ELSEVIER

Gold–ruthenium compounds containing bridging phosphide or thiolate groups: Crystal structures of the intermediate species $[Ru_3(CO)_8L(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC \equiv CSiMe_3\})]$ (L = NMe$_3$ or PPh$_2$H)

Esther Delgado [a,*], Elisa Hernández [a], Miguel A. Maestro [b], Angel Nievas [a], Maria Villa [a]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[b] *Departamento de Química Fundamental, Facultade de Ciencias, Universidad da Coruña, 15071 A Coruña, Spain*

Dedicated to Dr. J. Antonio Abad in occasion of his retirement.

Abstract

New tetranuclear complexes have been prepared using bridging phosphide or thiolate groups between phosphine gold fragments and the compound $[Ru_3(CO)_9(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC \equiv CSiMe_3\})]$. The crystal structures of the intermediates $[Ru_3(CO)_8(NMe_3)(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC \equiv CSiMe_3\})]$ and $[Ru_3(CO)_8(PPh_2H)(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)-CSC \equiv CSiMe_3\})]$ have been solved.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Ruthenium carbonyls; Gold–ruthenium compounds; Triruthenium complexes

1. Introduction

Mixed-metal compounds may exhibit an interesting chemistry from the point of view of organic synthesis, as a consequence of synergic interactions among the different metals. Many examples of polynuclear complexes containing mixed metals have been reported and among them, clusters of Group 8 metals bonded to the AuPPh$_3$ fragment have been prepared by the reaction of ionic complexes with the electrophilic fragment AuPPh$_3^+$. Thus, we have obtained the clusters Fe$_x$Au(CO)$_9$(μ-SR)PPh$_3$ (x = 2 or 3; R = alkyl or aryl group) [1] and Fe$_3$Au(CO)$_9$(μ-C≡CR)PPh$_3$ (R = Fc, Bu^t) [2] following this approach. However gold fragments attached to polynuclear compounds of the iron triad towards bridging phosphide or thiolate groups are almost unknown. In fact, as far as we

are aware, the recently reported cluster compound Os$_3$Au-(CO)$_{11}$(μ-PPh$_2$)PPh$_3$ [3] is the only example containing a bridging phosphide, while no derivatives have been described containing a thiolate bridge. In this paper we report the studies carried out on the compound $[Ru_3(CO)_9(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC \equiv CSi-Me_3\})]$ in order to prepare new gold–ruthenium compounds containing PPh$_2$ as well as SR (R = Et, Ph) bridging ligands. In addition to the analytical and spectroscopic data of the new complexes, crystallographic data on the intermediate derivatives $[Ru_3(CO)_8L(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC \equiv CSiMe_3\})]$ (L = NMe$_3$ or PPh$_2$H) are also reported.
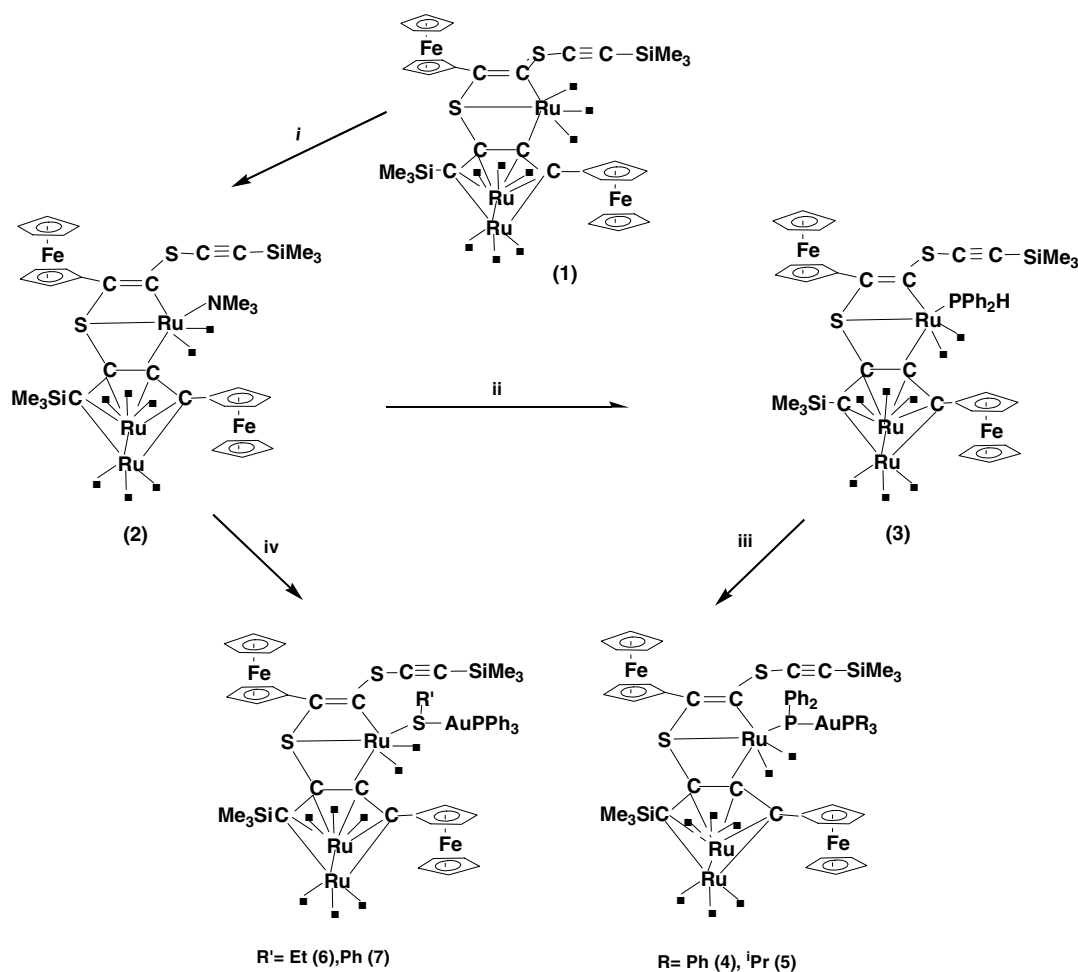
2. Results and discussion

