Triruthenium and triosmium carbonyl clusters containing chiral bidentate NHC-thiolate ligands derived from levamisole

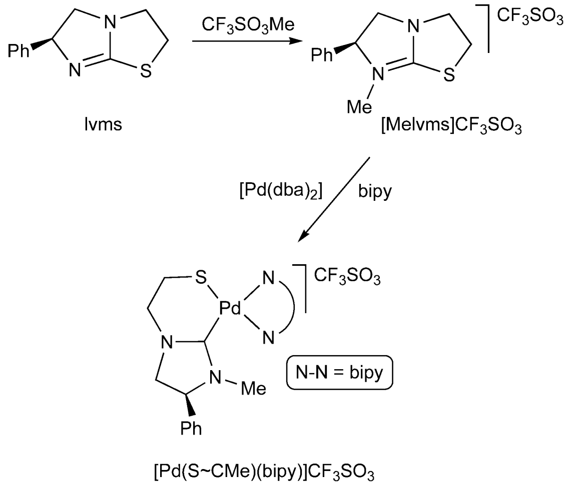
Javier A. Cabeza,* Iván da Silva, Ignacio del Río and M. Gabriela Sánchez-Vega

Received 15th May 2006, Accepted 22nd June 2006
First published as an Advance Article on the web 3rd July 2006
DOI: 10.1039/b606869c

The trinuclear complexes $[M_3(\mu\text{-}Cl)(\mu\text{-}S{\sim}CH)(CO)_9]$ (M = Ru, Os; S∼CH = 1-ethylenethiolate-3-*H*-4-(*S*)-phenylimidazolin-2-ylidene) and $[M_3(\mu\text{-}H)(\mu\text{-}S{\sim}CMe)(CO)_9]$ (M = Ru, Os; S∼CMe = 1-ethylenethiolate-3-methyl-4-(*S*)-phenylimidazolin-2-ylidene) have been prepared by treating $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ with levamisolium chloride or $[M_3(\mu\text{-}H)(CO)_{11}]^-$ with methyl levamisolium triflate, respectively. The chiral N-heterocyclic carbene-thiolate ligands S∼CH and S∼CMe arise from the oxidative addition of the C–S bond of levamisolium or methyl levamisolium cations to anionic trinuclear clusters.

Introduction

We have recently reported that reactions of methyl levamisolium triflate, [Melvms]CF_3SO_3, a methylated derivative of levamisole,[1] lvms, with $[Pd(dba)_2]$ (dba = dibenzylidene acetone), in the presence of appropriate ancillary ligands, lead, in one-pot processes, to cationic palladium(II) derivatives that contain the novel ligand 1-ethylenethiolate-3-methyl-4-(*S*)-phenylimidazolin-2-ylidene, S∼CMe. This ligand, that consists of a chiral NHC fragment (NHC = N-heterocyclic carbene) functionalized with a thiolate sidearm, arises from the cleavage, *via* oxidative addition, of the S–C(sp^2) bond of methyl levamisolium (see, for example, the reactions shown in Scheme 1).[2]



Scheme 1

These results, the current great interest in metal complexes having NHC ligands,[3,4] the recent discovery that some metal complexes containing chiral NHC ligands are efficient catalysts for asymmetric reactions,[5] and the fact that there is an increasing interest in metal complexes containing chiral ligands of this type,[5,6] led us to investigate whether the oxidative addition of the S–C(sp^2) bond of levamisolium salts could take place over complexes of low-valent metals different from palladium.

We now report that the treatment of levamisolium salts with some triruthenium and triosmium carbonyl cluster complexes leads, through processes that involve an S–C(sp^2) bond cleavage as a key reaction step, to trinuclear derivatives containing chiral bidentate NHC-thiolate ligands.

Levamisole hydrochloride (levamisolium chloride, [Hlvms]Cl), which is the most convenient precursor to levamisole and methyl levamisolium triflate,[1] is an inexpensive, commercially available, enantiomerically pure reagent. Levamisole and its hydrochloride have been used as drugs with anthelmintic[7] and anticancer[8] properties.

A small part of this work has been communicated in a preliminary form.[9]

Results and discussion

Levamisolium chloride reacted with $[Ru_3(CO)_{12}]$ in THF at reflux temperature (40 min) to give an apparently pure solid product (IR, CHN microanalysis, FAB MS, ^1H NMR) in high yield. However, the $^{13}C\{^1H\}$ NMR spectrum of this solid showed double lines for nearly all the carbon resonances, indicating the presence of two different, but very similar, products in a *ca.* 1 : 1 ratio (Fig. 1).[10] These compounds were subsequently identified as two diastereoisomers of formula $[Ru_3(\mu\text{-}Cl)(\mu\text{-}S{\sim}CH)(CO)_9]$ (**1** and **2**; S∼CH = 1-ethylenethiolate-3-*H*-4-(*S*)-phenylimidazolin-2-ylidene; Scheme 2). Column chromatography and TLC failed to separate **1** and **2**. A small amount (9%) of pure **2** was obtained by repeated recrystallization of the crude reaction mixture from combinations of dichloromethane and hexane.

