Reactivity of 2-(Diphenylphosphanyl)thiophenol ($HSC_6H_4PPh_2$) with Ruthenium and Osmium Carbonyl Complexes; Breaking of $HSC_6H_4PPh_2$ into Sulfide, Phenyl and Diphenylphosphanyl Ligands on a Triruthenium Cluster

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2-(Diphenylphosphanyl)thiophenol ($HSC_6H_4PPh_2$) reacts with the carbonyl clusters $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ to give mixtures of products, the composition of which depends upon the reaction conditions and the ratio of the reactants. The derivatives $[M_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)(CO)_9]$ (**1a**: M = Ru; **1b**: M = Os), $[Ru_3(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}Ph)(\mu\text{-}PPh_2)(PPh_3)(CO)_6]$ (**2**), and $[Ru_2(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)_2(CO)_4]$ (**3**) have been isolated. The $SC_6H_4PPh_2$ ligand of compounds **1a** and **1b** has the sulfur atom spanning the same M−M edge as the hydride ligand and the phosphorus atom attached to one of the bridged metal atoms. Compound **2**, which contains sulfide, phenyl, diphenylphosphanyl and triphenylphosphane ligands that arise from $HSC_6H_4PPh_2$, has the Ru_3 triangle capped by the sulfide and two Ru−Ru edges spanned by bridging phenyl and diphenylphosphanyl ligands. In complex **3**, the two $SC_6H_4PPh_2$ ligands have the same coordination behavior as in **1a** or **1b**; this binuclear complex is more conveniently prepared by treating $[Ru_2(\mu\text{-}\eta^2\text{-}MeCO_2)_2(CO)_4(MeCN)_2]$ with $HSC_6H_4PPh_2$.

Introduction

The reactivity of unfunctionalized arenethiols with ruthenium[1][2] and osmium[3−7] carbonyl clusters has been studied in detail. Most of these investigations have attempted to shed light on the fundamental steps of catalytic hydrodesulfurization (HDS) reactions[8] in which sulfur is removed from thiols and other organosulfur compounds in fossil fuels.[9] However, despite the widespread use of HDS processes and their economic and environmental significance, the nature of the interaction of the organosulfur compounds with the catalysts and the mechanisms of the catalytic processes are still far from being well-known.[9]

Both $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ react with thiophenol to give $[M_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_{10}]$ (M = Ru,[2] Os[3]) as primary products. However, these compounds undergo facile C−S bond activation reactions, under thermal and/or photochemical conditions, leading to the sulfide derivatives $[M_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$ (M = Ru,[2] Os[4][5]), $[Os_3(\mu_3\text{-}S)_2(CO)_9]$,[3b,4,6] $[M_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ (M = Ru,[2] Os[4]), $[Ru_4(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_9]$[2] $[Os_4(\mu_3\text{-}S)_2(CO)_{13}]$,[3b] $[Os_4(\mu_3\text{-}S)_2(CO)_{12}]$,[3b] and $[Os_6(\mu_4\text{-}S)_2(CO)_{17}]$.[5] It has also been reported that $[Os_3(CO)_{11}(MeCN)]$ reacts with *m*- and *p*-thiocresol to give $[Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4Me)(CO)_{10}]$ and that this reaction proceeds *via* the intermediate $[Os_3(CO)_{11}(HSC_6H_4Me)]$, in which both the sulfur and the hydrogen atoms of the thiol group interact with an osmium atom.[7]

Despite this interesting reactivity of thiophenols with ruthenium and osmium carbonyl clusters, only a limited number of studies involving functionalized thiophenols have been published. We have previously reported that 1,2-benzenedithiol reacts with $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ to give the binuclear derivatives $[M_2(\mu\text{-}\eta^2\text{-}S_2C_6H_4)(CO)_6]$ (M = Ru, Os),[10] and that treatment of 2-aminothiophenol with $[Ru_3(CO)_{12}]$ gives $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4NH_2)(CO)_9]$.[11] However, the reaction of 2-aminothiophenol with $[Os_3(CO)_{10}(MeCN)_2]$ gives $[Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4NH_2)(CO)_{10}]$,[12] in which the NH_2 group is not coordinated. It is also known that $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2-mercaptobenzoic acid to give the hexanuclear compound $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}\eta^3\text{-}SC_6H_4CO_2)]$,[13] in which the $SC_6H_4CO_2$ ligand connects two triangles of osmium atoms through the thiolate and the carboxylate groups, each group bridging one edge of the corresponding trimetal fragment.

