Note

A new coordination mode for (pyrid-2-yl)thiolate (L) ligands: Synthesis and characterization of $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}L)(\mu\text{-}CO)(CO)_{15}]$

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Abstract

The hexaruthenium cluster complexes $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}L)(\mu\text{-}CO)(CO)_{15}]$, HL = 2-mercaptopyridine (**1**) and 2-mercapto-6-methyl-pyridine (**2**), have been prepared by heating $[Ru_3(CO)_{12}]$ with 0.5 equiv. of HL in THF at reflux temperature. An X-ray diffraction study on a crystal of complex **2** has determined that its metallic skeleton, a basal-edge-bridged square pyramid, is hold up by a (6-methylpyrid-2-yl)thiolate ligand. This ligand is attached to the four basal ruthenium atoms of the pyramid through the sulfur atom and to the edge-bridging ruthenium atom through the nitrogen atom. Such a coordination mode is unprecedented for (pyrid-2-yl)thiolate ligands.
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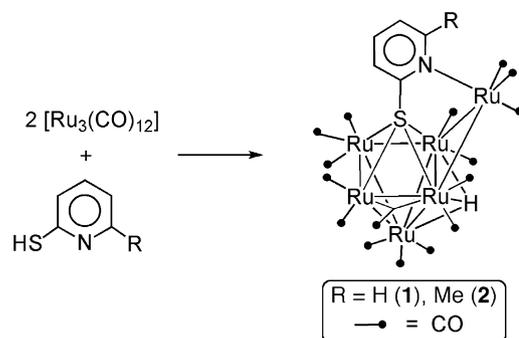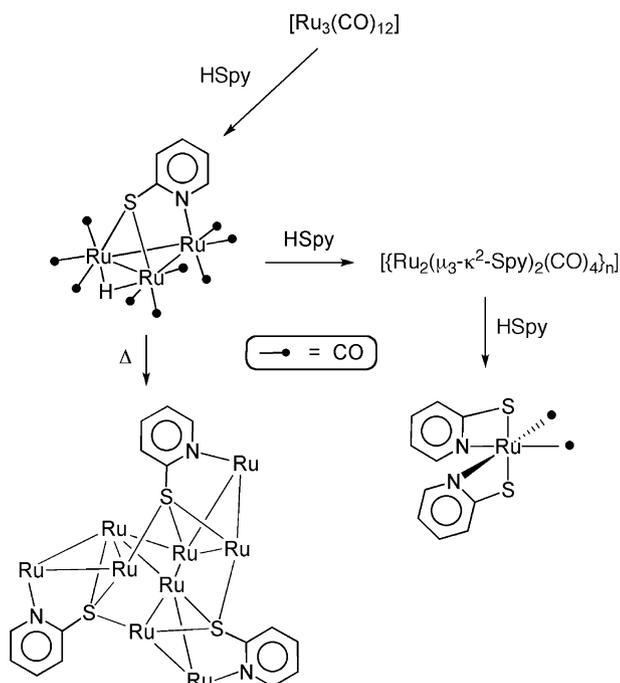
1. Introduction

We have recently reported the synthesis of the hexanu-clear derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ (H_2ampy = 2-amino-6-methylpyridine) by treatment of $[Ru_3(CO)_{12}]$ with H_2ampy in a 2:1 mole ratio [1,2]. The tri-ruthenium cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}Hampy)(CO)_9]$ is an intermediate in this reaction (Scheme 1). The unusual metallic skeleton of this cluster, a basal-edge-bridged square pyramid, is supported by a (6-methylpyrid-2-yl)i-mido ligand (ampy), which caps the metallic square through the imido N atom while its pyridine N atom is attached to the edge-bridging Ru atom. Its efficient synthe-sis has allowed us to investigate its reactivity with a variety of reagents, such as phosphines [2], alkynes [3], unsaturated cyclic hydrocarbons [4] and H_2ampy [5]. Its thermolysis at high temperature (196 °C) leads to interesting nonanuclear derivatives [6].