An X-ray diffraction study on the benzene solvate **2**·C_6H_6, reported in the preliminary communication of this work,[9] revealed that this compound is an open 50-electron trinuclear cluster in which the open edge is doubly bridged by a chlorine atom and by the sulfur atom of a 1-ethylenethiolate-3-*H*-4-(*S*)-phenylimidazolin-2-ylidene ligand. The NHC fragment of this ligand is also attached through its carbene carbon atom to one

---

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071, Oviedo, Spain. E-mail: jac@fq.uniovi.es; Fax: 34 985103446

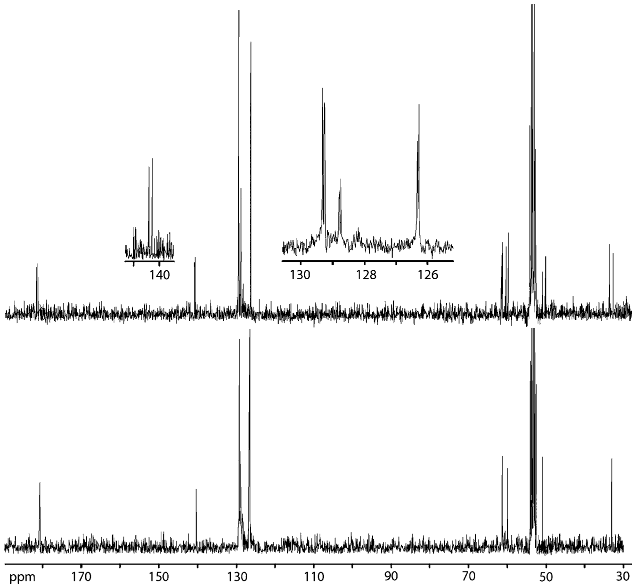
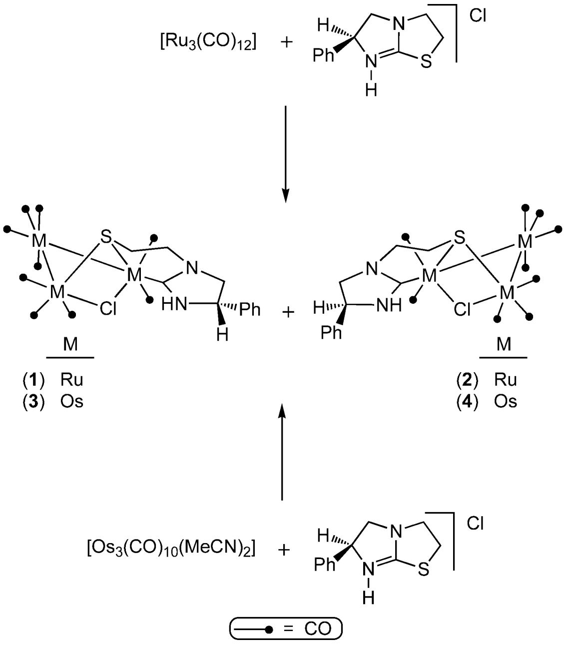


Fig. 1 $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, 293 K, 75.47 MHz) of the reaction mixture obtained from $[Ru_3(CO)_{12}]$ and [Hlvms]Cl (mixture of **1** and **2**, top spectrum) and pure **2** (bottom spectrum). In both spectra, the carbonyl region has been excluded for clarity.



Scheme 2

of the ruthenium atoms of the open edge (Scheme 2). The stereochemistry of the stereogenic carbon atom and the N–H hydrogen atom of the original levamisolium cation are maintained in compound **2**.

This structure helped assign the structure of diastereoisomer **1**. While both **1** and **2** should have the same absolute configuration of the phenyl-substituted carbon atom, their stereogenic metal atoms should have opposite absolute configurations.

Although the first chloro-[11] and thiolate-bridged[12] triruthenium carbonyl complexes were reported long time ago, the first report dealing with carbonyl metal clusters having NHC ligands has been published very recently. It describes the reactivity of $[Ru_3(CO)_{12}]$ with 1,3-dimethylimidazol-2-ylidene.[13]

In an analogous reaction to that described above, the treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with levamisolium chloride led to a solid material whose analytical and spectroscopic data, particularly the $^{13}C\{^1H\}$ NMR spectrum, confirmed that it contained a *ca.* 1 : 1 mixture of two diastereoisomers, analogous to **1** and **2**, that correspond therefore to the formula $[Os_3(\mu\text{-}Cl)(\mu\text{-}S{\sim}CH)(CO)_9]$ (**3** and **4**; Scheme 2). Unfortunately, this mixture could not be separated by recrystallization or by chromatographic techniques.

