in one of the isomers of the related osmium cluster $[Os_3(\mu_3\text{-}\eta^2\text{-}PhCCPh)(\mu\text{-}dppm)(PBu_3)(\mu\text{-}CO)(CO)_6]$ whose molecular structure has been determined by an X-ray study (Scheme 2(C)) [21], is similar to that proposed for **1b**–**1i** with a dppm and a semi-bridging CO ligands supporting the same Os_2 edge. Further evidence for axial coordination of the dppm ligand in our compounds comes from the observation that axially coordinated dppm phosphorus chemical shifts usually appear at relatively high frequencies and that the $J_{P\text{–}P}$ are large (over 110 Hz), which is the case with our compounds (see Table 2) [21].

Secondly, the diyne containing cluster $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2CCPh)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7]$ (**1j**), whose molecular structure, reported recently [14], is as proposed previously for the $C_2(CO_2Me)_2$ derivative (Scheme 2(D)), seems to exhibit in solution same structure as in the solid state. The $^{31}P\{^1H\}$ NMR spectrum of this cluster (which has not been reported previously) is rather different from those of the other clusters of the series (see Table 2) and exhibits two doublets at δ 33.5 and 12.6 ($J_{P\text{–}P} = 40$ Hz), which we attribute tentatively to the dppm phosphorus nuclei bonded to the metal atoms that interact with the alkyne in a σ- and π-fashions, respectively, by comparison with the chemical shifts observed for clusters **1a**–**1i**. The characterisation of **1j** was ambiguous, because this compound exhibits a different $^{31}P\{^1H\}$ NMR spectrum after each purification by TLC. We also observed that its IR spectrum (Table 1) is slightly different from those of clusters **1a**–**1i**.

Strangely, however, the $^{31}P\{^1H\}$ NMR spectrum of the analogous cluster containing the Fc substituted asymmetrical alkyne, $[Ru_3(\mu_3\text{-}\eta^2\text{-}FcCCC{\equiv}CFc)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_7]$, reported recently [22], was described to consist of two singlets at δ 35.85 and 36.17 and the compound was proposed to exhibit same structure as **1j** (Scheme 2D), although the alternative symmetrical structure was not ruled out [20]. In our opinion the spectral data seem to be incomplete, since the spectra of Ru_3 and Os_3 clusters of this series, which contain non equivalent dppm phosphorus nuclei, exhibit $J_{P\text{–}P}$ varying from 30 to above 100 Hz. Considering that the phosphorus chemical shift values reported for this compound are very close to those observed for the asymmetrical clusters **1b**–**1d**, **1h** and **1i** (see Table 2) it appears that also in this case, instead of singlets, the spectrum may consist of two second-order AB type doublets. Therefore the structure of this asymmetrical compound is probably similar to those of clusters **1b**–**1d**, **1h** and **1i**.

*2.3. Decarbonylation of **1a**–**1f**: formation of the unsaturated clusters $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-}dppm)(CO)_7]$ (**2a**–**2f**)*

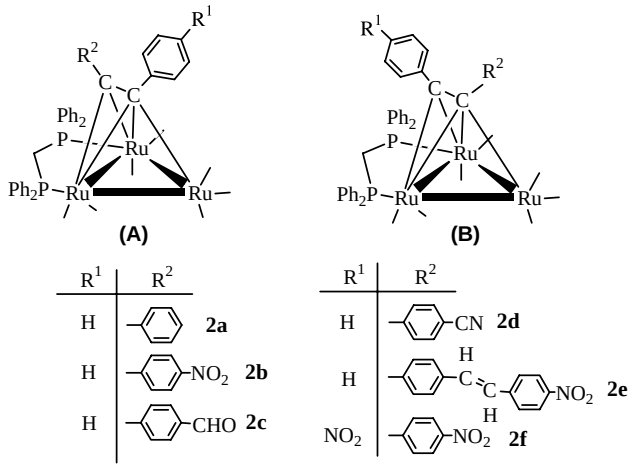
As described previously for cluster **1a**, heating purple compounds (**1b**–**1f**) in toluene at 70 °C for about 1 h under a stream of argon led to the formation of the unsaturated green compounds (**2b**–**2f**), which were obtained in yields varying from 76% to 88% after crystallisation from CH_2Cl_2/hexane (see Table 3 and Scheme 3). Compounds **1b**–**1f** were regenerated instantaneously upon bubbling CO through the solutions of the respective unsaturated species **2b**–**2f**, as previously described for **2a**.

