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C–H and C–C bond activations of terminal alkynes in the presence of a heteronuclear Ru_3Au cluster

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Dedicated to Professor Kenneth G. Caulton, on the occasion of his 70th birthday, in recognition of his many contributions to the field of organometallic chemistry.

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ABSTRACT

The reaction of compound $[Ru_3(CO)_{10}(\mu{-}Cl)(\mu{-}AuPPh_3)]$ (**1**) with terminal alkynes HC≡CR; (R = $C_6H_4{-}4{-}CH_3$, $C_6H_3{-}2,5{-}(CH_3)_2$, $C_6H_2{-}2,4,5{-}(CH_3)_3$, $C(CH_3) = CH_2$, $Si(CH_3)_3$), under very mild conditions yielded isostructural compounds $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CR)]$ (R = $C_6H_4{-}4{-}CH_3$ (**2**), $C_6H_3{-}2,5{-}(CH_3)_2$ (**3**), $C_6H_2{-}2,4,5{-}(CH_3)_3$ (**4**), $C(CH_3){=}CH_2$ (**5**), $Si(CH_3)_3$) (**6**)) respectively; where the alkynes suffer oxidative additions to the metallic fragment coordinating as acetylide groups in a $\mu_3{-}\eta^2{-}$perpendicular fashion by breaking the $C_{(sp)}$–H bond of the alkynes. The $AuPPh_3$ fragment remains without change in all compounds. All of these clusters have been characterized in solution by i.r. and n.m.r. spectroscopy and their structures have been established by single crystal X–ray diffraction studies.

1. Introduction

In the last three decades, the activation of C–H bonds of alkenes and alkynes promoted by transition-metal cluster complexes has been a major research theme in organometallic chemistry, as can be appreciated in the literature [1–7]. The alkyne–complexes obtained from these reactions have been considered as useful models for the chemisorption of small molecules on metal surfaces and as examples of reactions where carbon–carbon triple bond activation and reduction reactions occur [1]. Studies carried out so far involve both homo– and heteronuclear clusters [8,9], the potential advantage of this polynuclear compounds is related to the fact that several metal atoms linked together can provide specific sites of interaction between organic molecules and clusters [10]; besides the insertion of a different type of metal (heterometallic clusters) gives an inherit polarity to the heterometallic bond, which could direct and/or modify the substrate–catalyst interactions in catalytic processes for example in carbonylations [11], hydrogenations or HDS reactions of organic substrates [12].

To take advantage of this inherit polarity of the heterometallic bond in catalytic processes, the catalyst must be stable enough to produce the desire transformation in the substrate. It is well known that the carbonyl tetranuclear fragment $Ru_3(AuPPh_3)$ lacks of kinetic stability since easily transforms by breaking its Ru–Au and Au–P bonds [13], avoiding its possible use as catalyst. Therefore the substitution of carbonyl ligands in this cluster by diphosphines or acetylides enhances the metallic core stability [14–16].

Thus, the potential application of alkyne clusters in catalysis leads to the study of these systems, for example the synthesis of homo– and heteronuclear transition metal carbonyl cluster involving different types of main group heteroatoms, bonded to the metal core, have shown unique catalytic properties [11,17–21]. Several mixed Ru–Au metal clusters containing hydride or carbon atoms [22–25], thiolates [26], diphosphines [27] and alkynes [28–31] among other ligands [32,33] have been reported elsewhere. Besides, a novel dynamic process operating in the $[Fe_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CBu^t)]$ cluster has been

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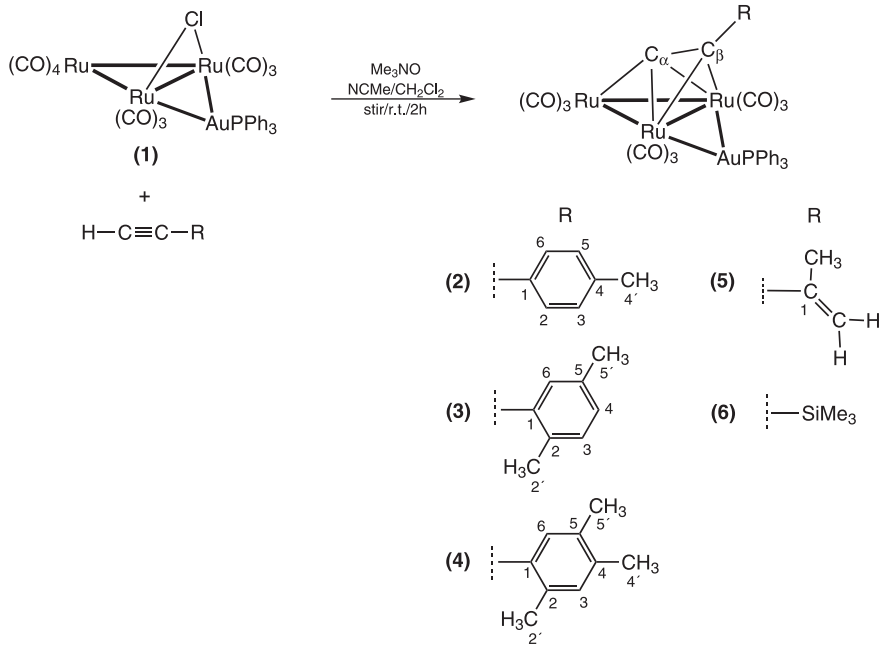

Scheme 1. Synthesis of the acetylide ruthenium–gold clusters **2**–**6**.

Table 1
^{1}H, ^{31}P{^{1}H}, ^{29}Si{^{1}H} and ^{13}C{^{1}H} NMR[a] data for compounds **2**–**6**.