Chloro-[14] and thiolate-bridged[15] triosmium carbonyl cluster complexes have been previously reported. Although osmium carbonyl clusters containing NHC ligands are unprecedented, some triosmium aminocarbene clusters, prepared by activation of tertiary amines, are known.[16]

Looking for reaction intermediates that could shed light on the reaction pathway that leads to the mixture of **1** and **2** from $[Ru_3(CO)_{12}]$ and levamisolium chloride, we treated the activated cluster $[Ru_3(CO)_{10}(MeCN)_2]$ with levamisolium chloride in dichloromethane at room temperature ($[Ru_3(CO)_{12}]$ does not react with levamisolium chloride at this temperature). The anionic chloro complex $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ was observed immediately by IR spectroscopy.[11a] A spot TLC analysis of the solution also indicated the presence of small amounts of **1** + **2**, $[Ru_3(CO)_{12}]$, and a yellow species that decomposed on the TLC plate after a couple of minutes. Heating this solution to reflux temperature led to **1** and **2** as the major products. In a subsequent experiment, $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ (formed *in situ* from $[Ru_3(CO)_{12}]$ and [PPN]Cl)[11a] was treated with $[Hlvms][BF_4]$ (prepared from levamisole and $[HOEt_2][BF_4]$). Again, a mixture of **1** + **2**, $[Ru_3(CO)_{12}]$, and the above-mentioned yellow species was observed at room temperature. Unfortunately all attempts to isolate this yellow product were unsuccessful, since chromatographic supports promote its transformation into the mixture of **1** and **2**. Interestingly, no reaction was observed when $[Ru_3(CO)_{12}]$ was treated with $[Hlvms][BF_4]$ in THF at reflux temperature.

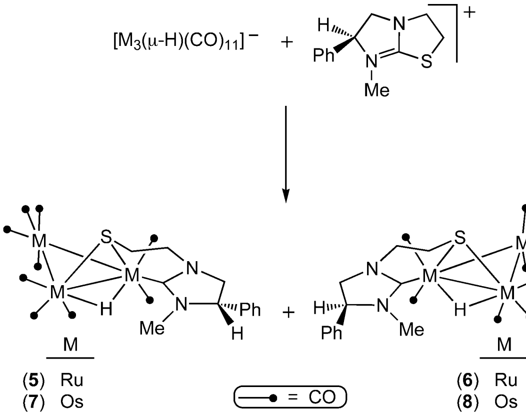
The above data suggest that upon treatment with levamisolium chloride, $[Ru_3(CO)_{12}]$ or $[Ru_3(CO)_{10}(MeCN)_2]$ are attacked by the chloride anion to give $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$. A subsequent attachment of $[Hlvms]^+$ to either of the chloro-bridged metal atoms of $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ should lead to a mixture of two transient neutral diastereoisomers, which may correspond to the unstable uncharacterized yellow species observed by TLC, that would readily undergo an S–C(sp^2) bond activation reaction (accompanied by CO elimination) to give the mixture of **1** and **2**.

Additionally, no reaction was observed when $[Ru_3(CO)_{12}]$ was treated with $[Hlvms][BF_4]$ and $[Melvms]CF_3SO_3$ in refluxing THF. As the tetrafluoroborate and triflate anions do not react with $[Ru_3(CO)_{12}]$, these experiments further support the deduction that levamisolium cations react with anionic clusters but not with neutral ones.

These data led us to study the reactivity of anionic hydrido-bridged triruthenium and triosmium carbonyl clusters of the type $[M_3(\mu\text{-}H)(CO)_{11}]^-$ with methyl levamisolium, expecting that the diastereomeric products of these reactions would have solubility and/or polarity different enough to allow the isolation of pure products.

As expected, a mixture of two diastereoisomers of formula $[Ru_3(\mu\text{-}H)(\mu\text{-}S{\sim}CMe)(CO)_9]$ was obtained form the reaction of

$[NEt_4][Ru_3(\mu\text{-}H)(CO)_{11}]$ with $[Melvms]CF_3SO_3$ in THF at reflux temperature (**5** and **6**; Scheme 3). Similarly, treatment of $[PPN][Os_3(\mu\text{-}H)(CO)_{11}]$ with $[Melvms]CF_3SO_3$ in THF at reflux temperature also led to two diastereoisomers, corresponding to the formula $[Os_3(\mu\text{-}H)(\mu\text{-}S{\sim}CMe)(CO)_9]$ (**7** and **8**; Scheme 3). In these two cases, both the ^1H NMR spectra (which showed separated singlet resonances for the hydride and methyl group of each diastereoisomer) and the $^{13}C\{^1H\}$ NMR spectra of the crude reaction mixtures indicated that they contained two compounds in *ca.* 1 : 1 ratio.