Two research groups have previously reported reactions of $[Ru_3(CO)_{12}]$ with 2-mercaptopyrine (HSpy). Our group has described that the thermal treatment of these two reagents, in a 1:1 mole ratio, leads to $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}Spy)(CO)_9]$. This trinuclear cluster reacts further with more HSpy to give, sequentially, the polymeric material $[\{Ru_2\text{-}(\mu_3\text{-}\kappa^2\text{-}Spy)_2(CO)_4\}_n]$ and the monomeric complex $[Ru\text{-}(\kappa^2\text{-}Spy)_2(CO)_2]$ (Scheme 2) [7]. Deeming's group has reported that $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}Spy)(CO)_9]$ is thermally unstable, undergoing trimerization in refluxing cyclohex-ane to give $[\{Ru_3(\mu_3\text{-}H)(\mu_4\text{-}\kappa^2\text{-}Spy)(CO)_7\}_3]$ (Scheme 2) [8].

Therefore, although the chemistry involving $[Ru_3(CO)_{12}]$ and 2-mercaptopyridine has already been developed to a considerable extent, the polynuclear ruthenium carbonyl chemistry commented above for 2-aminopyridines has no parallel in the chemistry of 2-mercaptopyridines. In addi-tion, the $\mu_5\text{-}\kappa^2$-coordination mode displayed by the ampy ligand in $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ has never been observed for (pyrid-2-yl)thiolate ligands.

These considerations prompted us to revisit the reactiv-ity of $[Ru_3(CO)_{12}]$ with 2-mercaptopyridines, but this time using a 2:1 mole ratio of the reagents. We now report that

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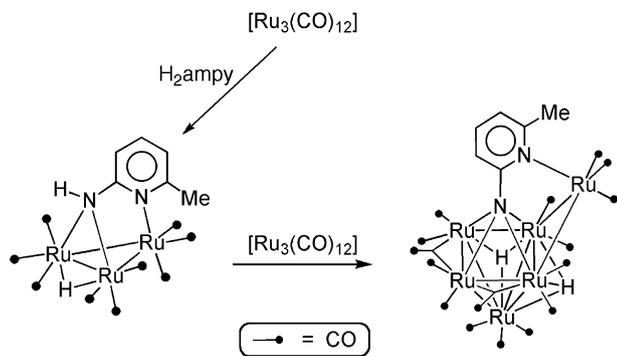
Scheme 1. Synthesis of [Ru$_6$(μ_3-H)$_2$(μ_5-κ^2-ampy)(μ-CO)$_2$(CO)$_{14}$].

Scheme 2. Reported reactivity of [Ru$_3$(CO)$_{12}$] with 2-mercaptopyridine. The hydride and CO ligands of the nonanuclear complex [{Ru$_3$(μ_3-H)(μ_4-κ^2-Spy)(CO)$_7$}$_3$] have been omitted for clarity.

Scheme 3. Synthesis of compounds **1** and **2**.

this approach has led to the synthesis of the hexaruthenium cluster complexes [Ru$_6$(μ_3-H)(μ_5-κ^2-L) (μ-CO)(CO)$_{15}$], HL = 2-mercaptopyridine (HSpy) and 2-mercapto-6-methyl-pyridine (Smpy), in which the (pyrid-2-yl)thiolate (L) ligands display an unprecedented μ_5-κ^2-coordination mode.

2. Results and discussion

The reaction of [Ru$_3$(CO)$_{12}$] with 0.5 equiv. of 2-merca-ptopyridine in THF at reflux temperature led to a mixture of products from which the dark green hexanuclear derivative [Ru$_6$(μ_3-H)(μ_5-κ^2-Spy)(μ-CO)(CO)$_{15}$] (**1**) was separated by chromatographic methods (38% yield) (Scheme 3). The trinuclear cluster [Ru$_3$(μ-H)(μ-κ^2-Spy)(CO)$_9$] was observed as a transient intermediate when the reaction was moni-tored by IR and spot TLC. In fact, complex **1** could also

be prepared in comparable yield by heating [Ru$_3$(CO)$_{12}$] and [Ru$_3$(μ-H)(μ-κ^2-Spy)(CO)$_9$] (1:1 mole ratio) in refluxing THF. The methylated derivative [Ru$_6$(μ_3-H)(μ_5-κ^2-Smpy)-(μ-CO)(CO)$_{15}$] (**2**) was similarly obtained from 2-mer-capto-6-methylpyridine (28% yield).