In contrast, it was impossible to obtain the unsaturated products from the decarbonylation of compounds **1g**, **1h** and **1i**. Whereas **1g** ($PhCCC_6H_4$-4-OMe containing cluster) underwent decomposition above room temperature, **1h** ($FcCCC_6H_4$-4-NO_2 containing cluster) was stable at 70 °C, even after heating for 6 h, but raising the reaction temperature to 90 °C led to the

Table 3
Analytical and spectroscopic data for the $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(CO)_7]$ (**2a**–**2f**) derivatives

Cluster (% yield)	Elemental analyses Found (Calc.) %	IR[a] (ν_{CO})/cm^{-1}
$R^1 = H$, $R^2 = Ph$ (**2a**) (82%)	$C_{46}H_{32}O_7P_2Ru_3C$: 51.62(51.89); H: 3.09(3.03)	2055s, 1987vs, 1925m
$R^1 = NO_2$, $R^2 = Ph$ (**2b**) (85%)	$C_{46}H_{31}NO_9P_2Ru_3C$: 49.12(49.78); H: 2.92(2.82); N: 1.32(1.26)	2062s, 1993vs, 1929m
$R^1 = CHO$, $R^2 = Ph$ (**2c**) (88%)	$C_{47}H_{32}O_8P_2Ru_3C$: 51.47(51.65); H: 3.02(2.95)	2059s, 1991vs, 1927m
$R^1 = CN$, $R^2 = Ph$ (**2d**) (76%)	$C_{47}H_{31}NO_7P_2Ru_3C$: 51.72(51.80); H: 2.94(2.87); N: 1.36(1.29)	2225w (CN), 2058s, 1991vs, 1926w
$R^1 = CHCHC_6H_4\text{-}4\text{-}NO_2$, $R^2 = Ph$ (**2e**) (78%)	$C_{54}H_{37}NO_9P_2Ru_3C$: 53.39(53.51); H: 3.01(3.08); N: 1.22(1.16)	2063s, 1992vs, 1930m
$R^1 = NO_2$, $R^2 = C_6H_4\text{-}4\text{-}NO_2$ (**2f**) (86%)	$C_{46}H_{30}N_2O_{11}P_2Ru_3C$: 47.73(47.84); H: 2.74(2.62); N: 2.51(2.43)	2065s, 1993vs, 1929m

[a] Measured in CH_2Cl_2.



Scheme 3. Structures proposed for the two isomers of unsaturated clusters **2b**–**2e** ($R^1 = -NO_2$ (**2b**), –CHO (**2c**), –CN (**2d**), $-C_6H_4CHCHC_6H_4\text{-}4\text{-}NO_2$ (**2e**)).

formation of several unidentified species in minute amounts according to TLC. Thermolysis of **1i** ($PhCCC_6H_4\text{-}4\text{-}CNW(CO)_5$ containing cluster) only led to the unsaturated compound **2d** as a result of the dissociation of "$W(CO)_5$" possibly via scavenging of the free CO.