We report herein the reactivity of 2-(diphenylphosphanyl)thiophenol ($HSC_6H_4PPh_2$) with $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$.

Results and Discussion

Treatment of a THF solution of $[Ru_3(CO)_{12}]$ with $HSC_6H_4PPh_2$, in a 1:1 ratio, at reflux temperature for 1.5 h gave $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)(CO)_9]$ (**1a**) as the major component of a mixture of at least three products. The compound was isolated in 56% yield after a chromatographic workup. On the other hand, the osmium derivative $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)(CO)_9]$ (**1b**) was isolated in 48% yield after a chromatographic separation from a mixture of at least four compounds, formed from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $HSC_6H_4PPh_2$, in a 1:1 ratio, in THF at room temperature.

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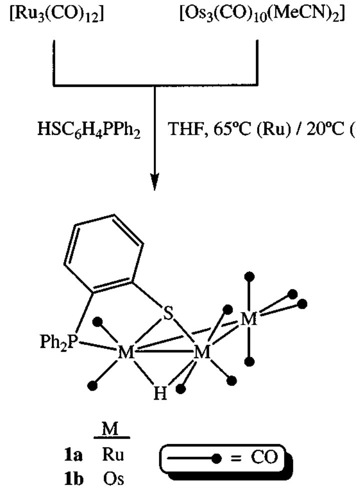
In both cases, longer reaction times, higher temperatures or the use of larger amounts of $HSC_6H_4PPh_2$ resulted in lower yields of **1a** or **1b** and in the formation of complex mixtures. In the case of the ruthenium reactions, we managed to isolate and characterize some of these products (vide infra), but the osmium reactions did not allow the identification of more products, since they afforded a plethora of compounds in very small amounts as soon as the temperature was raised.



Scheme 1. Synthesis of compounds **1a** and **1b**

The structure depicted for compounds **1a** and **1b** in Scheme 1 is based on their analytical and spectroscopic data and on an X-ray diffraction study on the ruthenium derivative **1a**. Both compounds give molecular ions in their FAB MS corresponding to the proposed formulation. Their ^1H NMR spectra contain a hydride resonance as a doublet with a small J_{H-P} coupling constant (8.3 Hz for **1a** and 8.1 Hz for **1b**), which indicates a *cis* arrangement of the hydride and the phosphorus atom in the clusters.[14–16] All these data, in addition to their microanalyses and IR spectra, indicate that both compounds have analogous structures. In order to precisely assign the coordination of the $SC_6H_4PPh_2$ ligand to the clusters, the structure of the ruthenium derivative **1a** was determined by X-ray diffraction methods.

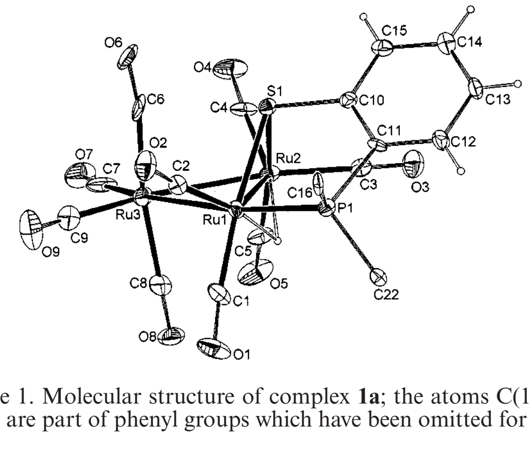


Figure 1. Molecular structure of complex **1a**; the atoms C(16) and C(22) are part of phenyl groups which have been omitted for clarity