Compound	^{1}H δ(ppm) J(Hz)	^{31}P{^{1}H} δ(ppm)	^{29}Si{^{1}H} δ(ppm) J(Hz)	^{13}C{^{1}H} δ(ppm) J(Hz)		[$C_\alpha + C_\beta$] {C_α–C_β}
2	7.50 (m, 15H, Ph) 7.44 ($H_{AA'}$, 2H, H(2,6)) 7.13 ($H_{BB'}$, 2H, H(3,5)) J_{AB}, $J_{A'B'}$ = 7.9, $J_{AA'}$ = 6.2, $J_{BB'}$ = 1.8 2.37 (s, 3H, CH_3(4′))	62.0 (s)	–	171.7 (s, C_α) 138.0 (s, C(4)) 134.1 (d, C_o) $^{2}J_{^{13}C-^{31}P}$ = 14.6 133.0 (s, C(1)) 131.2 (d, C_i) $^{1}J_{^{13}C-^{31}P}$ = 48.4	131.4 (d, C_p) $^{4}J_{^{13}C-^{31}P}$ = 2.3 131.1 (s, C(2, 6)) 129.5 (s, C(3, 5)) 129.3 (d, C_m) $^{3}J_{^{13}C-^{31}P}$ = 10.8 100.2 (s, C_β) 21.4 (s, CH_3(4′))	[271.9] {71.5}
3	7.50 (m, 15H, Ph) 7.21 (s, 1H, H(2)) 7.11 (d, 1H, H(5)) $^{3}J_{^{1}H-^{1}H}$ = 7.4 6.95 (d, 1H, H(4)) $^{3}J_{^{1}H-^{1}H}$ = 7.4 2.52 (s, 3H, CH_3(3′)) 2.29 (s, 3H, CH_3(6′))	61.9 (s)	–	172.2 (s, C_α) 135.6 (s, C(1)) 135.3 (s, C(3)) 134.9 (s, C(6)) 134.0 (d, C_o) $^{2}J_{^{13}C-^{31}P}$ = 14.5 133.3 (s, C(2)) 131.4 (d, C_p) $^{4}J_{^{13}C-^{31}P}$ = 2.1	131.2 (d, C_i) $^{1}J_{^{13}C-^{31}P}$ = 48.5 129.5 (s, C(4)) 129.3 (d, C_m) $^{3}J_{^{13}C-^{31}P}$ = 11.2 128.5 (s, C(5)) 96.3 (s, C_β) 22.3 (s, CH_3(5′)) 21.0 (s, CH_3(2′))	[268.5] {75.9}
4	7.51 (m, 15H, Ph) 7.17 (d, 1H, H(6)) 7.00 (d, 1H, H(3)) 2.49 (s, 3H, CH_3(2′)) 2.25 (s, 3H, CH_3(4′)) 2.20 (s, 3H, CH_3(5′))	62.5 (s)	–	171.7 (s, C_α) 136.5 (s, C(1)) 135.3 (s, C(5)) 134.3 (s, C(4)) 134.0 (d, C_o) $^{2}J_{^{13}C-^{31}P}$ = 14.6 133.8 (s, C(6)) 132.5 (s, C(2)) 131.3 (d, C_p) $^{4}J_{^{13}C-^{31}P}$ = 2.3	131.3 (d, C_i) $^{1}J_{^{13}C-^{31}P}$ = 48.4 131.0 (s, C(3)) 129.2 (d, C_m) $^{3}J_{^{13}C-^{31}P}$ = 11.5 96.5 (s, C_β) 22.1 (s, CH_3 (2′)) 19.5 (s, CH_3 (4′)) 19.3 (s, CH_3 (5′))	[268.3] {75.2}
5	7.47 (m, 15H, Ph) 5.26 (s, 1H, CH_{2cis}) 5.14 (m, 1H, CH_{2trans}) $^{4}J_{^{1}H-^{1}H}$ = 1.7 2.15 (s, 3H, CH_3)	61.7 (s)	–	172.9 (s, C_α) 139.0 (s, C(1)) 134.0 (d, C_o) $^{2}J_{^{13}C-^{31}P}$ = 14.6 131.3 (d, C_p) $^{4}J_{^{13}C-^{31}P}$ = 2.3	131.0 (d, C_i) $^{1}J_{^{13}C-^{31}P}$ = 48.3 129.2 (d, C_m) $^{3}J_{^{13}C-^{31}P}$ = 10.8 117.9 (s, CH_2) 102.7 (s, C_β) 26.7 (s, CH_3)	[275.6] {70.2}
6	7.47 (m, 15H, Ph) 0.32 (s, 9H, CH_3) $^{2}J_{^{1}H-^{29}Si}$ = 6.6 $^{2}J_{^{1}H-^{29}Si}$ = 13.2 $^{1}J_{^{1}H-^{13}C}$ = 119.9 $^{1}\Delta^{13/12}C$ = −1.1 ppb	62.3 (s)	0.8 (s) $^{2}J_{^{29}Si-^{1}H}$ = 6.6 $^{2}J_{^{29}Si-^{1}H}$ = 13.2	184.5 (s, C_α) 134.0 (d, C_o) $^{2}J_{^{13}C-^{31}P}$ = 14.6 131.3 (d, C_p) $^{4}J_{^{13}C-^{31}P}$ = 2.3	131.2 (d, C_i) $^{1}J_{^{13}C-^{31}P}$ = 48.4 129.2 (d, C_m) $^{3}J_{^{13}C-^{31}P}$ = 10.8 83.0 (s, C_β) 1.6 (s, 3C, CH_3)	[267.5] {101.5}

[a] Obtained at r. t. in $CDCl_3$. (s) singlet, (d) doublet, (m) multiplet, *o*, *ortho*; *p*, *para*; *m*, *meta*; *i*, *ipso*.

described, which involves the reversible rupture of a Au–Fe/Au–$C_{(acetylide)}$ bonds [34]. Examples like this may produce useful information about bond cleavage that take place between the metallic fragment and organic substrate in catalytic reactions.

Despite all cluster reactions involving terminal alkynes that have been described [8,35]; there are some examples of Ru–Au tetranuclear complex with this type of ligands [36]. The methods to produce the desire Ru_3Au–Acetylide clusters mainly have been based on reactions between $[Ru_3(CO)_{12}]$ or $[Ru_3(CO)_{10}(NCMe)_2]$ and an Au–alkynyl ligand [15,16] or between the hydride acetylide ruthenium cluster and a suitable Au fragment as $AuClPPh_3$ [29] or $[AuPPh_3]_3O^+$ [37]. Since the major previously reported synthetic method to prepare Ru_3Au acetylide complexes involves the preparation of a suitable gold–alkynyl precursor followed by a reaction with the Ru_3 homonuclear cluster [15,16,27,38,39], this prevents its wide use to produce this type of compounds. Therefore, in an effort to expand the available information on these systems, in this paper we report the synthesis and characterization of five new tetranuclear heterometallic ruthenium–gold clusters complexes containing acetylide ligands that arise from the cleavage of the $C_{(sp)}$–H bonds of terminal alkynes: $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CR)]$ (R = C_6H_4–4–CH_3 (**2**), C_6H_3–2,5–$(CH_3)_2$ (**3**), C_6H_2–2,4,5–$(CH_3)_3$ (**4**), $C(CH_3){=}CH_2$ (**5**), $Si(CH_3)_3$) (**6**)). All compounds were prepared under mild conditions by the *in situ* reaction of compound $[Ru_3(CO)_{10}(\mu\text{–}Cl)(\mu\text{–}AuPPh_3)]$ (**1**) and 1–etynyl–2–methylbenzene, 1–etynyl–2,5–dimethylbenzene,1–etynyl–2,4,5–trimethylbenzene, 2–methyl–1–buten–3–yne or trimethylsilylacetylene respectively. All synthesized compounds were characterized in solution by Infrared and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy. Full assignment of carbon atoms for all compounds was accomplished by 2–D heteronuclear correlation experiments. The molecular structures of all compounds in the solid state were determined by single crystal X–ray diffraction studies.

2. Results and discussion

Treatment of a CH_2Cl_2 solution of $[Ru_3(CO)_{10}(\mu\text{–}Cl)(\mu\text{–}AuPPh_3)]$ (**1**), prepared *in situ* as previously described [26] with an excess of the appropriate terminal alkyne at room temperature (r. t.) for 2 h in the presence of Me_3NO as activating agent, leads to the formation of the new clusters $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CR)]$ (R= C_6H_4–4–CH_3 (**2**), C_6H_3–2,5–$(CH_3)_2$ (**3**), C_6H_2–2,4,5–$(CH_3)_3$ (**4**), $C(CH_3){=}CH_2$ (**5**), $Si(CH_3)_3$) (**6**)) respectively in moderated yields (Scheme 1), In the case of methylated aryl series small amounts of isolobal compounds were observed, in which the $AuPPh_3$ fragment is replaced by a hydride ligand. In each reaction the main product is obviously derived from the $C_{(sp)}$–H bond cleavage in every alkyne and the substitution of the chlorine atom in the parent cluster. We employed different substituents: a series of variously methylated aryl derivatives, an olefinic fragment and a silicon group, to see if any steric or electronic inductive effect on the triple bond towards the reactivity of the heteronuclear cluster could be observed.