Secondary phosphines PR$_2$H or PRR′H exhibit very reactive P–H bonds and as a consequence they may undergo easy deprotonation reactions affording phosphide

* Corresponding author. Tel.: +34 914975268; fax: +34 914974833.
E-mail address: esther.delgado@uam.es (E. Delgado).

groups. Thus, it has been recently described [3] that the deprotonation of the phosphine PPh_2H in the cluster $Os_3(CO)_{11}PPh_2H$ followed by the reaction of different metal halides, allows the addition of MLn fragments to the molecule. In order to establish whether this synthetic method could be useful in our case, we have initially prepared the phosphine derivative of compound $[Ru_3(CO)_9(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC\equiv CSiMe_3\})]$ (**1**). Among the few examples reported of polynuclear derivatives containing a PPh_2H ligand, the compounds $[HMCo_3(CO)_{11}(PPh_2)]$ (M = Fe or Ru) [4], $Ru_3(\mu-H)(\mu-N\equiv CPh_2)(PPh_2H)(CO)_9$ [5], $Os_3(CO)_9$-$(\mu-dppm)(PPh_2H)$ [6] and $Os_3Ru(CO)_{11}(\mu-PPh_2)(\mu-H)_3$-$PPh_2H$ [7] have been prepared by direct decarbonylation or substitution of labile ligands. The substitution of CO by NMe_3 requires mild conditions avoiding the degradation of polynuclear species. As compound **1** consists of a ruthenole group joined to one $Ru(CO)_3$ fragment towards a dithioether, an additional aspect of interest for us was to determine in which metal fragment the substitution

should take place. The ruthenole entity is made up of the $Ru_2(CO)_6$ fragment and a C_4 ligand showing a σ, π coordination mode. The organic group forms a ruthenacyclopentadiene which is bonded to the other ruthenium atom. Treatment of the triruthenium compound **1** with $ONMe_3$ in toluene led to CO_2 evolution and formation of new compound $[Ru_3(CO)_8(NMe_3)(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)-SC(Fc)CSC\equiv CSiMe_3\})]$ (**2**) (Scheme 1).

The presence of NMe_3 ligand was inferred from ^1H NMR spectroscopy. Thus, the resonance at 2.79 ppm, in the range observed for other amine derivatives [8], was assigned to the methyl group of the NMe_3 ligand. Additionally, the IR spectrum in the carbonyl region [2096 (vw), 2071 (m), 2034 (vs), 2020 (m), 2002 (sh), 1998 (m)] is modified in comparison to the one that shows the precursor $[Ru_3(CO)_9(\mu_3-\eta^2,\eta^4,\eta^3-\{Me_3SiCC(C_2Fc)SC(Fc)CSC\equiv CSiMe_3\})]$ [9]. The molecular peak (m/z 1264) as well as the corresponding to the sequential loss of eight CO ligands observed in the FAB-mass spectrum seem to suggest that the substitution of one CO by one NMe_3 has taking place.

R'= Et (6), Ph (7)

R= Ph (4), ^iPr (5)

$\blacksquare$ = CO

i= $ONMe_3$, Toluene, r.t., 1h; ii= PPh_2H, Toluene, r.t., 2.5h;
iii= $AuClPR_3$, DBU, $TIBF_4$, Cl_2CH_2, r.t., 2h; iv= $Au(SR')PPh_3$, Toluene, r.t., 1.5h

Scheme 1.