Scheme 3

For both reactions, we succeeded in separating the mixture of diastereoisomers using TLC. This allowed us not only to confirm that the components of each pair of diastereoisomers have identical FAB MS and IR spectra, but also to get single crystals of the ruthenium compound **5**, determine its structure by X-ray diffraction, and subsequently assign the structures of compounds **6–8**.

The structure of compound **5** is shown in Fig. 2. A selection of bond distances is collected in Table 1. The compound is a closed 48-electron trinuclear cluster with an edge doubly bridged by a hydride and by the sulfur atom of a 1-ethylenethiolate-3-methyl-4-(*S*)-phenylimidazolin-2-ylidene ligand that is also attached through its carbene carbon atom to one of the ruthenium atoms of the bridged edge. The cluster shell is completed with nine terminal CO ligands.

The stereochemistry of the stereogenic carbon atom C(5) should be the same in compounds **5** and **6**, but the stereochemistry of the ruthenium atom attached to the carbene atom C(1) should be just opposite in compounds **5** and **6**, as shown in Scheme 3.

Table 1 Selected interatomic distances (Å) in compound **5**[a]

Ru(1)–Ru(2)	2.8754(6)	C(1)–N(2)	1.344(8)
Ru(1)–Ru(3)	2.8712(6)	C(2)–N(2)	1.454(8)
Ru(2)–Ru(3)	2.8317(7)	C(2)–C(3)	1.518(9)
S(1)–Ru(1)	2.372(2)	C(3)–S(1)	1.810(7)
S(1)–Ru(3)	2.388(2)	C(4)–N(2)	1.471(7)
H(100)–Ru(1)	1.91(5)	C(4)–C(5)	1.529(9)
H(100)–Ru(3)	1.64(5)	C(5)–N(1)	1.471(8)
C(1)–Ru(1)	2.069(6)	C(12)–N(1)	1.450(8)
C(1)–N(1)	1.354(8)		

[a] Data for one of the two independent molecules found in the unit cell.

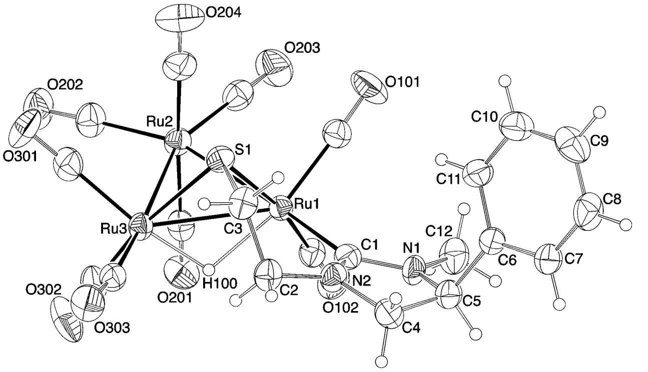


Fig. 2 Structure of one of the two independent but chemically equivalent molecules found in the crystals of **5** (30% thermal ellipsoids). The carbonyl C atoms have the same numbers as the corresponding O atoms.

As we could not get crystals of the osmium compounds **7** and **8** suitable for X-ray diffraction analysis, their structures (Scheme 3) were assigned on the basis of TLC elution rates. Using the same eluent, compounds **5** and **7** moved on their TLC plates faster than their diastereoisomers **6** and **8**, respectively. Consequently, we assigned to the osmium compounds **7** and **8** the same structures as the those of the ruthenium complexes **5** and **6**, respectively.

Therefore, the chiral NHC-thiolate ligands of compounds **1–8** arise from the oxidative addition of the S–C(sp^2) bond of levamisolium or methyl levamisolium to zerovalent metal species. Metal-mediated S–C bond cleavage processes are not unusual,[17] in fact, they are key steps in hydrodesulfurization processes,[18] but they generally require high temperatures. The oxidative addition of the C–Cl bond of 2-chloro-1,3-disubstituted imidazolinium salts has also been used to prepare metal complexes with NHC ligands.[5f]

Very few inorganic derivatives of levamisole have been hitherto reported. They are the above-mentioned cationic palladium(II) derivatives $[Pd_2(\mu\text{-}S{\sim}CMe)_2L_2]^{2+}$ (L = PPh_3, py) and $[Pd(S{\sim}CMe)L_2]^+$ (L_2 = bipy, phen), which contain NHC-thiolate ligands,[2] and the complexes $[MCl_2(lvms)_2]$ (M = Co, Ni, Cu, Zn),[19] $[Pd(aminoacidato)(lvms)_2]Cl$,[20] and $[PtCl(en)(lvms)]Cl$ (en = ethylenediamine),[21] which all have intact levamisole ligands coordinated through the sp^2 N atom.