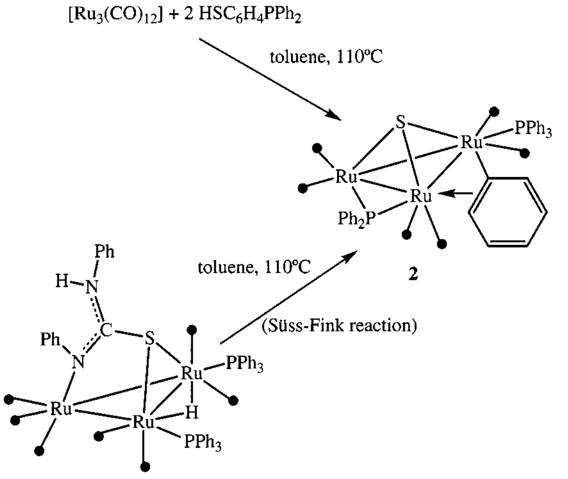
Table 1. Selected structural parameters of complex **1a**

Bond Lengths [Å]		Bond Angles [°]	
Ru(1)−Ru(2)	2.841(2)	C(1)−Ru(1)−P(1)	96.2(5)
Ru(1)−Ru(3)	2.824(2)	C(2)−Ru(1)−P(1)	99.1(6)
Ru(2)−Ru(3)	2.833(2)	C(1)−Ru(1)−S(1)	169.5(7)
Ru(1)−S(1)	2.381(4)	C(2)−Ru(1)−S(1)	98.2(6)
Ru(2)−S(1)	2.404(4)	P(1)−Ru(1)−Ru(3)	166.7(1)
Ru(1)−P(1)	2.309(4)	P(1)−Ru(1)−Ru(2)	107.1(1)
Ru(1)−C(1)	1.84(2)	P(1)−Ru(1)−S(1)	84.7(1)
Ru(1)−C(2)	1.90(2)	Ru(2)−Ru(1)−Ru(3)	60.01(6)
Ru(2)−C(3)	1.95(2)	C(3)−Ru(2)−S(1)	94.6(5)
Ru(2)−C(4)	1.91(2)	C(4)−Ru(2)−S(1)	94.9(5)
Ru(2)−C(5)	1.91(2)	C(5)−Ru(2)−S(1)	169.3(6)
Ru(3)−C(6)	1.93(2)	Ru(1)−Ru(2)−Ru(3)	59.70(5)
Ru(3)−C(7)	1.94(2)	Ru(1)−Ru(3)−Ru(2)	60.29(5)
Ru(3)−C(8)	1.94(2)	C(10)−S(1)−Ru(1)	105.2(6)
Ru(3)−C(9)	1.97(2)	C(10)−S(1)−Ru(2)	105.0(5)
		Ru(1)−S(1)−Ru(2)	72.8(1)

Figure 1 shows the molecular structure of compound **1a**. A selection of bond lengths and angles is given in Table 1. The cluster consists of an irregular triangle of ruthenium atoms in which the longest edge [Ru(1)−Ru(2) 2.841(2) Å], is spanned by the sulfur atom of a $SC_6H_4PPh_2$ ligand [Ru(1)−S(1) 2.381(4) Å, Ru(2)−S(1) 2.404(4) Å] and by a hydride ligand. The phosphorus atom of the $SC_6H_4PPh_2$ ligand is also attached to one of the ruthenium atoms of the same edge [Ru(1)−P(1) 2.309(4) Å] in a position approximately *trans* to the Ru(1)−Ru(3) edge [P(1)−Ru(1)−Ru(3) 166.7(1)°]. The cluster shell is completed by nine CO ligands, four of which are attached to Ru(3), three to Ru(2), and two to Ru(1). An analogous structure has been reported for the aminothiolate derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SC_6H_4NH_2)(CO)_9]$.[11] The structures of the ruthenium and osmium compounds $[M_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HNC_6H_4PPh_2)(CO)_9]$ (M = Ru,[15] Os[16]), derived from 2-(diphenylphosphanyl)aniline, have also been determined by X-ray diffraction methods and they are also similar to that of **1a**, although their bridged edges are shorter than the unbridged ones, in contrast to that of **1a**, probably as a consequence of the different sizes of the bridgehead atoms (N *vs* S).[17]