The reaction of compound **2** with the stoichiometric amount of PPh$_2$H led to the formation of compound [Ru$_3$(CO)$_8$(PPh$_2$H)(μ_3-η^2,η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)-CSC≡CSiMe$_3$})] (**3**), with IR spectrum in the carbonyl region similar to the one of the amine precursor. The presence of the coordinated PPh$_2$H ligand was confirmed by a single resonance in the ^{31}P NMR spectrum at 15.7 ppm. The peak corresponding to the parent ion (*m/z* 1391) appears in its FAB$^+$ mass spectrum.

The proposed structures for compounds **2** and **3** on the bases of analytical and spectroscopic data have been confirmed by X-ray diffraction methods (Figs. 1 and 2).

[Ru$_3$(CO)$_8$(NMe$_3$)(μ_3-η^2,η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)-CSC≡CSiMe$_3$})] (**2**) is one of the rare examples of clusters containing the amine ligand being crystallographically determined. The scarcity of this type of derivatives, formed by extrusion of CO using ONMe$_3$ as initiator showing stability in solid state maybe due to the lability of the NMe$_3$ ligand.

A dichloromethane solution of compound **3** was treated at room temperature with AuPPh$_3$Cl and TlBF$_4$, as chloride abstractor, in the presence of DBU, leading after 2 h to compound [AuRu$_3$(CO)$_8$(μ-PPh$_2$)(μ_3-η^2,η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$}PPh$_3$)] (**4**). This formulation is in accord with the spectroscopic data. A doublet resonance that appears at 32.1 ppm, with a $^2J_{P-P}$ coupling of 255 Hz in ^{31}P{^{1}H} NMR is assigned to a bridg-
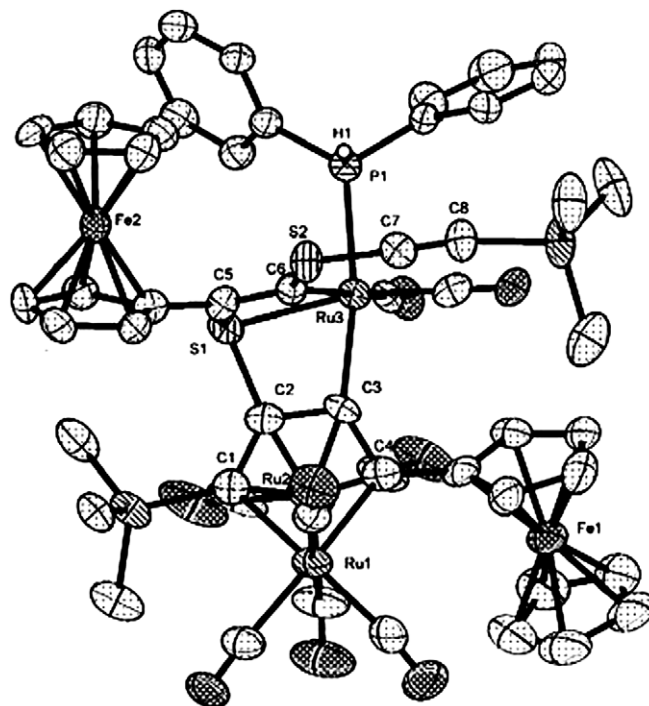

Fig. 2. View of the crystal structure of compound **3**. Selected bond distances (Å) and angles (°). Ru(1)–Ru(2) 2.7060(8), Ru(3)–S(1) 2.4458(18), Ru(3)–P(1) 2.3548(18), C(1)–C(2) 1.403(9), C(2)–C(3) 1.432(10), C(3)–C(4) 1.402(10), C(5)–C(6) 1.339(9), C(7)–C(8) 1.189(10), C(6)–S(2)–C(7) 104.2(3), C(3)–Ru(3)–P(1) 169.8(2), C(2)–S(1)–C(5) 95.6(3).

ing PPh$_2$ group between the ruthenium and gold atoms while a second doublet at 44.8 ppm ($^2J_{P-P}$ = 255 Hz) has been assigned to the presence of the AuPPh$_3$ group. By comparison, the compound [Au(C$_6$F$_5$)$_3$(μ-PPh$_2$)AuPPh$_3$] shows in the ^{31}P{^{1}H} NMR spectrum resonances at 31.1 and 44.6 ppm for the PPh$_2$ and PPh$_3$, respectively, [10].