Conclusions

The present work describes the synthesis of trinuclear carbonyl cluster complexes of ruthenium and osmium containing chiral NHC-thiolate ligands (*i.e.*, S∼CH and S∼CMe ligands) that arise from reactions of anionic metal cluster precursors with levamisolium and methyl levamisolium cations. While the levamisolium-derived ligand S∼CH of compounds **1–4** is unprecedented, the methyl levamisolium-derived ligand S∼CMe of compounds **5–8** has only been observed previously in palladium complexes.[2]

Therefore, this work demonstrates that the oxidative addition of the S–C(sp^2) bond of levamisolium cations is not restricted to palladium(0) complexes, but it can also be accomplished over other low-valent metal complexes, contributing to generalize the use of levamisolium cations as precursors to metal complexes containing chiral NHC-thiolate ligands.

Finally, the incorporation of different substituents, including chiral groups, on the sp^2 N atom of levamisole may lead to a wide variety of levamisolium cations that may be used as precursors to many new chiral NHC-thiolate ligands.

Experimental

General data

Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) 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 (carbonyl stretching region) and spot TLC. Levamisole,[2] methyl levamisolium triflate,[2] $[Os_3(CO)_{10}(MeCN)_2]$,[22] $[NH_4][Ru_3(\mu\text{-}H)(CO)_{11}]$,[23] and $[PPN][Os_3(\mu\text{-}H)(CO)_{11}]$[24] were prepared following published methods. The remaining reagents were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on a Bruker DPX-300 instrument, at 293 K, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$ for ^1H and 53.2 for ^{13}C). Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; the m/z value given for a molecular ion corresponds to that of the most abundant isotopomer.

Reaction of $[Ru_3(CO)_{12}]$ with [Hlvms]Cl. A mixture of $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and [Hlvms]Cl (42 mg, 0.173 mmol) was stirred in THF (25 mL) at reflux temperature for 40 min. The color changed from orange–yellow to dark orange. The solution was cooled down to room temperature and was left aside for 24 h. The excess of [Hlvms]Cl precipitated as a white solid and was filtered off. Concentration to *ca.* 5 mL and addition of hexane (15 mL) led to precipitation of an orange solid that was washed with hexane and dried *in vacuo* (105 mg, 93%). This solid was identified as a *ca.* 1 : 1 mixture of diastereoisomers **1** and **2** by ^{13}C NMR spectroscopy. Repeated recrystallizations from mixtures of dichloromethane and hexane allowed the isolation of a small amount of pure complex **2** (14 mg, 9%). Calc. for $C_{20}H_{13}ClN_2O_9Ru_3S$ (796.09): C, 30.18; H, 1.65; N, 3.52. Found: C, 30.26; H, 1.71; N 3.42%. FAB MS: 797 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2085 (m), 2048 (s), 2003 (s, br), 1993 (m, sh), 1948 (w). ^1H NMR (CD_2Cl_2): δ 7.62–7.25 (m, 5 H, Ph), 6.44 (s, br, 1 H, NH), 5.05 (m, 1 H, CH), 4.40–3.98 (m, 2 H, CH_2), 3.90–3.30 (m, 2 H, CH_2), 3.30–2.90 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, DEPT): δ 202.9, 202.1, 201.9, 201.2, 200.6, 199.3, 199.0, 195.9, 190.1 (9 CO); 180.4 (C), 140.7, (C); 129.2 (2 CH), 128.7 (CH), 126.2 (2 CH), 61.4 (CH); 60.2 ($\mathit{C}H_2$), 50.8 ($\mathit{C}H_2$), 32.6 ($\mathit{C}H_2$).

Reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with [Hlvms]Cl. Solid [Hlvms]Cl (21 mg, 0.087 mmol) was added to a dichloromethane solution (15 mL) of $[Ru_3(CO)_{10}(MeCN)_2]$ (0.078 mmol, prepared *in situ*[25] from $[Ru_3(CO)_{12}]$, Me_3NO and acetonitrile). An immediate color change from yellow to dark orange was accompanied by the observation of the anionic complex $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ by IR spectroscopy.[11a] After 2 min, the color changed from dark orange to orange. A spot TLC analysis (silica gel) of the solution also indicated the presence of small amounts of $[Ru_3(CO)_{12}]$ and a new yellow complex that decomposed on the plate after *ca.* 2 min to give orange **1** + **2**. Heating this solution to reflux temperature for 1 h led to a mixture of **1** + **2**.