The symmetry of the i.r. spectra of all complexes is similar to those of the previously reported compounds $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CBu^t)]$ [29] and $[Os_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CPh)]$ [30] (see experimental section). All compounds have isolobal structures to the well known trinuclear hydride acetylide complexes $[Ru_3(CO)_9(\mu\text{–}H)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CR)]$ (R = Bu^t, $SiMe_3$, $SiPh_3$ [8], and C_6H_4–4–CH_3, C_6H_3–2,5–$(CH_3)_2$, C_6H_2–2,4,5–$(CH_3)_3$ (this work, see experimental section). There was no evidence of any influence of the substituent in the alkyne, that affects the CO stretch frequency, but the presence of a gold atom instead of the hydride ligand on the metallic skeleton indeed lowers the CO stretching frequencies.

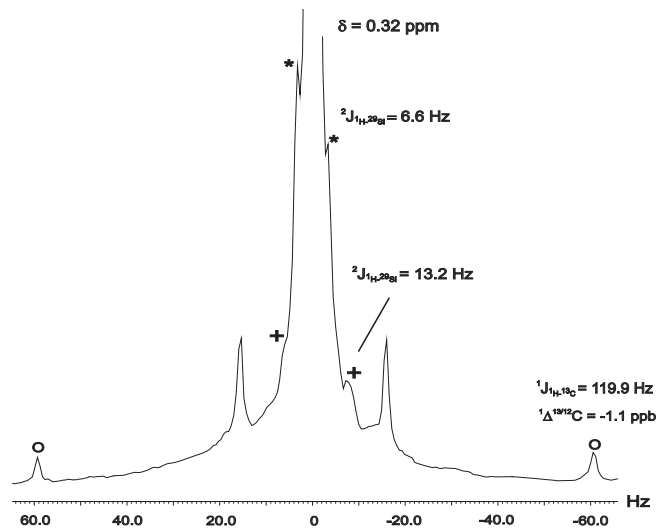

Fig. 1. ^1H NMR spectrum in the methyl region for compound **6**.

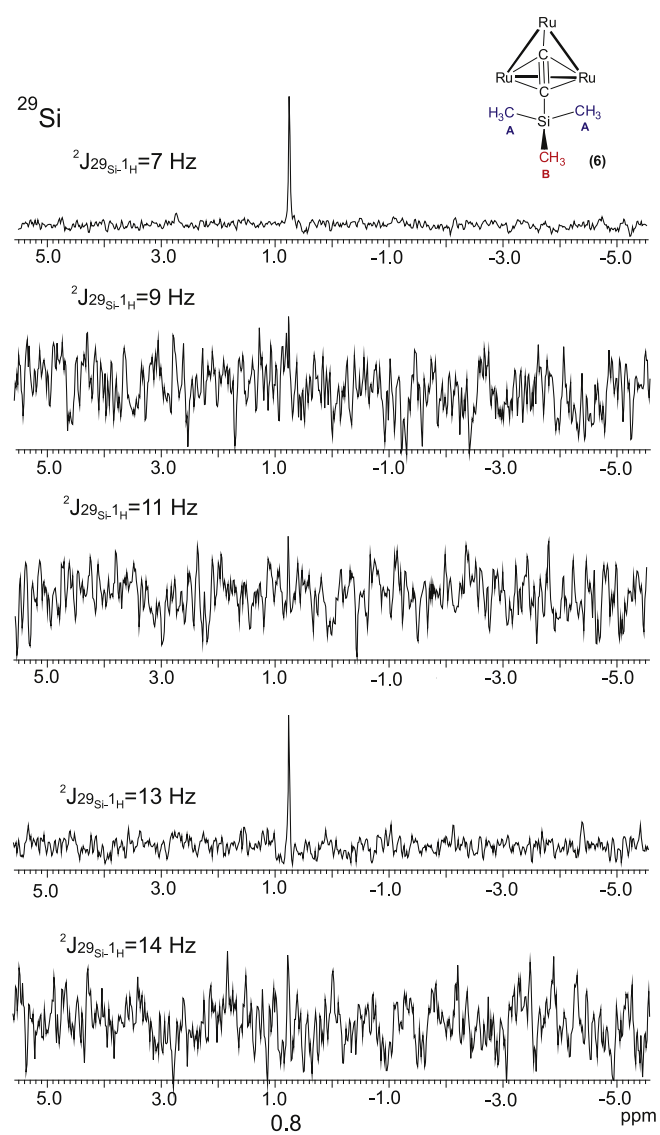

Fig. 2. ^{29}Si NMR spectra for **6**. CO and $AuPPh_3$ groups in the structure have been omitted for clarity.

The NMR spectroscopic data for compounds **2**–**6** are given in Table 1. All spectra were obtained at r. t. in $CDCl_3$. The $^{31}P\{^1H\}$ NMR spectra of all compounds showed singlet signals between 61.9 and 62.5 ppm, indicating that the gold phosphine group remain coordinated to the ruthenium cluster. Chemical shifts are similar to those described for other clusters containing a μ–$AuPPh_3$ bridge group [24,25]. The change of substituents in the acetylide fragment, did not affect the ^{31}P chemical shift.

The ^1H NMR spectrum for compound **2** showed two signals at 7.44 and 7.13 ppm, belonging to the characteristic AA'BB' system of the *p*–Me phenyl ring, the reported coupling constants were determined using a simulation NMR program [40]. The proton NMR spectra for compounds **3** and **4** showed the characteristic signals for substituted phenyl rings. The ^1H NMR spectrum for compound **5** showed a multiple signal at 5.14 ppm coupled to the methyl group to four bonds in a zig–zag mode; this signal was assigned to the CH_{2tras} and corroborated by a 2D–NOESY experiment. In the ^1H NMR spectrum for compound **6** a singlet at 0.32 ppm was observed and it was assigned to the methyl groups in the silyl fragment (Fig. 1); this signal showed a set of satellites caused by the coupling with ^{13}C nuclei with a $^1J_{^1H-^{13}C}$ coupling of 119.9 Hz. This set of satellites are unsymmetrically centered around the signal, which is characteristic for an isotopomeric effect $^1\Delta^{13/12}C$ (secondary isotope effects on the nuclear shielding of a signal), the value found was $^1\Delta^{13/12}C = -1.1$ ppb, in which the negative sign denotes a low frequency shift with respect to the lighter isotope [41]. Also, it was possible to observed another pair of satellites assigned to the coupling with the ^{29}Si nuclei, with a $^2J_{^1H-^{29}Si} = 6.6$ and 13.2 Hz, with relative intensities of 2:1 (6.6:13.2 Hz).

To corroborate the assignment and the values of this ^1H–^{29}Si coupling constants, we carried out several ^{29}Si NMR experiments changing the values of the coupling constant to acquire each of the ^{29}Si spectrums, (Fig. 2). We found that using $^2J_{^1H-^{29}Si}$ of 7.0 and 13.0 Hz the intensity of the silicon signal is maximized, confirming the values found in the ^1H spectrum. This can be explained on the magnetically nonequivalent methyl groups, bonded to the Si atom, two of them equal to each other (CH_{3A}) and different to the third one (CH_{3B}) (see structure in Fig. 2).