It is interesting to speculate about the relative stability of cluster **1h** with respect to CO loss. Formation of unsaturated $Ru_3(\mu_3\text{-}\eta^2\text{-alkyne})$ clusters containing the alkyne bonded in the perpendicular mode has been shown to be rather sensitive to the electronic density on the metal frame available for back donation to the alkyne in the unsaturated derivative. Thus, of the saturated compounds $[Ru_3(\mu_3\text{-}\eta^2\text{-PhCCPh})(CO)_{10}]$, $[Ru_3(\mu_3\text{-}\eta^2\text{-PhCCPh})(PPh_3)(CO)_9]$ and $[Ru_3(\mu_3\text{-}\eta^2\text{-PhCCPh})(dppm)(CO)_8]$, only the latter loses CO to give the unsaturated derivative [10b]. Therefore, formation and stabilisation of clusters **2b** and **2f** might be favoured by the electron withdrawing ability of one and two $-NO_2$ groups, respectively, on the alkyne (Scheme 3). In cluster **1h**, however, the effect of the $-NO_2$ group in the coordinated $FcCCC_6H_4\text{-}4\text{-}NO_2$ seems to be counteracted by that of the electron donating Fc group at the other end of the alkyne. Certainly, further investigation still needs to be carried out on these systems.

2.4. Characterisation of $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(CO)_7]$ (**2b**–**2f**)

The unsaturated clusters **2b**–**2f** were characterised by analytical and spectroscopic data (see Tables 2 and 3) and by comparison with the spectroscopic data reported for compound **2a**, whose structure was confirmed by an X-ray diffraction study [10]. These compounds exhibit IR spectra in the ν_{CO} region, which are very similar to that of **2a**, and ^1H NMR spectra, similar to those of the clusters from which they originated (**1b**–**1f**, see Table 2).

The $^{31}P\{^1H\}$ NMR spectrum of cluster **2f** containing the symmetrical alkyne $O_2N\text{-}4\text{-}C_6H_4CCC_6H_4\text{-}4\text{-}NO_2$ exhibits a singlet at δ 42.2, indicating that the two dppm phosphorus nuclei are equivalent and therefore that its structure is similar to that of cluster **2a**, which contains the alkyne bonded in a $\mu_2\text{-}\eta^2$-mode perpendicular to the Ru_2 edge supported by the dppm ligand on pseudo-equatorial coordination sites.

The $^{31}P\{^1H\}$ NMR spectra of compounds **2b**–**2e**, which contain asymmetrical alkynes indicated the presence of two isomers (A and B) in solution (see Table 2), as they exhibited two singlets, whose relative intensities and chemical shifts were sensitive to the nature of the substituent R^1 on the $R^1\text{-}4\text{-}C_6H_4CCPh$ coordinated alkyne. In the cases of compounds **2b**–**2d** (A:B = 1:3) only the highest frequency peak due to the least abundant isomer was sensitive to the electron withdrawing effect of R^1 [($\delta\Delta = \delta_{PA} - \delta_{PB}$/Hz, **2b** ($-NO_2$, 219) > **2c** (–CHO, 146) > **2d** (–CN, 134)]. For cluster **2e**, the influence of R^1 [$-C_6H_4CHCHC_6H_4\text{-}4\text{-}NO_2$, $\delta\Delta = 12$ Hz)] was minute and the isomer ratio A:B = 1:1 confirmed the electronic nature (rather than steric) of the effect. The structures of these two isomers, illustrated in Scheme 3, are thus proposed to differ with respect to the orientation of the

coordinated alkyne. Intuitively the structure of the major isomer (B) would be expected to contain the C_6H_4-4-NO_2 group directed towards the parallel Ru_2(dppm) edge, i.e. bonded to the least electron poor alkyne carbon, which is involved only in a π-interaction with the metal frame. Minor isomer A would contain the electron-withdrawing group bonded to the alkyne carbon, which also donates electron density to the cluster via a σ-interaction. The $–NO_2$ group could be expected to communicate better with the dppm phosphorus in isomer A than in B, due to their *transoid* orientation and this is indeed observed.

2.5. Synthesis and characterisation of $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7]$ (3a–3f)

The unsaturated compound **2a** has been shown previously to react rapidly with PhCCH and dppm to yield $[Ru_3\{\mu\text{-HCC(Ph)C(O)(Ph)CCPh}\}(\mu\text{-dppm})(CO)_6]$ and $[Ru_3(\mu_3\text{-}\eta^2\text{-PhCCPh})(\mu\text{-dppm})_2(CO)_6]$, respectively, which have been fully characterised [10a].