Although the molecular ion was not observed in the FAB$^+$ or MALDI mass spectra, a peak at *m/z* = 459 confirmed the presence of the AuPPh$_3^+$ fragment in the complex. The reaction using the AuP^{i}Pr$_3^+$ fragment yielded the analogous compound [AuRu$_3$(CO)$_8$(μ-PPh$_2$)(μ_3-η^2, η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$}P^{i}Pr$_3$)] (**5**). As can be observed the higher steric hindrance of the ^{i}Pr group does not affect the outcome of this reaction.

Since the phosphide and thiolate groups are isoelectronic, we considered of interest to study the possibility of joining the AuPPh$_3^+$ fragment to the [Ru$_3$(CO)$_9$-(μ_3-η^2,η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$})] (**1**) using the metalloligands AuSRPPh$_3$ (R = Et, Ph). Thus, treatment of [Ru$_3$(CO)$_8$(NMe$_3$)(μ_3-η^2,η^4,η^3-{Me$_3$SiCC-(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$})] (**2**) with the stoichiometric amount of AuSRPPh$_3$ in toluene at room temperature afforded to compounds [AuRu$_3$(CO)$_8$(μ-SR)(μ_3-η^2,η^4,η^3-{Me$_3$SiCC(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$})PPh$_3$][R = Et (**6**); Ph (**7**)]. Both complexes have been characterized by analytical and spectroscopic techniques. Resonances corresponding to the organic groups (Et, Ph, SiMe$_3$, Fc) present in
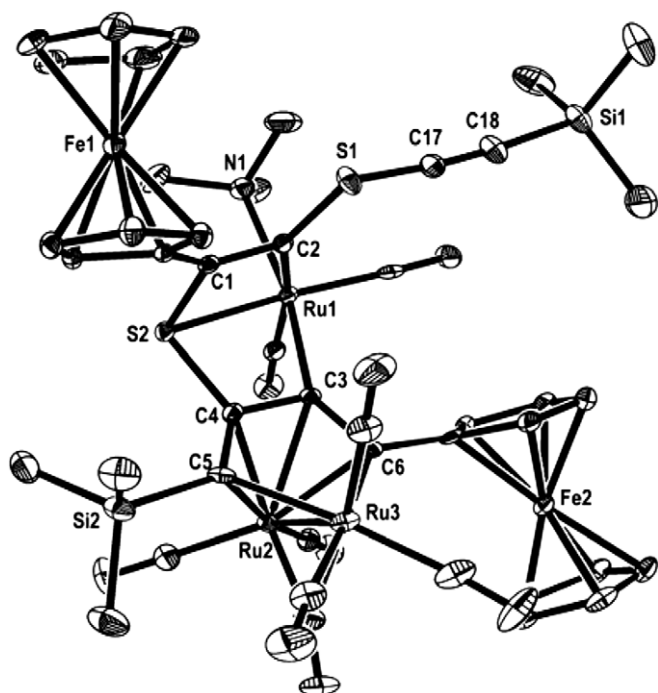

Fig. 1. View of the crystal structure of compound **2**. Selected bond distances (Å) and angles (°). Ru(2)–Ru(3) 2.7024(6), Ru(1)–S(2) 2.4708(12), Ru(1)–N(1) 2.289(4), C(3)–C(4) 1.444(6), C(4)–C(5) 1.407(6), C(3)–C(6) 1.419(6), C(17)–C(18) 1.199(6), C(1)–C(2) 1.345(6), C(2)–S(1)–C(17) 105.2(2), C(1)–S(2)–C(4) 93.34, C(3)–Ru(1)–N(1) 167.54(16) 167.54(6).

these molecules have been assigned in their ^{1}H NMR spectra. The IR pattern in the carbonyl region is similar in both compounds and related to complexes [AuRu₃(CO)₈(μ-PPh₂)(μ₃-η², η⁴, η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃}-PPh₃)] (**4**) and [AuRu₃(CO)₈(μ-PPh₂)(μ₃-η², η⁴, η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃}P^{i}Pr₃)] (**5**).

2.1. Crystal structures determination

The molecular structures of compound **2** and **3** are depicted in Figs. 1 and 2. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths and angles are collected as figure captions. The core of the two compounds is similar. It contains the units Ru₂(CO)₆ and Ru(CO)₂L (L = NMe₃ or PPh₂H) linked towards a polycarbon sulfur chain. A pseudo-octahedral geometry is located around each of the ruthenium atoms. The crystallographic data of **2** and **3** reveal the structure arising from the substitution of one CO ligand in the metal–metal unbonding Ru(CO)₃ fragment of the precursor **1**, by an amine or phosphine ligand in position *trans* to the carbon atom of the ruthenol group towards it is linked. The Ru–Ru bond distances of [2.7024(6) Å] in **2** and [2.7060(8) Å] **3** are comparable with those found in com-