The composition of **1** and **2** was obtained from CHN microanalysis and positive FAB mass spectra (the latter contain the peaks of the expected molecular ion isotopo-mers). Both compounds display a similar band pattern in their IR spectra, indicating related structures. Their ^{1}H NMR spectra contain the resonances expected for the cor-responding pyridyl ligands in addition to a high-field reso-nance attributed to a hydride ligand.

The structure of these complexes was definitively ascertained studying a crystal of compound **2** by X-ray diffraction (Fig. 1, Table 1). The cluster consists of a basal-edge-bridged square pyramid of ruthenium atoms anchored to an Smpy ligand in such a way that the four basal ruthenium atoms Ru(1), Ru(2), Ru(4) and Ru(5) are attached to the thiolate S atom and the edge-bridging Ru(3) atom is bound to the pyridine N atom. A hydride ligand caps the Ru(1)–Ru(2)–Ru(6) face of the pyramid.
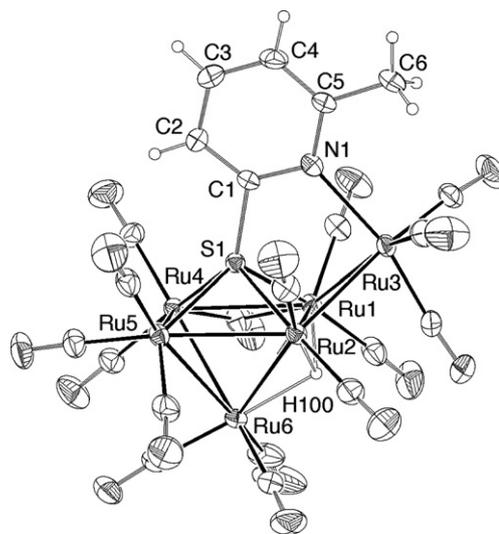

Fig. 1. Molecular structure of compound **2**. Ellipsoids are drawn at the 30% probability level.

Table 1
Selected interatomic distances (Å) in compound **2**

Ru(1)–Ru(2)	2.931(1)	Ru(1)–Ru(3)	2.7825(9)
Ru(1)–Ru(4)	2.8428(9)	Ru(1)–Ru(6)	2.963(1)
Ru(2)–Ru(3)	2.736(1)	Ru(2)–Ru(5)	2.8503(9)
Ru(2)–Ru(6)	2.8907(9)	Ru(4)–Ru(5)	2.896(1)
Ru(4)–Ru(6)	2.862(1)	Ru(5)–Ru(6)	2.843(1)
S(1)–Ru(1)	2.362(2)	S(1)–Ru(2)	2.329(2)
S(1)–Ru(4)	2.413(1)	S(1)–Ru(5)	2.382(2)
N(1)–Ru(3)	2.271(4)		

The cluster shell is completed by 15 terminal and one edge-bridging carbonyl ligands.

Overall, the structure of **2** reminds that of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ [2] because both have a common metallic skeleton and a similar arrangement of the corresponding bridging ligand, but some remarkable differences are also observed between these clusters. (a) The ampy derivative has two hydrides, whereas complex **2** has only one. This compensates the fact that the imido fragment contributes four electrons to the cluster count whereas the thiolate group contributes five (both compounds obey the EAN rule with their 88 electrons and 10 Ru–Ru bonds). (b) In $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)\text{-}(\mu\text{-}CO)_2(CO)_{14}]$, the distances between the apical Ru atom and those of the pyramid base are 0.1–0.2 Å longer than those involving the remaining ruthenium atoms, which are those bound to the bridging ampy ligand. However, the bond lengths between the basal ruthenium atoms of complex **2**, are 0.1–0.2 Å longer than those between the basal ruthenium atoms of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$, the remaining Ru–Ru distances being very similar for both clusters. This is attributed to the larger volume of the sulfur atom as compared to that of the nitrogen atom. (c) While the line defined by the bridgehead N atom and the C(1) atom of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2\text{-}(CO)_{14}]$ deviates only 3.2(8)° from the perpendicular to the plane defined by the four basal Ru atoms, the line defined by the bridgehead S atom and the C(1) atom of compound **2** deviates 11.62(1)° from the perpendicular to the basal plane. Again, this is undoubtedly due to the larger volume of the sulfur atom, which is more separated from the basal plane, 1.215(1) Å, than the imido N atom of the ampy complex, 1.04(1) Å. (d) Although $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ and compound **2** have the same number of CO ligands, they have a different distribution of terminal and edge-bridging CO ligands, 14 and 2 for the former cluster and 15 and 1 for the later.