The reactions of the unsaturated green clusters **2a**–**2f** with a series of nucleophiles were investigated in an attempt to tune both the electron density in the metal frame and the electronic communication between the metal frame and the substituent on the coordinated alkynein the addition products.

Clusters **2a** and **2b** did not react with the nitrogenated Lewis bases pyridine, 2,2′-bipyridil and benzonitrile, at room temperature in CH_2Cl_2 or toluene, after 10h, even in the presence of an excess of the nucleophile, and upon heating at 50 °C, only decomposition products were detected on the TLC plates. In contrast, these clusters reacted rapidly with phenylisocyanide, to give a number of products, which could not be characterised. Best results were obtained from the reactions with PPh_3, PCy_3 and PPh_2-2-py.

Clusters **2a**–**2f** reacted rapidly with PPh_3 (one equivalent or a 2-fold excess) in CH_2Cl_2 or in toluene, at room temperature, to give the purple addition products **3a**–**3f** in yields above 90% after crystallisation. Elemental analyses (see Table 4) confirmed that these compounds resulted from the addition of a single PPh_3 molecule to **2a**–**2f**, and their IR spectra in the ν_{CO} region, although shifted to lower frequencies with respect to those of the saturated analogous compounds **1a**–**1f**, also exhibited a weak band in the bridging CO region. As in the case of the precursors **1a**–**1f**, only very small ν_{CO} shifts were observed in the spectra of **3a**–**3f** as the result of changing the substituent on the alkyne.

The reactions of clusters **2a** and **2b** with one equivalent of PPh_2-2-py and PCy_3 proceeded similarly to those with PPh_3, and gave after about 10 min at room temperature, analogous adducts, identified in situ by IR spectroscopy. However, these adducts reacted further if left in solution for longer periods of time to give several unidentifiable products according to the TLC.

The room temperature $^{31}P\{^1H\}$ NMR spectra of clusters **3a**–**3f** revealed two broad peaks around δ 15 and 42. Upon lowering the temperature to −90 °C, the spectrum of the PhCCPh containing cluster, **3a**, (in CD_2Cl_2) showed two sharp singlets at δ 47.6 and 41.9 (approximate intensities ratio = 3:1), due to the coordinated PPh_3, and two broad peaks at δ 17.2 and 16.8 due to two dppm ligands, thus indicating the presence of two isomers in solution that still undergo some fluxional process involving the dppm ligand. In contrast, the variable temperature spectra of cluster **3b**, which contains the asymmetrical alkyne $PhCCC_6H_4$-4-NO_2, indicated clearly that this compound exists in solution as a mixture of three isomers (of approximate ratio A:B:C = 5:5:1), as the two broad singlets due to the dppm and PPh_3 ligands in the room temperature spectrum separated into six well defined doublets and three singlets, respectively, at −90 °C (in CD_2Cl_2/CS_2) (see Fig. 1).

Attempts at growing crystals of species **3a**–**3f** were frustrated, as only needle-like crystals were formed in a variety of solvent systems, and therefore the structures proposed below for the isomers of **3a** and **3b** are only speculative, although they were based on the structures of the isomers of the analogous osmium clusters $[Os_3(\mu_3\text{-}$

Table 4
Analytical and spectroscopic data for the $[Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7]$ (**3a**–**3f**) derivatives