Reaction of $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ with $[Hlvms][BF_4]$. Solid $[Hlvms][BF_4]$ (25 mg, 0.086 mmol) was added to a dichloromethane solution (15 mL) of $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ (0.078 mmol, prepared *in situ*[11a] from $[Ru_3(CO)_{12}]$ and [PPN]Cl). This solution behaved similarly to that prepared as described in the previous paragraph.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with [Hlvms]Cl. Solid [Hlvms]Cl (28 mg, 0.114 mmol) was added to a THF solution (30 mL) of $[Os_3(CO)_{10}(MeCN)_2]$ (89 mg, 0.095 mmol) and the resulting solution was stirred at reflux temperature for 40 min. The original yellow color was maintained. The solvent was removed under reduced pressure, the solid residue was dissolved in dichloromethane (3 mL), and the resulting solution was placed onto a silica gel chromatographic column (2 × 15 cm) packed in hexane. Hexane–dichloromethane (4 : 1) eluted two minor yellow bands. Hexane–dichloromethane (1 : 1) eluted a major bright yellow band that was worked up to give a *ca.* 1 : 1 mixture of compounds **3** and **4** (62 mg, 60%), which could not be separated. Calc. for $C_{20}H_{13}ClN_2O_9Os_3S$ (1063.54): C, 22.59; H, 1.23; N, 2.63. Found: C, 22.64; H, 1.32; N, 2.54. FAB MS: 1064 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2087 (m), 2050 (s), 2003 (s, br), 1994 (m, sh), 1948 (w). ^1H NMR (CD_2Cl_2): δ 7.51–7.34 (m, 5 H, Ph), 6.56 (s, br, 1 H, NH), 5.17 (m, 1 H, CH), 4.50–3.02 (m, 6 H, 3 CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, DEPT): δ 202.9, 202.7, 202.1, 202.0, 201.9, 201.5, 201.3, 201.2, 200.6, 200.4, 199.6, 199.3, 199.1, 199.0, 195.9, 193.8, 190.2, 190.1 (18 CO); 180.4 (C), 180.3 (C), 140.7 (C), 140.5 (C), 129.3 (2 CH), 129.2 (2 CH), 128.7 (CH), 128.5 (CH), 126.7 (2 CH), 126.2 (2 CH), 61.6 (CH), 61.2 (CH); 60.2 ($\mathit{C}H_2$), 59.7 ($\mathit{C}H_2$), 50.9 ($\mathit{C}H_2$), 50.1 ($\mathit{C}H_2$), 33.7 ($\mathit{C}H_2$), 33.2 ($\mathit{C}H_2$).

Reaction of $[NH_4][Ru_3(\mu\text{-}H)(CO)_{11}]$ with $[Melvms]CF_3SO_3$. A solution of $[NH_4][Ru_3(\mu\text{-}H)(CO)_{11}]$ (100 mg, 0.134 mmol) and $[Melvms]CF_3SO_3$ (59 mg, 0.161 mmol) in THF (40 mL) was stirred at reflux temperature for 1.5 h. The original red color was maintained. The solution was concentrated to *ca.* 5 mL and was supported on silica gel TLC plates. Repeated elution with hexane–diethyl ether (1 : 1) eluted two minor yellow bands. Hexane–dichloromethane (2 : 1) separated two pale yellow bands that were worked up to give, in order of elution, compounds **5** (20 mg, 18%) and **6** (26 mg, 24%). *Data for* **5***:* Calc. for $C_{21}H_{16}N_2O_9Ru_3S$ (775.64): C, 32.51; H, 2.07; N, 3.61. Found: C, 32.55; H, 2.08; N, 3.63%. FAB MS: 777 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2081 (m), 2039 (vs), 2005 (vs), 1996 (s, sh), 1973 (w, sh), 1941 (w). ^1H NMR (CD_2Cl_2): δ 7.41–7.12 (m, 5 H, Ph), 4.75 (m, 1 H, CH), 4.02 (m, 2 H, CH_2), 3.33 (s, 3 H, CH_3), 3.52–3.03 (m, 4 H, 2 CH_2), −15.34 (s, 1 H, μ-H). *Data for* **6**: Calc. for $C_{21}H_{16}N_2O_9Ru_3S$ (775.64): C, 32.51; H, 2.07; N, 3.61. Found: C, 32.66; H, 2.13; N 3.55%. FAB MS: 777 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2081 (m), 2039 (vs), 2005 (vs), 1996 (s, sh), 1973 (w, sh), 1941 (w). ^1H NMR (CD_2Cl_2): δ 7.42–7.13 (m, 5 H, Ph), 4.81 (m, 1 H, CH), 4.00 (m, 2 H, CH_2), 3.31 (s, 3 H, CH_3), 3.52–3.04 (m, 4 H, 2 CH_2), −15.43 (s, 1 H, μ-H).