Apart from $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ and some of its derivatives [2–6], the basal-edge-bridged square pyramidal metallic skeleton has only been observed in very few cluster complexes. In all cases, the four basal metal atoms are attached to the bridgehead atom of a quadruply-bridging sulfide [9], carbyne [10], carbide [11] or imido [12] ligand.

The (pyrid-2-yl)thiolate ligand has been found to be very versatile, being able to bind metal atoms in a monodentate manner through the sulfur atom [13], as a chelating ligand [7,13], as a bridging ligand through both nitrogen and sulfur and through sulfur alone [14], as a triply-bridging ligand [7,15] and as a quadruply-bridging ligand [8]. The quintuply-bridging coordination mode of the (pyrid-2-yl)thiolate ligands of **1** and **2** is unprecedented.

The μ_4-coordination mode of thiolate ligands is also very unusual. In fact, it has only been observed in some group-11 metal complexes [16] and in $[Et_4N][Fe_2Ru_3(\mu_4\text{-}SMe)(CO)_{14}]$ [17]. Curiously the bridging ligand of this mixed-metal complex does not arise from the corresponding thiol but from the methylation of the sulfide ligand of $[Et_4N]_2[Fe_2Ru_3\text{-}(\mu_4\text{-}S)(CO)_{14}]$ with methyl triflate. The Ru–S distances in this complex, 2.388, are comparable to the Ru–S distances found in compound **2**, which are in the range 2.329–2.413 Å. It is interesting to note that the Ru–S distances in these μ_4-thiolate complexes are similar to those reported for ruthenium cluster complexes containing μ_4-sulfide ligands, such as $[Ru_6(\mu_4\text{-}S)_2(CO)_{17}]$ [18], $[Ru_5(\mu_4\text{-}S)_2\text{-}(CO)_{14}]$ [18], $[Ru_4(\mu_4\text{-}S)_2(CO)_9(PMe_2Ph)_2]$ [19] and $[Ru_6(\mu\text{-}H)(\mu_4\text{-}S)(\mu_3\text{-}\kappa^2\text{-}ampy)(CO)_{17}]$ [20], being also comparable to those found in complexes having thiolate ligands bridging three or two metal–metal bonded ruthenium atoms, such as $[Ru_3(\mu\text{-}AuPPh_3)(\mu_3\text{-}S^tBu)(CO)_9]$ (2.301, 2.300 and 2.299 Å) [21], $[Ru_3(\mu\text{-}H)(\mu_3\text{-}S^tBu)(CO)_7(\mu\text{-}dppm)]$ (2.309, 2.322 and 2.334 Å) [22], $[Ru_3(\mu\text{-}H)(\mu\text{-}SEt)(CO)_{10}]$ (2.389, 2.391 Å) [23], and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}Spy)(CO)_9]$ (2.397, 2.401 Å) [8].

3. Experimental

3.1. General data

Solvents were dried over sodium diphenylketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC. All reagents were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument, using the residual dichloromethane solvent peak (5.30 ppm) as reference. Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

3.2. $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}Spy)(\mu\text{-}CO)(CO)_{15}]$ (**1**)

A mixture of $[Ru_3(CO)_{12}]$ (58 mg, 0.090 mmol) and 2-mercaptopyridine (5 mg, 0.045 mmol) was stirred in THF (10 ml) at reflux temperature for 6 h. Once cooled to room temperature, silica gel (4 g) was added and the solvent was removed under reduced pressure. The solid was placed onto a chromatographic silica gel column