Cluster (% yield)	Elemental analyses Found (Calc.) %	IR[a] (ν_{CO})/cm^{-1}
R^1 = H, R^2 = Ph (**3a**) (94%)	$C_{64}H_{47}O_7P_3Ru_3C$: 57.72(57.92); H: 3.62(3.57)	2021w, 1999vs, 1957vs, 1812w
$R^1 = NO_2$, R^2 = Ph (**3b**) (95%)	$C_{64}H_{46}NO_9P_3Ru_3C$: 55.97(56.02); H: 3.34(3.38); N: 1.08(1.02)	2026m, 2004vs, 1963vs, 1912w, 1817w
R^1 = CHO, R^2 = Ph (**3c**) (92%)	$C_{65}H_{47}O_8P_3Ru_3C$: 57.32(57.61); H: 3.50(3.50)	2024m, 2001vs, 1960vs, 1910w, 1816w
R^1 = CN, R^2 = Ph (**3d**) (89%)	$C_{65}H_{46}NO_7P_3Ru_3C$: 57.32(57.74); H: 3.37(3.43); N: 1.08(1.04)	2226w (CN), 2024m, 1999vs, 1960vs, 1909w, 1815w
$R^1 = CHCHC_6H_4$-4-NO_2, R^2 = Ph (**3e**) (98%)	$C_{72}H_{52}NO_9P_3Ru_3C$: 58.78(58.66); H: 3.56(3.56); N: 1.01(0.95)	2025m, 2002vs, 1962vs, 1910w, 1817w
$R^1 = NO_2$, $R^2 = C_6H_4$-4-NO_2 (**3f**) (96%)	$C_{64}H_{45}N_2O_{11}P_3Ru_3C$: 53.99(54.24); H: 3.21(3.20); N: 1.99(1.98)	2028m, 2005vs, 1963vs, 1910w, 1820w

[a] Measured in CH_2Cl_2.

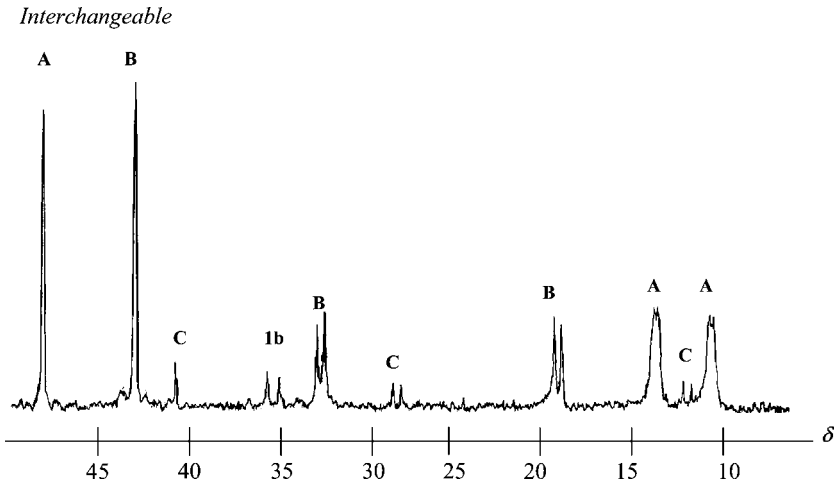


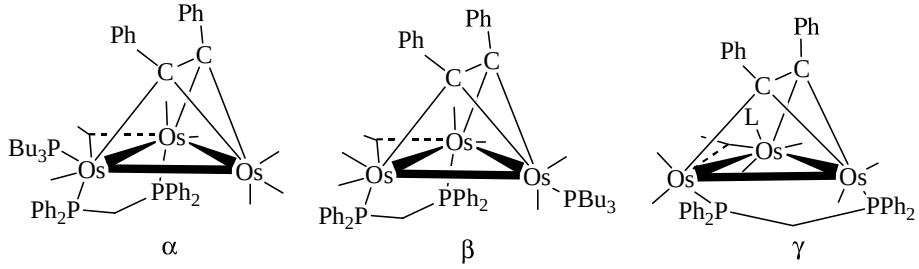
Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of cluster **3b** at −90 °C, showing the presence of three isomers A, B and C, and cluster **1b** present as an impurity.

η^2-PhCCPh)(μ-dppm)(L)(μ-CO)$(CO)_6$] (L = PBu_3, PPh_3, PMe_2Ph and $P(OMe)_3$) [21], which were established by a combination of X-ray diffraction and ^{31}P NMR spectroscopy studies. These compounds exist as a mixture of three inseparable isomers, whose structures are illustrated in Scheme 4. In isomer α, the dppm ligand is bonded axially to the same Os_2 edge that contains a semi-bridging CO, and the PR_3 ligand is coordinated to an Os atom that is also bonded to one of the dppm phosphorus atoms. The difference between this isomer and isomer β is that in the latter the PR_3 ligand is coordinated to the Os atom that is not bonded to the dppm. Isomer γ exhibits the alternative ligand arrangement that had been proposed for **1a**, with the CO and dppm bridging different Os edges, and with all phosphorus ligands occupying equatorial coordination sites on different Os atoms.