Treatment of THF or toluene solutions of $[Ru_3(CO)_{12}]$ with $HSC_6H_4PPh_2$, in 1:2 mol ratio, at reflux temperature, resulted in complex mixtures of products from which compounds **1a** and **2** could be separated by chromatographic means and subsequently identified. The best yield of complex **2** (13%) was obtained from a 1 h reaction in toluene at reflux temperature.

The structure depicted for compound **2** in Scheme 2 is based on an X-ray diffraction study, since little structural information was obtained from its analytical (microanalysis, FAB MS) and spectroscopic data (IR, ^1H and ^{31}P NMR). After having determined the structure, we found that Süss-Fink's group had previously synthesized the same compound by thermolysis of $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCNHPhNPh)(CO)_7(PPh_3)_2]$ in refluxing toluene (Scheme 2), in the course of a study of the reactivity of $[Ru_3(CO)_{12}]$ with *N,N'*-disubstituted thioureas.[18] They also reported its



Scheme 2. Synthesis of compound **2**

X-ray structure. Consequently, we will not describe the structural details here.

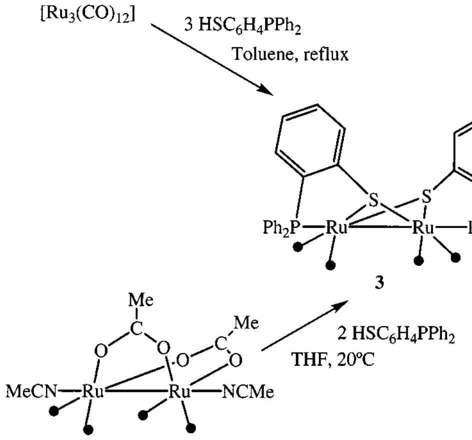
It should be noted that all the non-CO ligands of complex **2**, i.e. sulfide, phenyl, diphenylphosphanyl and triphenylphosphane, arise in our case from the degradation of 2-(diphenylphosphanyl)thiophenol, implying the cleavage of P−C, S−C, and S−H bonds and the formation of C−H bonds. To our knowledge, this is the first example in which such important processes occur in the same ligand in a metal complex.

As mentioned in the introduction, the reactions of arenethiols with carbonyl metal clusters often lead to stoichiometric desulfurization of the thiols, to give the arenes and sulfide-metal derivatives.[1−8] However, apart from compound **2**, few examples of cluster compounds containing phenyl ligands arising from the degradation of arylphosphane ligands have been reported, but in all of them the phenyl groups are η^1-coordinated in terminal[19] or bridging[20] modes. Cluster **2** is a rare example of a complex containing a bridging phenyl ligand which interacts in a monohapto manner with one metal atom and in a dihapto manner with the other metal atom. This type of coordination is frequently observed for bridging alkenyl ligands.

The reaction pathway by which complex **2** is formed appears to be quite intricate, since it involves the breaking and the formation of many bonds. The composition of **2** suggests that it may be formed from **1a** and two equivalents of $HSC_6H_4PPh_2$, but a sulfur atom is in excess from a stoichiometric point of view. This is in accordance with the fact that the formation of complex **2** is accompanied by the formation of other products which could not be characterized.

As a part of several attempts to shed light on the mechanism of formation of complex **2**, compound **1a** was thermolyzed in refluxing toluene for 1 h, both in the absence and presence of $HSC_6H_4PPh_2$. In the former case, a $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture revealed the presence of **2**, in low yield, among many other products with high ^{31}P chemical shifts ($\delta > 200$). In the latter case, compound **2** was formed in a greater amount, being the major component (*ca.* 15%) of a mixture of many products ($^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture). These data suggest that compound **1a** may be an early intermediate in the formation of **2** from $[Ru_3(CO)_{12}]$ and $HSC_6H_4PPh_2$, although other possibilities excluding the intermediacy of **1a** cannot be ruled out.