$(20 \times 2$ cm) packed in hexane. Hexane–diethyl ether (10:1) eluted a yellow-orange band that contained [$Ru_3(CO)_{12}$] contaminated with small amounts of compounds that were not investigated (3 mg). Hexane–diethyl ether (1:2) eluted a minor brown-green band that was not identified. Hexane–dichloromethane (1:1) eluted a dark green band that was evaporated to dryness to give complex **1** as a dark green solid (20 mg, 38%). A dark brown residue remained une-luted at the top of the chromatographic column. Anal. Calc. for $C_{21}H_5NO_{16}Ru_6S$: C, 21.64; H, 0.43; N, 1.20. Found: C, 21.69; H, 0.48; N, 1.25%. +FAB MS (m/z): 1166 [M$^+$]. IR, ν(CO) (CH$_2$Cl$_2$): 2086 (w), 2057 (s), 2027 (vs), 2007 (m, sh), 1975 (w, br), 1954 (w, sh) cm^{-1}. ^{1}H NMR, δ (CDCl$_3$): 8.65 (d, $J = 7.2$ Hz, 1H), 7.79 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 7.2$ Hz, 1H), −18.75 (s, 1H) ppm.

3.3. [Ru$_6$(μ$_3$-H)(μ$_5$-κ^2-Smpy)(μ-CO)(CO)$_{15}$] (2)

A mixture of [Ru$_3$(CO)$_{12}$] (500 mg, 0.782 mmol) and 2-mercapto-6-methylpyridine (49 mg, 0.391 mmol) was stir-red in THF (30 ml) at reflux temperature for 10 h. Once cooled to room temperature, silica gel (6 g) was added and the solvent was removed under reduced pressure. The solid was placed onto a chromatographic silica gel column $(20 \times 2$ cm) packed in hexane. Hexane eluted a yellow-orange band that contained [Ru$_3$(CO)$_{12}$] contaminated with small amounts of compounds that were not investigated (40 mg). Hexane–diethyl ether (1:2) eluted a minor brown-green band that was not identified. Hexane–dichloromethane (1:4) eluted a dark green band that was evaporated to dryness. The residue was recrystallized twice from THF–hexane to give **2** as a dark green solid (130 mg, 28%). A dark brown residue remained uneluted at the top of the chromatographic column. Anal. Calc. for $C_{22}H_7NO_{16}Ru_6S$: C, 22.40; H, 0.60; N, 1.19. Found: C, 22.33; H, 0.63; N, 1.22%. +FAB MS (m/z): 1180 [M$^+$]. IR, ν(CO) (CH$_2$Cl$_2$): 2084 (w), 2054 (s), 2027 (vs), 2004 (m, sh), 1976 (w, br), 1954 (w, sh) cm^{-1}. ^{1}H NMR, δ (CDCl$_3$): 7.69 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.6$ Hz, 1H), 2.89 (s, 3H), −18.79 (s, 1H) ppm.

3.4. X-ray structure of compound 2

A selection of crystal, measurement and refinement data is given in Table 2. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffrac-tometer, using graphite-monochromatized Mo Kα radia-tion. An absorption correction was applied using SADABS [24]. The structure was solved by direct methods and refined by full matrix least-squares against F^2 with SHEL-XTL [25]. All non-hydrogen atoms were refined anisotropi-cally. The hydride atom H(100) was located using the program XHYDEX [26] and was refined with free coordinates and thermal parameters. All the remaining hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plot was made with the PLATON pro-

Table 2
Crystal data and structure refinement details for compound **2**

Formula	$C_{22}H_7NO_{16}Ru_6S$
Formula weight	1179.77
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.675(5)
b (Å)	14.684(5)
c (Å)	17.566(7)
β (°)	105.420(6)
V (Å^3)	3152(2)
Z	4
$F(000)$	2216
D_{calc} (g/cm^3)	2.486
Radiation (λ, Å)	Mo Kα (0.71073)
μ (mm^{-1})	2.940
Crystal size (mm)	$0.27 \times 0.20 \times 0.16$
Temperature (K)	296(2)
θ Limits (°)	1.78–23.32
Minimum/maximum h, k, l	−14/7, −16/16, −19/19
Number of reflections collected	13689
Unique reflections	4556
Reflections with $I > 2\sigma(I)$	4064
Absorption correction	SADABS
Maximum/minimum transmission	0.628/0.495
Parameters, restraints	421, 0
Goonness-of-fit on F^2	1.076
Final R_1 (on F, $I > 2\sigma(I)$)	0.0266
Final wR_2 (on F^2, all data)	0.0790
Minimum/maximum residuals (e/Å^3)	−0.621/0.536

gram package [27]. The WINGX program system [28] was used throughout the structure determination.

4. Supplementary material

CCDC 640542 contains the supplementary crystallo-graphic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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