The $^{13}C\{^1H\}$ NMR spectra of compounds **2**–**6** showed the characteristic chemical shifts for C_α and C_β (acetylide carbons). The $\delta(C_\beta)$ is shifted to higher frequencies in the silyl heteronuclear compounds respect to their isolobal analogs with R = $SiMe_3$ or $SiPh_3$, while the $\delta(C_\alpha)$ remains almost invariable [8]. Also, $\delta(C_\alpha) + \delta(C_\beta)$ and $\delta(C_\alpha) - \delta(C_\beta)$ values have been proposed to be related to the total charge alteration and the polarization of the C≡C triple bond respectively [2]. In our compounds, we found that the polarization of the acetylide C–C bond follow the tendency **6** > **3** > **4** > **2** > **5**; with compounds **5** and **6** showing the largest $\Delta\Delta\delta$

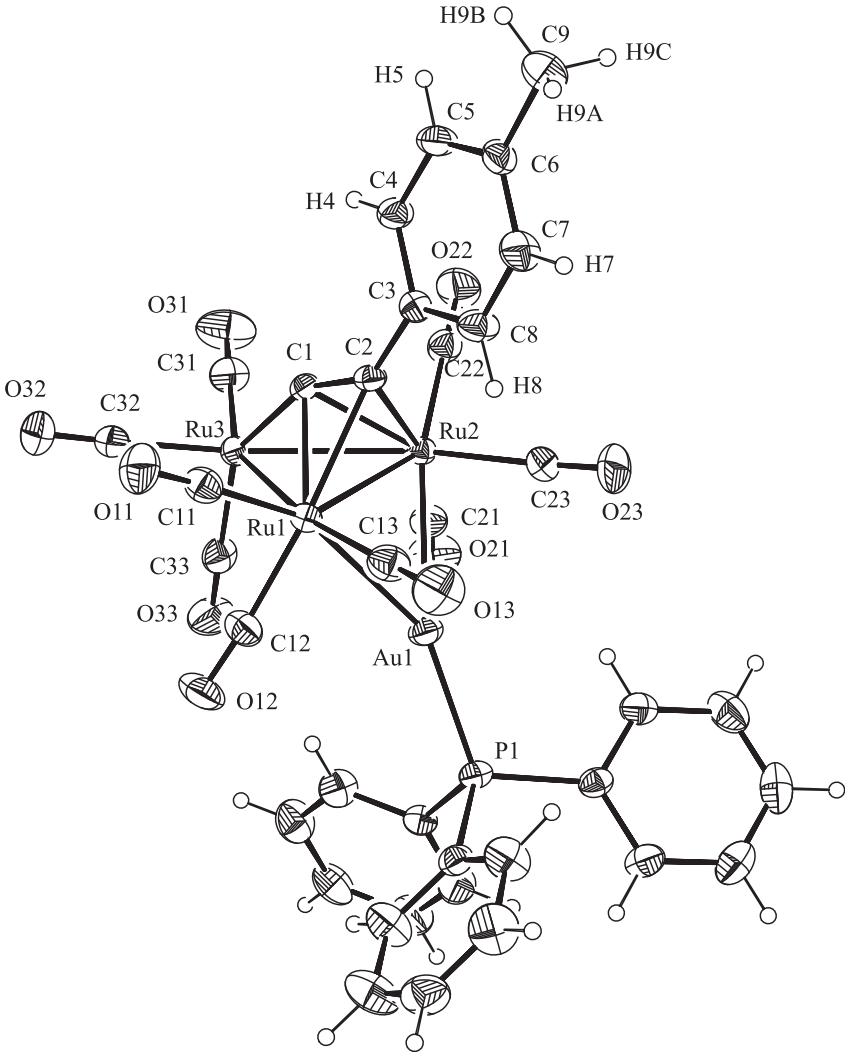

Fig. 3. ORTEP view of compound **2** (30% probability).

(31.3 ppm). The fact that the compound **5** has the lowest polarization on the triple bond could be associated to a delocalized electronic effect due to the presence of the C=C bond substituent. This is supported by the charge alteration over the triple bond assumed to be evaluated by the $\delta(C_\alpha) + \delta(C_\beta)$ value, since compound **5** shows the largest value of all compounds. This fact could be related to an electronic inductive effect of the substituents.

2.1. X-ray diffraction studies

Single crystal X–ray diffraction studies were carried out to confirm the solid state structures of all synthesized compounds and to verify that there were no important structural differences in the described complexes. ORTEP diagrams of the structures are shown in Figs. 3 to 7 and Table 2 collects some selected bond lengths and angles. Compound **3** contains two crystallographically independent molecules in the asymmetric unit; both are essentially identical and only one of the two molecules is shown in Fig. 4. All compounds have a "butterfly" metal framework array with the gold atom occupying a wing–tip position. No significant differences in bond distances and angles in compounds **2** to **6** and related complexes $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CBu^t)]$ [29], $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CFc)]$ [28] were observed. Similarly to compound $[Ru_3(CO)_{10}(\mu\text{–}AuPPh_3)(\mu\text{–}Cl)]$ [13] and some other ruthenium–gold clusters [24,28,29] the $AuPPh_3$ fragment is symmetrically coordinated bridging the largest Ru–Ru bond (Ru(1)–Ru(2) = 2.8415 Å av.). It is also worth noticing that this average distance is smaller than those observed in other tetranuclear ruthenium–gold clusters containing a μ_3–SBu^t (2.950(1) Å) [32] or μ_3–PPh (3.002(6) Å) [33] even though they have the same metal framework. Compounds **6** and **4** have larger Ru(1)–Ru(2) distances (2.8534(9) and 2.8507(11) Å respectively) than compounds **5**, **3** and **2**, [2.8331(6), 2.8416 av. and 2.8287(5) Å respectively]. Also, these bond distances are equal or slightly shorter than the "normal" Ru–Ru bond (2.854 Å av.) in $[Ru_3(CO)_{12}]$, while in the cluster $[Ru_3(CO)_{10}(\mu\text{–}Cl)(\mu\text{–}AuPPh_3)]$ (**1**) the doubly bridged Ru–Ru bond (2.8742(6) Å) being the largest of all [13]. The other two Ru–Ru distances, Ru(2)–Ru(3) and Ru(3)–Ru(1) [2.8088 and 2.8070 Å av. respectively] are the shortest ones, which could be related to a higher polarization in the coordinated acetylide fragment as mentioned previously. The phosphine ligand is terminally attached to the gold atom with a P(1)–Au(1) average distance of 2.296 Å. All the C(1)–C(2) distances (range from 1.302(7) to 1.330(14) Å) in the acetylide fragments are closer to a C–C double bond distance (C_{sp}–C_{sp} 1.21 Å; $C_{sp}2$–$C_{sp}2$ 1.34 Å; $C_{sp}3$–$C_{sp}3$ 1.53 Å [42]) reflecting the change in hybridization of these carbons upon coordination.

The Ru(3)–C(1)–C(2) angles are in the range of 153.3(4) – 155.6(8)°, while the C(1)–C(2)–C(3) angles for compounds **2**;141.0(5)°, **3**;145.5(5)° and 143.5(5)°, **4**;144.4(4)° and **5**; 143.1(6)° and C(1)–C(2)–Si(1) for **6**;144.0(8)°; both groups of angles are essentially the same than the corresponding values for $[Ru_3(CO)_9(\mu\text{–}AuPPh_3)(\mu_3\text{–}\eta^2\text{–}\perp\text{–}C{\equiv}CBu^t)]$ [29] and $[Ru_3(CO)_9(\mu\text{–}H)$