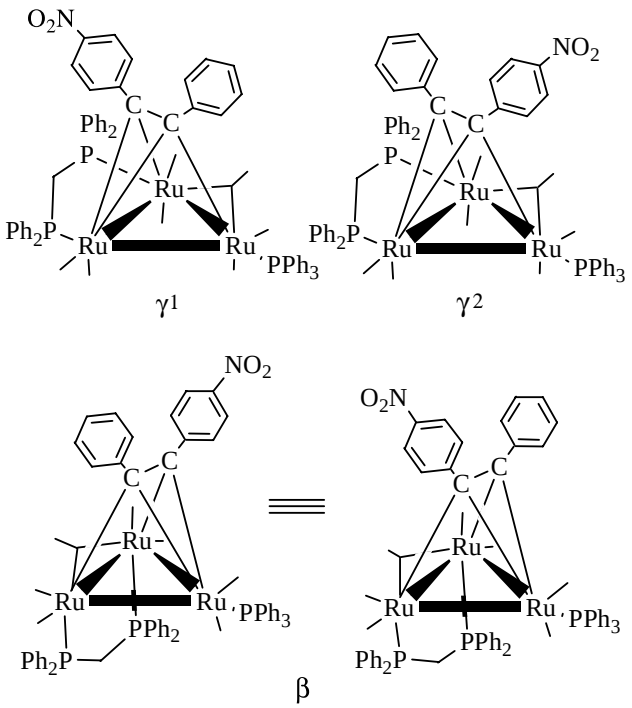
It was found that only isomers β and γ were obtained from the reactions of the unsaturated precursor [Os_3(μ$_3$-η^2-PhCCPh)(μ-dppm)$(CO)_7$] with PPh_3 or $P(OMe)_3$ in polar solvents, such as CH_2Cl_2, at room temperature, i.e. nucleophilic attack at the osmium centres bonded to the dppm ligand was disfavoured under these conditions [21].

A similar outcome is possible for the reactions of clusters **2a** and **2b** with PPh_3, which were investigated under the same conditions as described above for the osmium system. We therefore propose that the two isomers of cluster **3a** exhibit structures similar to those of isomers β (*symmetrical*) and γ (*asymmetrical*) of the osmium analogue shown in Scheme 4, with a PPh_3 in place of PBu_3 and L, respectively. Because the fluxional process involving the dppm ligand in cluster **3a** could not be frozen at −90 °C, the J_{P-P} between the phosphorus nuclei of this ligand could not be measured and it was therefore impossible to assign the chemical shifts observed to one or another structure. In any case, it is interesting that CO substitution for a PPh_3 in cluster **1a**, which exhibits a *symmetrical* structure, results in the stabilisation of both the "*symmetrical*" (β) and the "*asymmetrical*" (γ) structures, thus suggesting that the energy differences between the two structures is small.

Also in the case of cluster **3b**, we suggest that the three isomers exhibit one of the two structures, β or γ, for the same reason discussed above. As illustrated in Scheme 5, the two different orientations of the asymmetrical alkyne in structure β lead to identical structures, providing that the PPh_3 ligand occupies in the



Scheme 4. Structures of the isomers of [Os_3(μ$_3$-η^2-PhCCPh)(μ-dppm)(L)(μ-CO)$(CO)_6$] [L = PBu_3, PPh_3, PMe_2Ph and $P(OMe)_3$]. The molecular structures of isomers α and β of the PBu_3 derivative were determined by X-ray diffraction studies and the structure of isomer γ was proposed on the basis of its reactivity and ^{31}P NMR studies [21].