In a further attempt to shed light on the mechanism of formation of complex **2**, $[Ru_3(CO)_{12}]$ was heated with three equivalents of $HSC_6H_4PPh_2$ in refluxing THF for 2 h. In this case, complex **2** was also formed in a small amount, but the major component of the mixture (*ca.* 20%) was a complex that could be separated by TLC and subsequently identified as the binuclear derivative $[Ru_2(\mu\text{-}\eta^2\text{-}SC_6H_4PPh_2)_2(CO)_4]$ (**3**). Similar results were obtained carrying out the reaction in refluxing toluene for 1 h.



Scheme 3. Synthesis of compound **3**

The microanalysis and FAB MS data of **3** support its binuclear formulation. Its $^{31}P\{^1H\}$ NMR spectrum, which only contains a singlet at $\delta = 75.3$, and its IR spectrum, which shows four absorptions in the carbonyl region, confirm the C_2 symmetry shown in Scheme 3 for this complex.

Complex **3** can be more efficiently prepared (45% yield) by treatment of the binuclear acetate dimer $[Ru_2(\mu\text{-}\eta^2\text{-}MeCO_2)_2(CO)_4(MeCN)_2]$[21] with $HSC_6H_4PPh_2$ (1:2 mol ratio) in THF at room temperature. The carboxylate bridges of $[Ru_2(\mu\text{-}\eta^2\text{-}RCO_2)_2(CO)_4(MeCN)_2]$ are labile in the presence of acids (HX) whose conjugate bases (X) are able to act as bridging ligands, the carboxylate bridge being released as the corresponding carboxylic acid. This synthetic method has previously been used to prepare some ligand-bridged diruthenium complexes, such as $[Ru_2(\mu\text{-}SR)_2(CO)_4(PPh_3)_2]$[22] or $[Ru_2(\mu\text{-}pz)_2(CO)_4(PPh_3)_2]$[23] (pz = pyrazolate). The preparation of complex **3** by this method, which starts from a binuclear precursor, also supports its binuclear nature.

In conclusion, the present work describes the synthesis of some bi- and trinuclear ruthenium and osmium carbonyl complexes derived from the reactions of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ with 2-(diphenylphosphanyl)thiophenol. We have shown that these reactions are not selective, since this thiol is very fragile once it is coordinated to a metal cluster, being liable to undergo a series of S−H, S−C and P−C bond cleavage reactions that often lead to mixtures of many products, as has been proven with the isolation and characterization of compound **2**

Experimental Section

General: Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. − Unless otherwise stated, the reactions were carried out under nitrogen, using standard Schlenk techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC on silica gel. − The compounds $[Ru_3(CO)_{12}]$,[24] $[Os_3(CO)_{12}]$,[25] $[\{Ru_2(\mu\text{-}\eta^2\text{-}MeCO_2)_2(CO)_4\}_n]$[21] and $HSC_6H_4PPh_2$[26] were prepared as described in the literature. Anhydrous Me_3NO was prepared by azeotropic distillation of a toluene solution of $Me_3NO\cdot 2H_2O$ and was stored under nitrogen. $RuCl_3\cdot nH_2O$ and OsO_4 were purchased from Pressure Chemicals, all other reagents were purchased from Aldrich. − Microanalyses: University of Oviedo Analytical Service. − FAB MS (positive ion): Finnigan Mat-95 spectrometer, nitrobenzyl alcohol as matrix, cesium as bombarding gas. − IR: Perkin−Elmer FT 1720-X. − NMR: Bruker AC-200 and AC−300, 23°C, $SiMe_4$ (internal, for ^1H) or 85% H_3PO_4 (external, for ^{31}P) as standards ($\delta = 0$).