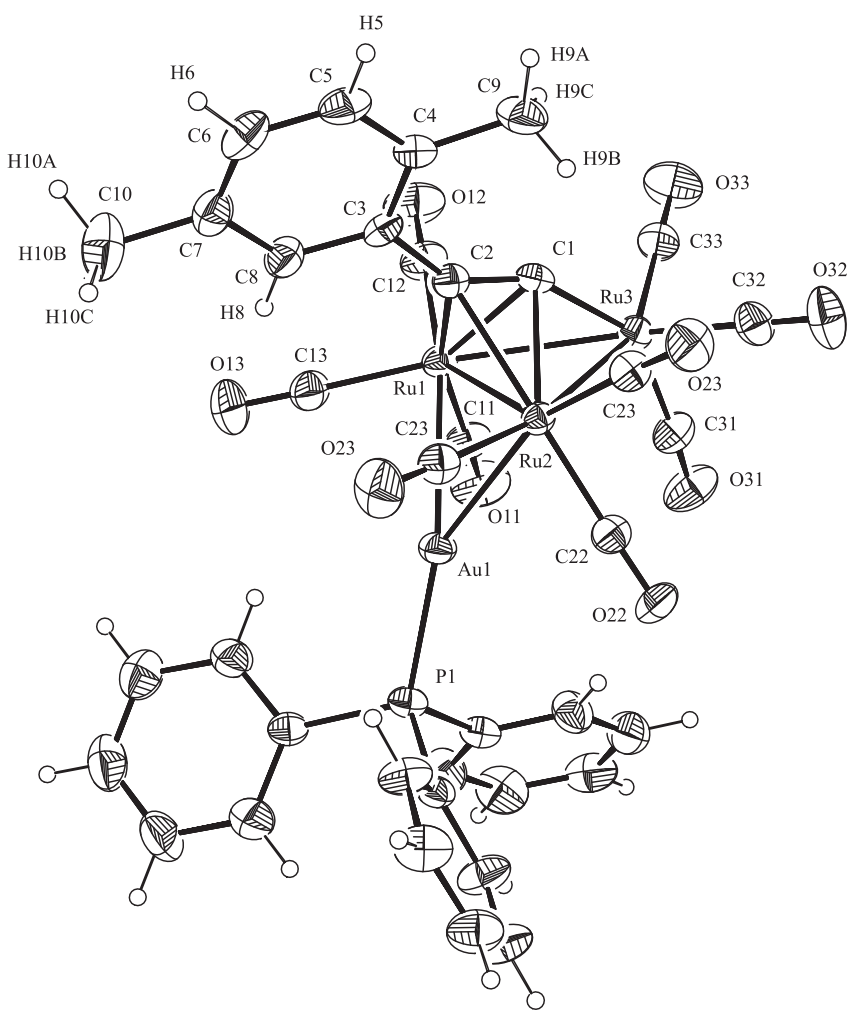

Fig. 4. ORTEP view of compound **3** (30% probability).

(μ_3–η^2–⊥–C≡CR)] [8]. The trend observed in C(1)–C(2)–R angles among compounds $\mathbf{3}_{(1)} \cong \mathbf{4} \cong \mathbf{6} > \mathbf{5} > \mathbf{2}$ could be associated with a decrease in size of the substituent. The dihedral angles formed by the two planes [Ru(3)–Ru(1)–Ru(2) and Ru(1)–Ru(2)–Au(1)] for the heteronuclear butterfly core, are in the range of 110.30(2) to 121.28(1)°, with the $SiMe_3$ substituted acetylide showing the lowest value; this is probably due to its inherent hindrance properties. On the other hand, the type of substituents on C(2) (C_β), does not affect the interline angle between C(1)–C(2) and Ru(1)–Ru(2) with an average of 89.1°. No significant intermolecular short contacts were found in any crystal packing of collected compounds.

3. Conclusions

The study of tetraheteronuclear ruthenium–gold clusters of general formula [$Ru_3(CO)_9$(μ–$AuPPh_3$)(μ_3–η^2–⊥–C≡CR)] shows that change in the substituents on the terminal alkynes does not significantly affect either the spectroscopic data or the main skeletal fragments of these clusters in the solid state. However, the ^{13}C NMR data shows that there is some degree of polarization of the acetylide C–C bond being the lowest in compound **5**, which could be associated to a delocalized electronic effect due to the unsaturated substituent.

The synthesis of this type of compounds is a clear example of the ease of activation of $C_{(sp)}$–H and $C_{(sp)}$–$C_{(sp)}$ bonds in alkynes promoted by a heterometallic ruthenium–gold cluster, through the rupture of the C–H bond and the re–hybridization of the acetylenic carbon atoms, establishing a simple synthetic route to this well–known class of compounds.

On the other hand, the well known thermodynamically stability of the $Ru_3(AuPPh_3)(C_2R)$ fragment was confirm since no decomposition in solution or in the solid state were observed for all compounds; this can be exploited, as mention before, in future potential catalytic applications as hydrogenation or HDS processes.

4. Experimental section

4.1. General procedures and materials

All reactions were carried out under nitrogen atmosphere. Solvents were dried prior to use by standard techniques and trimethylamine *N*–oxide dihydrate was sublimed several times in high-vacuum to remove water. All chemicals were supplied by Aldrich Company except chloro(triphenylphosphine)gold(I) which was supplied by Strem Chemicals, all reagents were used without further purifications. Commercial TLC plates (silica gel 60 F254) were used to monitor the progress of the reactions. Infrared spectra for all compounds were recorded in KBr pellets on a GX PERKIN Elmer 2000 FT–IR instrument. NMR spectra were measured on a JEOL Eclipse 400, JEOL GSX-270 and VARIAN 400 spectrometers in $CDCl_3$, with ^1H, ^{13}C and ^{29}Si spectra relative to $SiMe_4$, and ^{31}P spectra relative to 85% aq. H_3PO_4. Mass spectra were recorded at CINVESTAV–México (HR–LC 1100/MSD TOF Agilent Technology equipment). Compound **1** was prepared accordingly to published procedure [26].

4.2. General procedure for the synthesis of compounds [$Ru_3(CO)_9$(μ–$AuPPh_3$)(μ_3–η^2–⊥–C≡CR)] (R = C_6H_4–4–CH_3 (**2**), C_6H_3–2,5–$(CH_3)_2$ (**3**), C_6H_2–2,4,5–$(CH_3)_3$ (**4**), C(CH_3)=CH_2 (**5**), Si$(CH_3)_3$) (**6**))

To the solution of [$Ru_3(CO)_{10}$(μ–Cl)(μ–$AuPPh_3$)] (**1**) was added "*in situ*" an excess of the corresponding alkyne and 1.5 equivalent amount of dry Trimethylamine *N*–oxide, $(CH_3)_3NO$. Every reaction mixture was stirred for 2 h. The solvent was removed under low pressure and the resulting residue was redissolved in a minimum amount of chloroform and separated by TLC (eluent: hexane–-chloroform (80:20 v/v).

4.3. [$Ru_3(CO)_9$(μ–$AuPPh_3$)(μ_3–η^2–⊥–C=CR)] (R = C_6H_4–4–CH_3) (**2**)

The above procedure was employed for the preparation of **2**. The following compounds were used: [$Ru_3(CO)_{10}$(μ–Cl)(μ–$AuPPh_3$)] (**1**) (50.0 mg, 0.050 mmol), 1-etynyl-2-methylbenzene (16 mg; 0.111 mmol) and $(CH_3)_3NO$, (6 mg, 0.080 mmol). The first band was identified as traces of starting material, the second band was identified as compound [$Ru_3(CO)_9$(μ–H)(μ_3–η^2–⊥–C≡CC_6H_4–4–CH_3)] Yield: (yellow solid, 4 mg, 12%). ^1H NMR in $CDCl_3$ at 298 K: 7.46 (d, 2H, H(2,6), ^3J = 7.5 Hz), 7.16 (d, 2H, H(3,5), ^3J = 7.5 Hz), 2.38 (s, 3H, CH_3(4′)), −20.51 (s, 1H, Ru–H–Ru). IR ν(CO): 2097(w), 2073(m), 2053(m), 2022(vs), 1986(w) cm^{-1}. The sixth band corresponds to compound [$Ru_3(CO)_9$(μ–$AuPPh_3$)(μ_3–η^2–⊥–C≡CC_6H_4–4–CH_3)] (**2**). Yield: (yellow solid, 16 mg, 32%). HR–MS (ESI–TOF); $[MH]^+$ for ($C_{36}H_{23}O_9PRu_3Au$) calcd 1132.7870, found +1132.7862. IR ν(CO): 2072 (m), 2053 (sh), 2033 (vs), 2004 (s), 1991 (sh), 1985 (s), 1959 (s), 1943 (sh) cm^{-1}. The remaining bands were not studied because they did not contain coordinated ligands accordingly to their ^1H NMR spectrums.