Scheme 5. Structures proposed for the isomers of **3b**.

two structures, either an axial site, or an equatorial site *transoid* to the phenyl group bearing the same 4-substituent X = H or $-NO_2$. In the case of structure γ though, the two different orientations of the asymmetrical alkyne lead to two different structures γ_1 and γ_2, as shown in Scheme 5. In the absence of further structural information, we do not feel comfortable to attribute the chemical shifts observed to the three structures proposed.

3. Experimental

All preparations, and manipulations were carried out under an atmosphere of argon. Starting materials were purchased from Aldrich and/or Strem and used without further purification. The alkynes were prepared as described in the literature [23,24]. Solvents were dried and distilled by standard procedures. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF254, 0.5 mm thickness). The progress of the reactions was monitored by analytical TLC (precoated plates, silica gel F254, 0.25 mm thick; Merck) and IR spectroscopy. All Ru_3-clusters were stored under inert atmosphere to avoid some decomposition observed in some compounds stored for long time in the solid state.

Infrared spectra were recorded on a Bomen (FT-IR Michelson) spectrophotometer between 2200 and 1600 cm^{-1} (ν_{CO}), $^{31}P\{^1H\}$ and ^1H NMR spectra on a Bruker AC 300P and/or Varian Gemini 300 spectrometers using, as references, 85% H_3PO_4 (external) for the former and $SiMe_4$ for ^1H. Elemental analyses were carried out at the Instituto de Química, UNICAMP.

3.1. Synthesis of precursors [PPN][Ru_3(CO)$_9$(μ-Cl)(RC CR)] (PPN 1a–1h)

Precursors **PPN1a**–**1h** were prepared as described in the literature [8c]. Spectroscopic data for **PPN1a** (coordinated alkyne: PhCCPh): IR (ν_{CO}(THF)/cm^{-1}): 2056 m, 2035 vs, 1985 vs, 1952m e 1920w. The spectra of **PPN1b** (PhCCC$_6$H$_4$-4-NO$_2$), **PPN1c** (PhCCC$_6$H$_4$-4-CHO), **PPN1d** (PhCCC$_6$H$_4$-4-CN), **PPN1e** (PhCCC$_6$H$_4$-CH=CHC$_6$H$_4$-4-NO$_2$), **PPN1f** (O$_2$N–C$_6$H$_4$CCC$_6$H$_4$-4-NO$_2$), **PPN1g** (PhCCC$_6$H$_4$-4-OCH$_3$), and **PPN1h** (Fc-CCC$_6$H$_4$-4-NO$_2$) are all very similar, with bands shifted by a maximum of ±6 cm^{-1} from those of **PPN1a**.

3.2. Preparation of clusters [Ru_3(μ$_3$-η^2-R^1-4-C$_6$H$_4$CCR^2)(μ-dppm)(μ-CO)(CO)$_7$] (1b–1h)

Clusters **1b**–**1h** were prepared by slight modification of a literature method [10] and obtained in yields varying from 50% to 77%, after crystallisation (Table 1).

Cluster **1i** [R^1 = –H and R^2 = C$_6$H$_4$-4-CN–W(CO)$_5$] was obtained by slow addition of a THF solution of freshly prepared [W(CO)$_5$THF] (from W(CO)$_6$, 14 mg, 0.04 mmol) to cluster **1d** (45 mg, 0.04 mmol) in THF (15 ml) [15]. The mixture was left under stirring for further 20 min. The solvent was then evaporated under vacuum and the product, purified by TLC (CH_2Cl_2/hexane, 1:1) to give compounds **1d** (11 mg, 25%) and **1i** (23 mg, 56%). Clusters **1a**–**1i** were characterised by elemental analyses, IR (Table 1), ^1H and ^{31}P NMR spectroscopy (Table 2).

3.3. Decarbonylation of (1b–1f): formation of the unsaturated clusters [Ru_3(μ$_3$-η^2-R^1-4-C$_6$H$_4$CCR^2)(μ-dppm)(CO)$_7$] (2b–2f)

Clusters **2b**–**2f** were obtained according to a literature method [10] in yields varying from 76% to 86%, after crystallisation (Table 2).