Synthesis of 1a: A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and $HSC_6H_4PPh_2$ (50 mg, 0.158 mmol) in THF (15 mL) was stirred at reflux temperature for 1.5 h. The color changed from orange to deep red. After addition of neutral alumina (*ca.* 100 mg) to the solution, the solvent was removed under vacuum. The solid residue was poured on top of a column (2 × 15 cm) of neutral alumina (activity I) packed in hexane. Elution with dichloromethane/hexane (1:6) afforded to yellow bands. A dark residue remained uneluted at the top of the column. The second band was very weak and was discarded. The first band gave compound **1a**, as a yellow/orange solid, when the solvent was evaporated under vacuum. − Yield: 75 mg (56%). − $C_{27}H_{15}O_9PRu_3S$: calcd. C 38.17, H 1.78; found C 37.98, H 1.72. − IR (THF): $\nu(CO)$ = 2086 (m), 2050 (s), 2017 (m), 2005 (s), 1988 (m), 1961 (w), 1944 (w). − ^1H NMR ($CDCl_3$): δ = 7.86−7.10 (m, 14 H), −15.76 (d, J_{H-P} = 8.3 Hz, 1 H). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 69.8 (s). − FAB MS: *m*/*z* = 850 $[M]^+$.

Synthesis of 1b: A solution of $[Os_3(CO)_{12}]$ (50 mg, 0.055 mmol) and anhydrous Me_3NO (10 mg, 0.14 mmol) in dichloromethane (15 mL) and acetonitrile (2 mL) was stirred at room temperature for 1 h. The resulting solution, containing the complex $[Os_3(CO)_{10}(MeCN)_2]$[27] (IR identification) was evaporated to dryness under vacuum. The residue was extracted into THF (10 mL) and was treated with $HSC_6H_4PPh_2$ (16 mg, 0.055 mmol). After stirring for 1 h at room temperature, the solution was concentrated to *ca.* 2 mL and was applied onto preparative silica gel TLC plates. Elution with dichloromethane/hexane (2:5) afforded four bands. The major band, yellow, was extracted with dichloromethane to give compound **1b**, as a yellow solid, after crystallization from dichloromethane/hexane. − Yield: 30 mg (48%). − $C_{27}H_{15}O_9Os_3PS$: calcd. C 29.03, H 1.35; found C 29.31, H 1.38. − IR (CH_2Cl_2): $\nu(CO)$ = 2110 (w), 2091 (m), 2052 (s), 2010 (s), 1990 (m), 1970 (w), 1951 (w). − ^1H NMR ($CDCl_3$): δ = 7.84−7.18 (m, 14 H), −17.42 (d, J_{H-P} = 8.1 Hz, 1 H). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 43.8 (s). − FAB MS: *m*/*z* = 1117 $[M]^+$.

Synthesis of 2: A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and $HSC_6H_4PPh_2$ (97 mg, 0.330 mmol) in toluene (20 mL) was stirred at reflux temperature for 1 h. The color changed from orange to deep red. The solution was concentrated to *ca.* 2 mL and the concentrate was applied onto preparative silica gel TLC plates. Elution with dichloromethane/hexane (2:5) afforded five bands and a residue at the base line. The major band, pink, was extracted with dichloromethane to give compound **2**, as a dark pink solid, after crystallization from dichloromethane/hexane. − Yield: 21 mg (13%). − $C_{42}H_{30}O_6P_2Ru_3S$: calcd. C 49.08, H 2.94; found C 49.03, H 2.87. − IR (THF): $\nu(CO)$ = 2002 (vs), 1977 (s), 1943 (m), 1927 (w). − ^1H NMR ($CDCl_3$): δ = 8.10 (d, J_{H-P} = 8.0 Hz, 1 H), 7.80−7.20 (m, 26 H), 7.06 (t, J_{H-P} = 8.0 Hz, 1 H), 6.52 (t, J_{H-P} = 8.0 Hz, 1 H), 6.09 (d, J_{H-P} = 8.0 Hz, 1 H) − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 215.1 (s, 1 P) 40.0 (s, 1 P). − FAB MS: *m*/*z* = 1028 $[M]^+$.