4.4. [$Ru_3(CO)_9$(μ–$AuPPh_3$)(μ_3–η^2–⊥–C≡CR)] (R = C_6H_3–2,5–$(CH_3)_2$) (**3**)

The general procedure was employed for the preparation of **3**. The following compounds were used: [$Ru_3(CO)_{10}$(μ–Cl)(μ–$AuPPh_3$)] (**1**) (50.0 mg, 0.050 mmol), 1-etynyl-2,5-dimethylbenzene (18 μl;

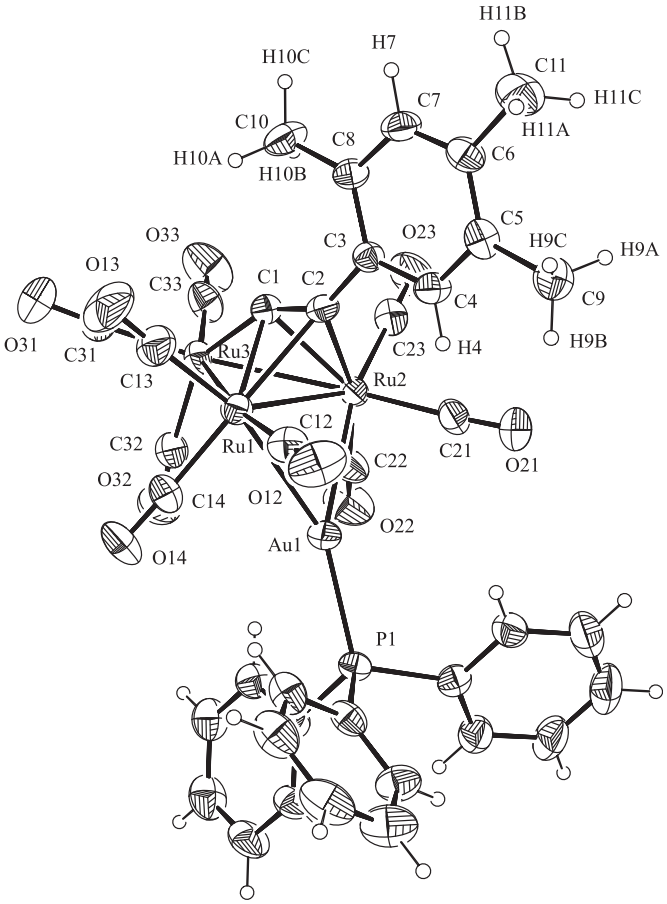

Fig. 5. ORTEP view of compound **4** (30% probability).

0.130 mmol) and $(CH_3)_3NO$, (6 mg, 0.080 mmol). The first band was identified as traces of starting material, the second band was identified as compound $[Ru_3(CO)_9(\mu{-}H)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CC_6H_4{-}2,5{-}(CH_3)_2)]$ Yield: (yellow solid, 3.2 mg, 9%). ^{1}H NMR in $CDCl_3$ at 298 K: 7.26 (s, 1H, H(6)), 7.16 (d, 1H, H(3), $^3J = 7.7$ Hz), 7.04 (d, 1H, H(4), $^3J = 7.7$ Hz), 2.52 (s, 3H, $CH_3(5')$), 2.34 (s, 3H, $CH_3(2')$), −20.37 (s, 1H, Ru–H–Ru). IR ν(CO): 2071 (m), 2052 (sh), 2030 (vs), 1990 (s, br), 1968 (sh), 1959 (sh) cm^{-1}. The fifth band corresponds to compound $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CC_6H_4{-}2,5{-}(CH_3)_2)]$ (**3**). Yield: (yellow solid, 11 mg, 22%). HR–MS (ESI–TOF); $[MH]^+$ for $(C_{37}H_{25}O_9PRu_3Au)$ calcd 1146.8026, found +1146.8028. IR ν(CO): 2071(m), 2030(vs), 1987(s, br), 1961(sh) cm^{-1}. The remaining bands were not studied because they did not contain coordinated ligands accordingly to their ^{1}H NMR spectrums.

4.5. $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CR)]$ ($R = C_6H_2{-}2,4,5{-}(CH_3)_3$) (**4**)

The general procedure was employed for the preparation of **4**. The following compounds were used: $[Ru_3(CO)_{10}(\mu{-}Cl)(\mu{-}AuPPh_3)]$ (**1**) (50.0 mg, 0.050 mmol), 1-etynyl-2,4,5-trimethylbenzene (35 μl; 0.276 mmol) and $(CH_3)_3NO$, (6 mg, 0.080 mmol). The first band was identified as traces of starting material, the second band was identified as compound $[Ru_3(CO)_9(\mu{-}H)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CC_6H_4{-}2,4,5{-}(CH_3)_3)]$ Yield: (yellow solid, 4.5 mg, 13%). ^{1}H NMR in $CDCl_3$ at 298 K: 7.19 (s, 1H, H(6)), 7.03 (s, 1H, H(3)), 3.73 (s, 3H, $CH_3(2')$), 2.48 (s, 3H, $CH_3(4')$), 2.26 (s, 3H, $CH_3(5')$), −20.37 (s, 1H, Ru–H–Ru). IR ν(CO): 2096(m), 2068 (vs), 2049(vs), 2013(vs), 1983(s) cm^{-1}. The fifth band corresponds to compound $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CC_6H_2{-}2,4,5{-}(CH_3)_3)]$ (**4**). Yield: (yellow solid, 15 mg, 30%). HR–MS (ESI–TOF); $[MH]^+$ for $(C_{38}H_{27}O_9PRu_3Au)$ calcd 1160.8183, found +1160.8191. IR ν(CO): 2069 (m), 2038 (sh), 2027 (vs), 1998 (s), 1987 (s), 1978 (s), 1967 (m), 1961 (m) cm^{-1}. The remaining bands were not studied because they did not contain coordinated ligands accordingly to their ^{1}H NMR spectrums.

4.6. $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CR)]$ ($R = C(CH_3){=}CH_2$ (**5**)

The general procedure was employed for the preparation of **5**. The following compounds were used: $[Ru_3(CO)_{10}(\mu{-}Cl)(\mu{-}AuPPh_3)]$ (**1**) (50.0 mg, 0.050 mmol), 2-methyl-1-buten-3-yne (28 μl; 0.300 mmol) and $(CH_3)_3NO$, (6 mg, 0.080 mmol). The first band was identified as traces of starting material and the second band corresponds to compound $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CC(CH_3){=}CH_2)]$ (**5**). Yield: (yellow solid, 11 mg, 22%). HR–MS (ESI–TOF); $[MH]^+$ for $(C_{32}H_{21}O_9PRu_3Au)$ calcd 1082.7713, found +1082.7735. IR ν(CO): 2093 (m), 2069 (s), 2049 (sh), 2033 (vs), 1990 (vs, br), 1969 (m), 1963 (m), 1958 (m) cm^{-1}.