The following procedure described for the synthesis of cluster **2b** was carried out for the syntheses of **2c**–**2f** (Table 3). A wine coloured toluene solution (20 ml) of **1b** (20 mg, 0.02 mmol) was stirred at 80 °C for 90 min (until the colour had changed to green). The reaction was also monitored by TLC and IR spectroscopy in the ν_{CO} region. The product was purified by TLC (CH_2Cl_2/hexane, 2:3), recrystallised from the same solvent system and obtained in 85% yield. Clusters **2b**–**2f** were characterised by elemental analyses, IR (Table 2), ^1H and ^{31}P NMR spectroscopy (Table 2).

3.4. Attempts at decarbonylating 1g–1i

Treatment of cluster **1g** under the conditions described above only led to its decomposition, into various products in very small amounts, according to the TLC. Heating **1i** under the conditions described for the syntheses of **2b**–**2f** led to the formation of cluster **2d** which was obtained in 82% yield. Burgundy cluster **1h** was stable when heated under the same conditions, even after 6 h. Upon increasing the temperature to 90 °C, it underwent decomposition, after 10 h, into several unidentified species according to the TLC (CH_2Cl_2:hexane, 1:3).

3.5. Preparation of clusters [$Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7$] (3a–3f): general procedure

PPh_3 (0.025 mmol) was added as a solid to solutions of clusters **2a**–**2f** (0.025 mmol) in CH_2Cl_2 (10 ml). The colour of the solutions changed immediately from dark green to burgundy. After 15 min stirring, the volume of the solutions was reduced to about 1 ml and the products were purified by TLC, using CH_2Cl_2/hexane, 2:1 as eluent. Compounds **3a**–**3f** were recrystallised from the same solvent system and obtained in yields varying from 89% to 98% (Table 4). Clusters **3b**–**3f** were characterised by elemental analyses, IR (Table 3), ^1H and ^{31}P NMR spectroscopy (Table 2).

4. Conclusions

Systematic ^{31}P NMR studies of triruthenium μ_3-η^2-alkynyl clusters containing electronically symmetrical and asymmetrical alkynes [$Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(\mu\text{-CO})(CO)_7$] (**1**), [$Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(CO)_7$] (**2**), and [$Ru_3(\mu_3\text{-}\eta^2\text{-}R^1\text{-}4\text{-}C_6H_4CCR^2)(\mu\text{-dppm})(PPh_3)(CO)_7$] (**3**), and correlations with X-ray structural data of related compounds available in the literature made it possible to propose structures for these three series of clusters. ^{31}P NMR data for analogous clusters are scarce in the literature and structures for compounds related to saturated clusters **1** had been proposed based on the very few solid state structures determined by X-ray studies. However, our results clearly show that the distribution of CO and dppm ligands with respect to the μ_3-η^2-coordinated alkyne is sensitive both to the nature of the alkyne and to the presence of a PPh_3 in place of a CO ligand. Thus, whereas all clusters of series **1** exhibit a *symmetrical* structure in which a CO and a dppm ligands bridge the same edge which is also parallel to the μ_3-η^2-alkyne, saturated clusters of series **3**, which contain a PPh_3 ligand in place of a CO, exist in solution as mixtures of isomers of *symmetrical* and *asymmetrical* structures, the latter containing the dppm ligand on a different edge to that bridged by the CO ligand. The fact that the dppm phosphorus chemical shifts are sensitive to the alkyne electronic asymmetry made it possible to show that both *symmetrical* and *asymmetrical* clusters containing electronically asymmetrical alkynes exist in two isomeric forms, which differ with respect to the alkyne orientation. Furthermore, all clusters **2** exhibit a *symmetrical* structure in which the dppm and the alkyne, bonded in the perpendicular mode, bridge the same Ru_2 edge, however, the derivatives which contain asymmetrical alkynes also exist in solution as a mixture of two isomers which differ with respect to the orientation of the alkyne.

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