pounds containing the ruthenol fragment [Ru₃(CO)₉-(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃})] [9] and [Ru₄Ni(CO)₁₂(μ-PPh₂)₂(μ₄₋η¹,η¹,η²,η⁴-Bu^{t}C≡CC₄C≡CBu^t)] [11]. The substitution of the one CO ligand by amine or phosphine seems not to affect to the S–Ru distance [2.4708(12) Å for **2** and 2.4458(18) Å for **3**] in comparison with the parent compound [Ru₃(CO)₉(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃})][2.4414(10) Å]. Angles of 167.54(16)° for C3–Ru1–N1 in compound **2** and 169.8(2)° for C3–Ru3–P1 in **3** are in agreement with the substitution of the CO in position *trans* to one C atom of the ruthenol unit present in [Ru₃(CO)₉(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃}). The C(3)–C(4) 1.444(6), C(4)–C(5) 1.407(6) and C(3)–C(6) 1.419(6) distances for compound **2** and C(1)–C(2) 1.403(9), C(2)–C(3) 1.432(10) and C(3)–C(4) 1.402(10) for **3** are in the range expected for a ruthenol unit. A value of 1.199(6) Å for the C(17)–C(18) distance observed in compound **2** and 1.189(10) Å for C(7)–C(8) in **3**, confirm the presence of a free alkynethiolate group in both molecules.

3. Experimental

All reactions were carried out under argon atmosphere using Schlenk techniques. Solvents were dried according to standard methods. IR spectra were recorded on a Perkin–Elmer 1650 FTIR spectrophotometer using NaCl cells. ^{1}H NMR and ^{31}P NMR spectra were registered on a Bruker AMX-300 instrument. Elemental analyses were performed on a Perkin–Elmer 240-B microanalyzer. FAB mass spectra were carried out on a WG AutoSpec spectrometer, using 3-nitrobenzylalcohol as matrix. Me₃SiC≡CSC≡CFc [12], [AuClPPh₃] [13] and [AuSRPPh₃] [R = Et, Ph] [14] were prepared as previously reported.

3.1. Synthesis of [Ru₃(CO)₈(NMe₃)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃})] (2)

A mixture of [Ru₃(CO)₉(μ₃-η²,η⁴,η³-{Me₃SiCC-(C₂Fc)SC(Fc)CSC≡CSiMe₃})] (**1**) (0.062 g, 0.051 mmol) and ONMe₃ (0.006 g, 0.079 mmol), was stirred in toluene (15 ml), bubbling argon, during 1 h. The solvent was removed and the amine derivative [Ru₃(CO)₈(NMe₃)-(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃})] (**2**), extracted with hexane from the residue (0.048 mmol, 93% yield). Crystals of **2** were obtained in *n*-hexane at −20 °C. IR (hexane) cm⁻¹ ν_{CO} 2096 (vw), 2071 (m), 2034 (vs), 2020 (m), 2002 (sh), 1998 (m), 1980 (w), 1968 (m); ^{1}H NMR (CDCl₃, 300 MHz, 22 °C) δ: 4.48–4.22 [m, 4H, C₅H₄], 4.23 [s, 5H, C₅H₅], 4.17 [s, 5H, C₅H₅], 4.16–4.12 [m, 4H, C₅H₄], 2.79 [s, 9H, NMe₃], 0.10 [s, 9H, SiMe₃], 0.00 [s, 9H, SiMe₃]. MS(FAB⁺) *m/z* 1264 (M⁺+H), 1204 (M⁺+H-NMe₃), 1176–981 (M⁺+H-NMe₃-*n*CO, *n* = 1–8). Anal. Calcd. for C₄₅H₄₅O₈S₂Si₂NFe₂Ru₃ (Found): C, 42.76 (41.85); H, 3.56 (3.94); N, 1.11(1.07); S, 5.06 (4.81)%.