4.7. $[Ru_3(CO)_9(\mu{-}AuPPh_3)(\mu_3{-}\eta^2{-}\perp{-}C{\equiv}CR)]$ ($R = Si(CH_3)_3$) (**6**))

The general procedure was employed for the preparation of **6**. The following compounds were used: $[Ru_3(CO)_{10}(\mu{-}Cl)(\mu{-}AuPPh_3)]$ (**1**) (50.0 mg, 0.050 mmol), trimethylsilylacetilene (42 μl; 0.300 mmol) and $(CH_3)_3NO$, (6 mg, 0.080 mmol). The first band was identified as traces of starting material and the second

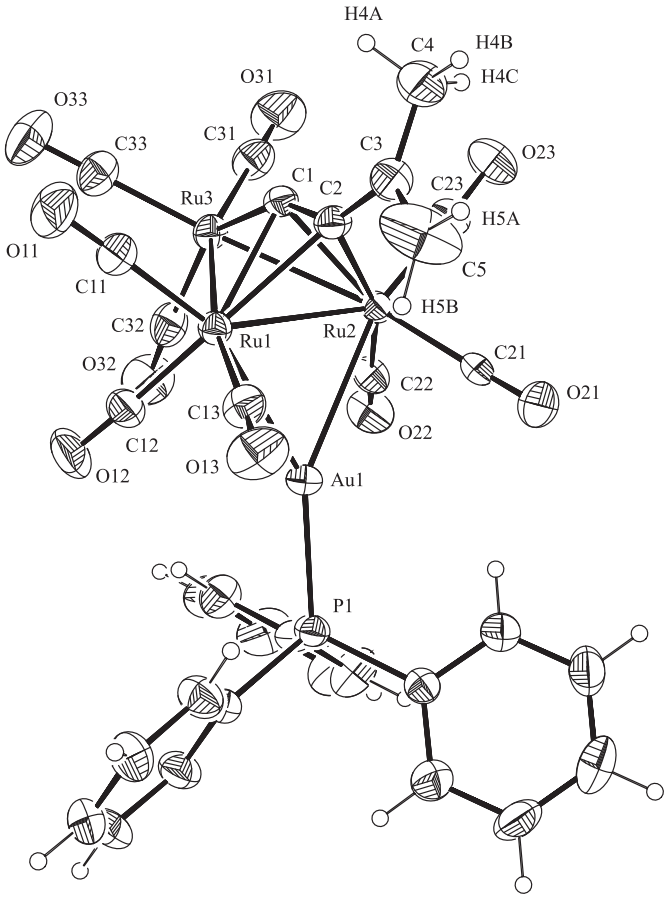

Fig. 6. ORTEP view of compound **5** (30% probability).

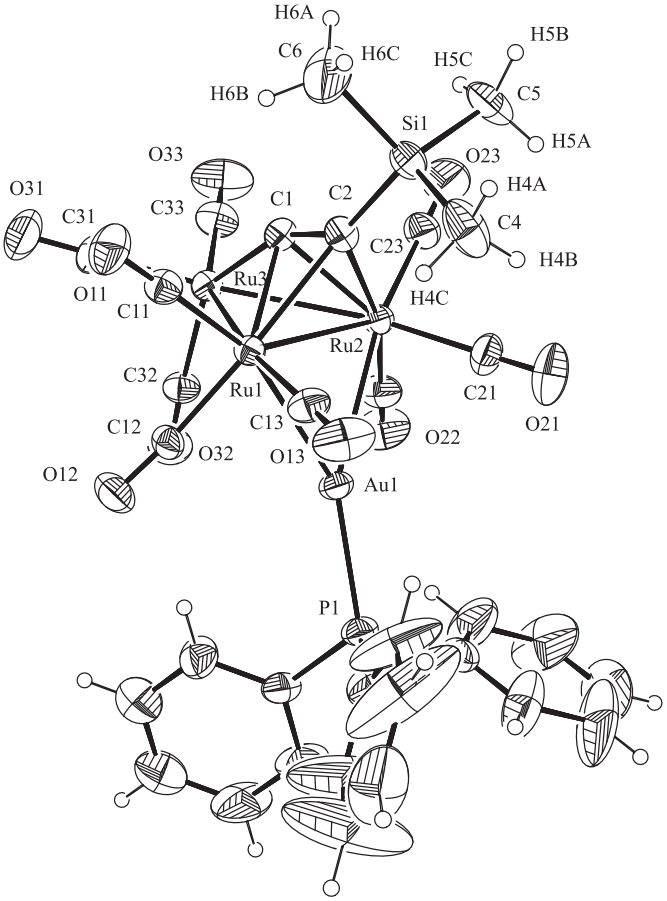

Fig. 7. ORTEP view of compound **6** (30% probability).

Table 2
Selected bond lengths (Å) and angles (°) for compounds **2**–**6**.

Compound	**2**	**3**		**4**	**5**	**6**
Bond lengths		Molecule1	Molecule2			
Ru(1)–Ru(2)	2.8287(5)	2.8448(6)	2.8383(6)	2.8507(11)	2.8331(6)	2.8534(9)
Ru(2)–Ru(3)	2.8103(5)	2.8138(6)	2.8036(7)	2.8167(12)	2.8023(7)	2.8063(10)
Ru(3)–Ru(1)	2.8269(6)	2.8088(6)	2.7869(6)	2.7996(12)	2.8100(7)	2.8099(9)
C(1)–C(2)	1.302(7)	1.314(7)	1.313(6)	1.330(14)	1.303(8)	1.330(13)
C(2)–Si(1)	–	–		–	–	1.855(10)
C(2)–C(3)	1.473(6)	1.461(7)	1.469(7)	1.444(13)	1.465(8)	–
Ru(1)–C(1)	2.185(5)	2.220(5)	2.197(5)	2.173(10)	2.202(6)	2.190(9)
Ru(1)–C(2)	2.231(4)	2.246(5)	2.244(5)	2.264(10)	2.237(6)	2.260(9)
Ru(2)–C(1)	2.190(5)	2.194(5)	2.182(5)	2.188(10)	2.192(6)	2.169(9)
Ru(2)–C(2)	2.254(4)	2.277(5)	2.241(5)	2.249(10)	2.247(6)	2.258(10)
Ru(3)–C(1)	1.947(5)	1.960(6)	1.941(5)	1.937(10)	1.950(6)	1.938(9)
Ru(1)–Au(1)	2.7652(4)	2.7734(5)	2.7739(5)	2.7487(9)	2.7597(5)	2.7659(7)
Ru(2)–Au81)	2.7645(4)	2.7505(5)	2.7684(5)	2.7712(9)	2.7616(5)	2.7590(7)
Au(1)–P(1)	2.293(1)	2.295(2)	2.296(2)	2.296(2)	2.291(2)	2.306(2)
Bond angles						
Ru(1)-Ru(2)-Ru(3)	60.172(13)	59.518(15)	59.200(16)	59.20(3)	59.817(17)	59.53(2)
Ru(2)–Ru(3)–Ru(1)	60.237(14)	60.791(15)	61.021(16)	61.00(3)	60.637(16)	61.07(2)
Ru(3)–Ru(1)–Ru(2)	59.592(12)	59.691(15)	59.779(16)	59.79(3)	59.546(16)	59.40(2)
Ru(3)–C(1)–C(2)	154.9(4)	153.3(4)	153.5(4)	155.4(8)	153.4(4)	155.6(8)
C(1)–C(2)–C(3)	141.0(5)	145.5(5)	143.5(5)	144.4(9)	143.1(6)	
C(1)–C(2)–Si(1)	–			–	–	144.0(8)
C(2)–Ru(1)–Au(1)	104.44(12)	101.11(14)	101.26(13)	101.5(2)	102.89(15)	104.6(3)
C(2)–Ru(2)–Au(1)	103.82(12)	100.96(13)	101.50(13)	101.3(3)	102.56(15)	104.8(2)
C(1)–Ru(1)–Au(1)	108.00(11)	107.92(13)	108.17(13)	108.3(3)	108.28(15)	105.9(2)
C(1)–Ru(2)–Au(1)	107.87(12)	109.50(13)	108.81(14)	107.1(3)	108.52(15)	106.8(2)
Interline and interplane angles						
C(1)–C(2)/Ru(1)–Ru(2)	89.5(2)	88.0(2)	89.6(3)	89.0(4)	89.3(3)	89.4(5)
C(1)–C(2)/Ru(3)–Ru(2)–Ru(1)	17.8(2)	17.2(3)	16.9(3)	17.5(4)	16.9(4)	18.4(5)
Ru(3)–Ru(1)–Ru(2)/Ru(1)–Ru(2)–Au(1)	114.32(1)	121.28(1)	119.83(1)	119.10(2)	117.15(2)	110.30(2)
C(1)–Ru(1)–Ru(2)/Ru(1)–Ru(2)–Au(1)	167.0(2)	174.6(2)	173.04(2)	172.0(3)	170.3(1)	163.1(3)
C(2)–Ru(1)–Ru(2)/Ru(1)–Ru(2)–Au(1)	148.2(1)	140.6(1)	141.6(1)	142.2(2)	144.9(2)	150.9(2)