Synthesis of 3: A suspension of $[\{Ru_2(\mu\text{-}\eta^2\text{-}MeCO_2)_2(CO)_4\}_n]$ (100 mg, 0.231 mmol) was stirred in acetonitrile (20 mL) at reflux temperature for 15 min to give a yellow solution containing $[Ru_2(\mu\text{-}\eta^2\text{-}MeCO_2)_2(CO)_4(MeCN)_2]$[21] (IR identification). The solvent was removed under reduced pressure, and $HSC_6H_4PPh_2$ (136 mg, 0.463 mmol) and THF (20 mL) were added. The resulting solution was stirred at room temperature for 6 h. The color changed from orange to red. The solution was concentrated to *ca.* 2 mL and the concentrate was applied to preparative silica gel TLC plates. Elution with dichloromethane/hexane (1:5) afforded four bands. The first and major band, yellow, was extracted with dichloromethane to give compound **3**, as a yellow solid, after crystallization from dichloromethane/hexane. − Yield: 95 mg (45%). − $C_{40}H_{28}O_4P_2Ru_2S_2$: calcd. C 53.33, H 3.13; found C 53.71, H 3.33. − IR (hexane): $\nu(CO)$ = 1999 (w), 1978 (vs), 1940 (s), 1924 (w). − ^1H NMR ($CDCl_3$): δ = 7.84−7.06 (m) − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 75.3 (s). − FAB MS: *m*/*z* = 901 $[M]^+$.

Crystal Structure Determination of 1a: Crystal data and details of the structure determination are listed in Table 2. The unit cell dimensions were determined from the angular settings of 25 reflections with 10° < Θ < 15°. The orthorhombic space group *P*bca

Table 2. Crystallographic and refinement data for complex **1a**

formula	$C_{27}H_{15}O_9PRu_3S$
fw	849.63
cryst syst	orthorhombic
space group	*P*bca
a, *b*, *c* [Å]	30.282(7), 19.893(3), 10.195(3)
V [Å^3]	6142(3)
Z	8
F(000)	3296
D_{calcd} [g cm^{-3}]	1.838
μ [mm^{-1}]	1.625
cryst size [mm]	0.26 × 0.16 × 0.10
radiation (λ [Å])	Mo Kα (0.71073)
diffractometer	Enraf−Nonius CAD4
monochromator	graphite
temp [K]	293 (2)
scan method	ω−2θ
min/max *h, k, l*	0 /35, 0/23, 0/12
θ range [°]	1.34 to 24.98
data set	6243
unique data	5386 (R_{int} = 0.171)
data with $I>2\sigma(I)$	1304
restraints, parameters	0, 367
$R(F)_{I>2\sigma(I)}$[a]	0.0487
$R_w(F^2)_{all\ data}$[b]	0.1342
GOF[c]	0.954
Δ/σ	0.001
max, min Δρ [e/Å^3]	0.500, −0.804

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. − [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

was determined from systematic absences and confirmed by the structure determination. The intensity was checked throughout data collection by monitoring three standard reflections every 60 min. Final drift correction factors were between 0.99 and 1.02. Profile analysis[28] was performed on all reflections. Lorentz and polarization corrections were applied and data were reduced to $|F_o|^2$ values.

The structure was solved by Patterson interpretation using the program DIRDIF92.[29] Anisotropic least-squares refinement, using a local version of SHELX,[30] was followed by an empirical absorption correction[31] (maximum and minimum correction factors 1.00 and 0.28, respectively). Full matrix anisotropic least squares refinement on F^2, using the program SHELXL92,[32] followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms. Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms were refined. All hydrogen atoms, except the bridging hydride ligand, were geometrically placed, and were isotropically refined. The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0236P)^2]$, with $\sigma(F_o)$ from counting statistics and $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from the literature.[33] The plot in Figure 1 was made with the EUCLID package.[34] Geometrical calculations were made with PARST.[35] All computations were performed on an Alpha AXP3000 workstation.

Crystallographic data (excluding structure factors) for compound **1a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133011. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk].

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