Table 1
Crystallographic data for compounds **2** and **3**

Compound	2	3
Formula	C₄₅H₄₅Fe₂NO₈ Ru₃S₂Si₂ · 0.5C₆H₁₄	C₅₄H₄₇Fe₂O₈P Ru₃S₂Si₂
F_w	1306.12	1390.10
Crystal size (mm)	0.26 × 0.12 × 0.02	012 × 0.06 × 0.03
Crystal system	Triclinic	Monoclinic
Space group	P$\bar{1}$	P2₁/c
Z	2	4
a (Å)	12.0217(10)	17.4064(8)
b (Å)	13.4150(11)	13.2576(10)
c (Å)	18.1263(15)	25.4584(10)
α (°)	80.380(2)	90
β (°)	73.979(2)	98.051(2)
γ (°)	72.073(2)	90
Temperature (K)	173(2)	100(2)
Volume (Å³)	2662.5(4)	5817.1(6)
ρ_{calc} (g cm⁻³)	1.629	1.587
μ (mm⁻¹)	1.54178	11.798
F(000)	1310	2776
θ Range (°)	1.83–28.32	2.56–68.25
Observed reflections	17,321	26,645
Independent reflections [R_{int}]	12,152 [0.0355]	10,285 [0.0823]
Index ranges	−16 to 15, −16 to 17, −16 to 23	−20 to 18, −14 to 15, −30 to 27
Reflections collected/unique	12,152/7781	10,285/6269
Goodness-of-fit on F^2	0.963	0.906
Largest difference in peak/hole (e Å⁻³)	0.732 and −0.729	1.318 and −1.103
Final R indices [$I > 2\sigma(I)$]		
R_1	0.0455	0.0531
wR_2	0.0806	0.1159

3.2. Synthesis of [Ru₃(CO)₈(PPh₂H)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃})] (3)

HPPh₂ (0.008 ml, 0.047 mmol) was added to a solution of compound **2** (0.06 g, 0.047 mmol) in toluene (20 ml). The mixture was stirred while bubbling argon for 2.5 h at room temperature and the solvent was evaporated to dryness. The orange residue was washed several times with cold hexane to afford to a solid compound corresponding to compound [Ru₃(CO)₈(PPh₂H)(μ₃-η²,η⁴,η³-{Me₃SiCC-(C₂Fc)SC(Fc)CSC≡CSiMe₃})] (**3**) (0.029 mmol, 61%). Crystals of **3** were obtained in CH_2Cl_2/*n*-hexane (1:2) at −20 °C. IR (hexane) cm⁻¹ ν_{CO} 2092 (vw), 2069 (m), 2040 (vs), 2023 (m), 1988 (s), 1976 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ: 7.67–7.46 (m, 10H, C₆H₅), 6.51 (d, 1H, P–H, J_{H-P}: 363.4 Hz), 4.34–4.20 (m, 4H, C₅H₄), 4.18 (s, 5H, C₅H₅), 4.12–4.10 (m, 4H, C₅H₄), 4.09 (s, 5H, C₅H₅), −0.02 (s, 9H, SiMe₃), −0.05 (s, 9H, SiMe₃). ³¹P{¹H} NMR (CDCl₃, 300 MHz, 22 °C) δ: 15.3. MS(FAB⁺) *m/z* 1391 (M⁺+H), 1363–1167 (M⁺+H-*n*CO, *n* = 1–8), 1204 (M⁺+H-PPh₂H). Anal. Calcd. for C₅₄H₄₇O₈S₂Si₂PFe₂Ru₃ (Found): C, 46.66 (46.69); H, 3.38 (4.11); S 4.61 (4.28)%.

3.3. Synthesis of [AuRu₃(CO)₈(μ-PPh₂)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃}PPh₃)] (4)

A dichloromethane solution (10 ml) of compound **3** (0.02 g, 0.014 mmol) was treated with the stoichiometric amount of DBU (0.002 ml, 0.015 mmol), followed of Au-ClPPh₃ (0.008 g, 0.015 mmol) and TlBF₄ (0.004 g, 0.015 mmol). The mixture was stirred 2 h at room temperature, the solvent was evaporated to dryness and the residue crystallized from CH_2Cl_2/hexane at −20 °C to afford [AuRu₃(CO)₈(μ-PPh₂)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)-SC(Fc)CSC≡CSiMe₃}PPh₃)] (**4**) (0.008 mmol, 60%). IR (hexane) cm⁻¹ ν_{CO} 2086 (vw), 2067 (m), 2028 (vs), 2014 (sh), 1991 (s), 1961 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ: 7.91–7.43 (m, 25H, C₆H₅), 4.35–4.16 (m, 5H, C₅H₄), 4.14 (s, 5H, C₅H₅), 4.08–3.92 (m, 3H, C₅H₄), 3.90 (s, 5H, C₅H₅), −0.11 (s, 9H, SiMe₃), −0.14 (s, 9H, SiMe₃). ³¹P{¹H} NMR (CDCl₃, 300 MHz, 22 °C) δ 44.8 (d, PPh₃, $^2J_{P-P}$: 255 Hz), 32.1 (d, PPh₂, $^2J_{P-P}$: 255 Hz). Anal. Calcd. for C₇₂H₆₁O₈S₂Si₂P₂Fe₂Ru₃Au · C₆H₁₄ (Found): C, 48.40 (48.03); H, 3.88 (4.10); S 3.31 (3.21)%.