Reaction of $[PPN][Os_3(\mu\text{-}H)(CO)_{11}]$ with $[Melvms]CF_3SO_3$. A solution of $[PPN][Os_3(\mu\text{-}H)(CO)_{11}]$ (100 mg, 0.070 mmol) and $[Melvms]CF_3SO_3$ (31 mg, 0.084 mmol) in toluene (30 mL) was stirred at reflux temperature for 1 h. The color changed from red to orange. The solution was evaporated to dryness, the residue was dissolved in dichloromethane (*ca.* 5 mL), and the resulting solution was supported on silica gel TLC plates. Hexane–dichloromethane (2 : 1) eluted several bands. The major ones, both yellow, were worked up to give, in order of elution, compounds **7** (18 mg, 24%) and **8** (24 mg, 16%). *Data for* **7**: Calc. for $C_{21}H_{16}N_2O_9Os_3S$ (1043.11): C, 24.18; H, 1.54; N, 2.68. Found: C, 24.22; H, 1.62; N, 2.62%. FAB MS: 1044 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2087 (m), 2043 (s), 2004 (vs), 1989 (m, sh), 1965 (w, sh), 1931 (w). ^{1}H NMR (CD_2Cl_2): δ 7.40–7.20 (m, 5 H, Ph), 4.86 (m, 1 H, CH), 4.11 (m, 2 H, CH_2), 3.49 (m, 2 H, CH_2), 3.31 (s, 3 H, CH_3), 3.22 (m, 2 H, CH_2), −17.41 (s, 1 H, μ-H). *Data for* **8**: Calc. for $C_{21}H_{16}N_2O_9Os_3S$ (1043.11): C, 24.18; H, 1.54; N, 2.68. Found: C, 24.25; H, 1.63; N, 2.60. FAB MS: 1044 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2087 (m), 2043 (s), 2004 (vs), 1989 (m, sh), 1965 (w, sh), 1931 (w). ^{1}H NMR (CD_2Cl_2): δ 7.40–7.20 (m, 5 H, Ph), 4.88 (m, 1 H, CH), 4.08 (m, 2 H, CH_2), 3.54 (m, 2 H, CH_2), 3.30 (s, 3 H, CH_3), 3.24 (m, 2 H, CH_2), −17.52 (s, 1 H, μ-H).

X-Ray crystallography

A selection of crystal, measurement, and refinement data is given in Table 2. Diffraction data for Diffraction data for **5** were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera on a κ-goniostat, using graphite-monochromated Cu-Kα radiation. Empirical absorption corrections were applied using XABS2,[26] with maximum and minimum transmission factors 0.161 and 0.157, respectively. The structure was solved by Patterson interpretation using DIRDIF-96.[27] Isotropic and full matrix anisotropic least squares refinements were carried out using SHELXL-97.[28] Two chemically identical but crystallographically independent molecules, both with an *S* configuration of the stereogenic phenyl-substituted carbon atom, were found in the asymmetric unit. H100 and H200 hydride atom positions were calculated using the program XHYDEX[29] and their coordinates and thermal parameters were refined. The remaining hydrogen atom positions were geometrically calculated and refined riding on their parent atoms. The molecular plot was made with the PLATON program package.[30] The WINGX program system[31] was used throughout the structure determination.

Table 2 Selected crystal, measurement and refinement data for **5**

Formula	$C_{21}H_{16}N_2O_9Ru_3S$
M_r	775.63
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	9.2786(3)
b/Å	16.3421(4)
c/Å	34.6797(6)
V/Å^3	5258.5(2)
Z	8
$F(000)$	3008
D_c/g cm^{-3}	1.959
Radiation (λ/Å)	1.54180 (Cu-Kα)
μ/mm^{-1}	14.978
Crystal size/mm	0.15 × 0.13 × 0.13
T/K	293(2)
θ limits/°	2.55–68.30
Min./max. h, k, l	−11/11, −19/19, −41/41
Collected reflections	17912
Unique reflections	9639
Reflections with $I > 2\sigma(I)$	8181
Parameters/restraints	657/0
GOF on F^2	1.017
R_1 (on F, $I > 2\sigma(I)$)	0.0352
wR_2 (on F^2, all data)	0.0670
Max./min. $\Delta\rho$/e Å^{-3}	0.473/−0.877
Flack parameter	−0.039(8)

CCDC reference number 605755.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606869c

Acknowledgements

This work was supported by the European Union (FEDER grants) and the Spanish MCyT-MEC research project BQU2002-2623. The University of Carabobo (Venezuela) is acknowledged for a research grant to M. G. S.-V.