Table 3
Crystal data and structure refinement parameters for compounds **2**–**6**.

Compound	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{22}Au_1O_9P_1Ru_3$	$C_{37}H_{24}AuO_9P_1Ru_3$	$C_{38}H_{26}Au_1O_9P_1Ru_3$	$C_{32}H_{20}Au_1O_9P_1Ru_3$	$C_{32}H_{24}Au_1O_9P_1Ru_3Si1$
Formula weight	1129.68	1143.71	1157.73	1079.63	1111.75
Crystal colour and shape	red prism	orange prism	red prism	orange plate	orange prism
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal size (mm)	0.3 × 0.2 × 0.1	0.28 × 0.11 × 0.1	0.25 × 0.21 × 0.15	0.41 × 0.39 × 0.21	0.25 × 0.19 × 0.091
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1$
Unit cell dimensions					
a (Å)	13.0243(2)	12.7175(3)	35.8213(11)	13.2217(2)	12.3295(2)
b (Å)	11.5864(2)	33.9779(8)	13.1804(5)	17.0832(3)	10.1494(2)
c (Å)	24.4145(4)	17.8827(4)	16.8224(5)	16.0699(3)	15.1613(3)
α (°)	90.00	90	90.00	90.00	90
β (°)	96.3720(10)	100.1460(10)	94.379(2)	107.9270(10)	102.2140(10)
γ (°)	90.00	90	90.00	90.00	90
V, (Å^3)	3661.50(10)	7606.5(3)	7919.3(5)	3453.47(10)	1854.29(6)
Z	4	8	8	4	2
$D_{calcd.}$ (Mg m^{-3})	2.049	1.997	1.942	2.076	1.991
μ, (mm^{-1})	5.304	5.108	4.907	5.618	5.265
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Mo-Kα)) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Scan type	ω–ϕ	ω–ϕ	ω–ϕ	ω–ϕ	ω–ϕ
2θ range (°)	3.07 to 27.47	2.93 to 27.43	3.54 to 27.49	3.45 to 27.48	3.4 to 27.48
Index ranges					
($h$min/$h$max, $k$min/$k$max, $l$min/$l$max)	−16/13, 13/15, −26/31	−16/13, 44/42, −22/23	−31/45, −15/17, −21/18	−17/16, −22/21, −20/20	−15/15, −13/11, −19/19
Reflections collected	22 163	41 476	18 593	37022	26051
Independent reflections	8112 (R_{int} = 0.0383)	16 544 (R_{int} = 0.0479)	8232 (R_{int} = 0.0635)	7878 (R_{int} = 0.0393)	4430 (R_{int} = 0.0393)
Observed reflections	5855($F > 4\sigma$(F))	4352 ($F > 4\sigma$(F))	5558 ($F > 4\sigma$(F))	5695 ($F > 4\sigma$(F))	4021 ($F > 4\sigma$(F))
Parameters/restrains	452/0	923/0	436/0	416/1	391/1
Rfinal; Rall data	0.0383, 0.0676	0.0412, 0.0643	0.0635, 0.1045	0.0393, 0.0681	0.0338, 0.0403
Rwfinal, Rwall data	0.0761, 0.0881[a]	0.0855, 0.0744[b]	0.1547, 0.1860[c]	0.0793, 0.0681[d]	0.0792, 0.0824[e]
GOF (all data)	0.97	1.014	0.909	0.909	0.996
Max, min peaks (eÅ^{-3})	0.937/−0.826	0.580/−0.746	0.782/−1.067	0.888/−1.148	0.781/−1.292

[a] $w^{-1} = \sigma^2(F_o^2)+(0.0400P)^2 + P$.
[b] $w^{-1} = \sigma^2(F_o^2)+(0.10.0062P)^2 + 5.5156P$.
[c] $w^{-1} = \sigma^2(F_o^2)+(0.1131P)^2 + 51.5217P$.
[d] $w^{-1} = \sigma^2(F_o^2)+(0.0322P)^2 + 4.6502P$.
[e] $w^{-1} = \sigma^2(F_o^2)+(0.0485P)^2 + 1.2819P$. Where $P = (F_o^2+2F_c^2)/3$.

band corresponds to compound $[Ru_3(CO)_9(\mu-AuPPh_3)(\mu_3-\eta^2-\perp-C\equiv CSi(CH_3)_3))]$ (**6**). Yield: (yellow solid, 13 mg, 25%). HR–MS (ESI–TOF); $[MH]^+$ for ($C_{32}H_{25}O_9PSiRu_3Au$) calcd 1114.7796, found +1114.7796. IR ν(CO): 2070 (m), 2040 (sh), 2029 (vs), 2004 (s), 1994 (sh), 1980 (s), 1971 (sh), 1960 (m), 1946 (m) cm^{-1}.

5. Crystallography

Suitable crystals for compounds **2** to **6** were obtained by slow evaporation of $CHCl_3$ solution at low temperature (5 °C) for several days. Table 3 shows details for data collection and structure refinement for all compounds. Data were collected in an Enraf–Nonius Cappa CCD area detector diffractometer using MoKα radiation. The samples were mounted in MicroMounts (MiTeGen company) www.mitegen.com. For all compounds, all non–hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized refined positions. Data collection, determination of unit Cell and integration of Frames of all compounds were carried out using the suite Collect software [43] and HKL Scalepack [44]. A semi–empirical absorption correction method (SADABS) [45] was applied in all cases. All structures were resolved by direct methods, completed by subsequent difference Fourier synthesis, and refined by full–matrix least–squares procedures using the SHELX–97 package [45]. All crystallographic programs were used under WINGX program [46].

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Appendix A. Supplementary data

CCDC 821994, 830621, 821993, 821996 and 821995 contain the supplementary crystallographic data for **2** to **6** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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