3.4. Synthesis of [AuRu₃(CO)₈(μ-PPh₂)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃}(PᶦPr₃))] (5)

Compound **5** was prepared following the method described for **4**. The solid residue was purified by TLC silica plates using hexane/CH_2Cl_2 (10:1) as eluent. IR (hexane) cm⁻¹ ν_{CO} 2092 (vw), 2065 (m), 2032 (vs), 2017 (sh), 1991 (s), 1965 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ: 7.83–7.30 (m, 10H, C₆H₅), 4.42–4.24 (m, 4H, C₅H₄), 4.17 (s, 5H, C₅H₅), 4.08 (s, 5H, C₅H₅), 4.07–3.92 (m, 4H, C₅H₄), 2.36 (m, 3H, C*H*(CH₃)₂), 1.30 (d, 9H, J = 7.1 Hz,

CH(C*H*₃)₂), 1.25 (d, 9H, J = 7.1 Hz, CH(C*H*₃)₂), 0.12 (s, 9H, SiMe₃), −0.09 (s, 9H, SiMe₃). ³¹P{¹H} NMR (CDCl₃, 300 MHz, 22 °C) δ: 72.6 (d, PᶦPr₃, $^2J_{P-P}$: 247 Hz), 32.0 (d, PPh₂, $^2J_{P-P}$: 247 Hz). MS(FAB⁺) *m/z*: 1522 (M⁺−8CO), 543 (HPPh₂AuPᶦPr₃), 357 (AuPᶦPr₃). Anal. Calcd. for C₆₃H₆₇O₈S₂Si₂P₂Fe₂Ru₃Au · 1/2CH₂Cl₂ (Found): C, 42.64 (42.57); H, 3.80 (3.87); S 3.58 (3.53)%.

3.5. Synthesis of [AuRu₃(CO)₈(μ-SEt)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃}PPh₃)] (6)

AuSEtPPh₃ (0.012 g, 0.023 mmol) was added to a solution of compound **2** (0.028 g, 0.022 mmol) in toluene (10 ml). The mixture was stirred while bubbling argon for 1.5 h at room temperature and the solvent was evaporated to dryness. Compound [AuRu₃(CO)₈(μ-SEt)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSC≡CSiMe₃}PPh₃)] (**6**) was obtained as red crystals from Cl_2CH_2/hexane (1:3) at −20 °C (0.018 g, 0.01 mmol, 47.5% yield). IR (hexane) cm⁻¹ ν_{CO} 2092 (vw), 2068 (s), 2028 (vs), 2030 (vs), 2016 (s), 1998 (sh), 1992 (s), 1961 (m), 1907 (vw). ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ: δ 7.65–7.50 (m, 10H, C₆H₅), 4.45–4.33 (m, 3H, C₅H₄), 4.19 (s, 5H, C₅H₅), 4.16–4.04 (m, 5H, C₅H₄), 4.11 (s, 5H, C₅H₅), 3.13 (m, 2H, C*H*₂CH₃), 1.56 (t, 3H, J = 7.24 Hz, CH₂C*H*₃), 0.01 (s, 9H, SiMe₃), −0.01 (s, 9H, SiMe₃). ³¹P{¹H} NMR (CDCl₃, 300 MHz, 22 °C) δ: 37.2 (s, PPh₃). MS(FAB⁺) *m/z*: 1584–1500 (M⁺−*n*CO, *n* = 5–8), 1472 (M⁺−8CO-Et), 520 (AuS-EtPPh₃), 459 (AuPPh₃). Anal. Calcd. for C₆₂H₅₆O₈S₃Si₂P-Fe₂Ru₃Au · CH₂Cl₂ (Found): C, 41.83 (41.87); H, 3.21 (3.69); S 5.31(4.92)%.

3.6. Synthesis of [AuRu₃(CO)₈(μ-SPh)(μ₃-η²,η⁴,η³-{Me₃SiCC(C₂Fc)SC(Fc)CSCCSiMe₃}PPh₃)] (7)

Compound **7** was obtained following the above procedure for **6**. IR (hexane) cm⁻¹ ν_{CO} 2091 (vw), 2067 (m), 2034 (vs), 2019(s), 1992 (s), 1970 (m). ¹H NMR (CDCl₃, 300 MHz, 22 °C) δ: 7.59 (m, 15H, PPh₃), 7.29 (m, 5H, SPh), 4.42–4.24 (m,4H, C₅H₄), 4.16 (s, 5H, C₅H₅), 4.09–3.93 (m, 4H, C₅H₄), 4.07 (s, 5H, C₅H₅), 0.00 (s, 9H, SiMe₃), −0.02 (s, 9H, SiMe₃). ³¹P{¹H} NMR (CDCl₃, 300 MHz, 22 °C) δ: 37.1 (s, PPh₃). MS(FAB⁺) *m/z*: 1548 (M⁺−8CO), 1208 (M⁺−8CO-Ph-PPh₃), 568 (AuSPhPPh₃), 459 (AuPPh₃). Anal. Calcd. for C₆₆H₅₆O₈S₃Si₂PFe₂-Ru₃Au · 1/2CH₂Cl₂ (Found): C, 44.01 (43.98); H, 3.14 (3.57); S 5.29 (4.88)%.

3.7. X-ray crystallographic studies

Data collection of compounds **2** and **3** were carried out at 100 and 173 K, respectively, on a Bruker SMART-CCD area diffractometer operating at 50 kV and 30 mA with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for **2** and Cu Kα radiation (λ = 1.54178 Å) for **3**.

Crystal data and structure refinement parameters for compounds **2** and **3** are listed in Table 1. The unit cell parameters were refined from the observed positions of all strong reflections in the complete data sets. Several sets of frames of intensity data were collected over a hemisphere of the reciprocal space by combination of exposure sets. A 0.2% decay was observed for compound **2** and no decay for **3**.

Absorption corrections were applied using the SADABS program [15]. The raw intensity data frames were integrated with the SAINT program [16], which also applied corrections for Lorentz and polarization effects. The software package SHELXTL [16] version 6.10 was used for space group determination, structure solution and refinement. The structure was solved by direct methods (SHELXS-97 [16], completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 [16] minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters unless highly disorder solvent (hexane). All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 programme library. The hydrogen atom positions were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic U.

4. Supplementary material

Crystallographic data for compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 274796 and 274797, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) E. Delgado, E. Hernández, O. Rossell, M. Seco, X. Solans, J. Chem. Soc., Dalton Trans. (1993) 2191;
(b) E. Delgado, E. Hernández, O. Rossell, M. Seco, E. Gutierrez, C. Ruiz, J. Organomet. Chem. 455 (1993) 177.

[2] (a) E. Delgado, B. Donnadieu, M.E. García, S. García, M.A. Ruiz, F. Zamora, Organometallics 21 (2002) 780;
(b) A. Cabrera, E. Delgado, C. Pastor, M.A. Maestro, F. Zamora, Inorg. Chim. Acta 9 (2005) 139.

[3] B. Ahrens, J.M. Cole, J.P. Hickey, J.N. Martin, M.J. Mays, P.R. Raithby, S.J. Teat, A.D. Woods, J. Chem. Soc., Dalton. Trans. (2003) 1389.

[4] P. Braunstein, J. Rosé, P. Granger, J. Raya, S-E. Bouaoud, D. Grandjean, Organometallics 10 (1991) 3686.

[5] J.A. Cabeza, I. Del Rio, V. Riera, J. Organomet. Chem. 548 (1997) 255.

[6] K.A. Azam, M.B. Hursthouse, Md. R. Islam, S.E. Kabir, K.M. Abdul Malik, R. Miah, C. Sudbrake, H. Vahrenkamp, J. Chem. Soc., Dalton. Trans. (1998) 1097.

[7] L.J. Pereira, K.S. Chan, W.K. Leong, J. Organomet. Chem. 690 (2005) 1033.

[8] (a) T. Akter, N. Begum, D.T. Haworth, D.W. Bennett, S.E. Kabir, Md. A. Miah, N.C. Sarker, T.A. Siddiquee, E. Rosenberg, J. Organomet. Chem. 689 (2004) 2571;
(b) J.-I. Terasawa, H. Kondo, T. Matsumoto, K. Kirchner, Y. Motoyama, H. Nagashima, Organometallics 24 (2005) 2713.

[9] B. Alonso, C. Castejón, E. Delgado, B. Donnadieu, E. Hernández, Organometallics 23 (2004) 5112.

[10] M.C. Blanco, E.J. Fernandez, J.M. López-de-Luzuriaga, M.E. Olmos, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Chem. Eur. J. 6 (2000) 4116.

[11] P. Blenkiron, G.D. Enright, A.J. Carty, Chem. Commun. (1997) 483.

[12] A.W.M. Lee, A.B.W. Yeung, M.S.M. Yuen, H. Zang, X. Zhao, W.Y. Wong, Chem. Commun. (2000) 2502.

[13] C. Kovala, J.M. Suan, Aust. J. Chem. 19 (1966) 547.

[14] E. Delgado, E. Hernández, Polyhedron 11 (1992) 3135.

[15] G.M. Sheldrick, SADABS, Program for Absorption Corrections using Bruker CCD Data, University of Göttingen, Germany, 1996.

[16] G.M. Sheldrick, SHELXTL-PC, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.