References

1 Levamisole = 2,3,5,6-tetrahydro-6-(*S*)-phenylimidazo[2,1-*b*]thiazole.

2 J. A. Cabeza, I. del Río, M. G. Sánchez-Vega and M. Suárez, *Organometallics*, 2006, **25**, 1831.

3 Selected reviews on complexes having NHC ligands: (*a*) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162; (*b*) A. Arduengo, *Acc. Chem. Res.*, 1999, **32**, 913; (*c*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; (*d*) D. Enders and H. Gielen, *J. Organomet. Chem.*, 2001, **617–618**, 70; (*e*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*f*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247.

4 Reviews on catalytic applications of complexes having NHC ligands: (*a*) ref. 3*e*; (*b*) M. T. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; (*c*) M. C. Perry and K. Burgess, *Tetrahedron: Asymmetry*, 2003, **14**, 951; (*d*) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239; (*e*) A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang and S. P. Nolan, *J. Organomet. Chem.*, 2002, **653**, 69; (*f*) V. César, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619.

5 Examples of catalytic applications of complexes with chiral NHC ligands: (*a*) V. César, S. Bellemin-Laponnaz, H. H. Wadepohl and L. H. Gade, *Chem. Eur. J.*, 2005, **11**, 2862; (*b*) A. R. Chianase and R. H. Crabtree, *Organometallics*, 2005, **24**, 4432; (*c*) H. Clavier, L. Coutable, L. Toupet, J. C. Guillemin and M. Mauduit, *J. Organomet. Chem.*, 2005, **690**, 5237; (*d*) C. Song, C. Ma, Y. Ma, W. Feng, S. Ma, Q. Chai and M. B. Merritt, *Tetrahedron Lett.*, 2005, **46**, 3241; (*e*) J. J. van Veldhuizen, J. E. Campbell, R. E. Hoveyda and H. Amir, *J. Am. Chem. Soc.*, 2005, **127**, 6877; (*f*) D. Kremzow, G. Seidel, C. W. Lehmann and A. Fuerstner, *Chem. Eur. J.*, 2005, **11**, 1833; (*g*) T. Focken, J. Rudolph and C. Bolm, *Synthesis*, 2005, 429; (*h*) L. G. Bonnet, R. E. Douthwaite and B. M. Kariuki, *Organometallics*, 2003, **22**, 4187; (*i*) C. Costabile and L. Cavallo, *J. Am. Chem. Soc.*, 2004, **126**, 9592.

6 Further examples of complexes with chiral NHC ligands: (*a*) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, J. Houghton, B. M. Kariuki and S. Simonovic, *Dalton Trans.*, 2004, 3528; (*b*) S. Gischig and A. Togni, *Organometallics*, 2004, **23**, 2479; (*c*) L. G. Bonnet, R. E. Douthwaite and R. Hodgson, *Organometallics*, 2003, **22**, 4384; (*d*) F. Glorious, G. Altenhoff, R. Goddard and C. Lehmann, *Chem. Commun.*, 2002, 2704.

7 W. K. P. Amery and J. P. J. M. Bruynseels, *Int. J. Immunopharmacol.*, 1992, **14**, 481, and references therein.

8 J. S. Kovach, P. A. Svingen and D. J. Schaid, *J. Natl. Cancer Inst.*, 1992, **84**, 515, and references therein.

9 J. A. Cabeza, I. del Río, S. García-Granda, V. Riera, M. G. Sánchez-Vega and M. Suárez, *Eur. J. Inorg. Chem.*, 2002, 2561.

10 In the preliminary communication of this work,[9] due to the absence of $^{13}C\{^1H\}$ NMR data, it was erroneously reported that the only product of the reaction of $[Ru_3(CO)_{12}]$ with [Hlvms]Cl is complex **2**.

11 (*a*) G. Lavigne and H. D. Kaesz, *J. Am. Chem. Soc.*, 1984, **106**, 4647; (*b*) C. E. Kampe, N. M. Boag, C. B. Knobler and H. D. Kaesz, *Inorg. Chem.*, 1984, **23**, 1390; (*c*) E. D. Morrison, G. L. Geoffroy, A. L. Rheingold and W. C. Fultz, *Organometallics*, 1985, **4**, 1413.

12 B. F. G. Johnson, D. R. Johnston, P. L. Josty, J. Lewis and I. G. Williams, *Nature*, 1967, **213**, 901.

13 J. A. Cabeza, I. del Río, D. Miguel and M. G. Sánchez-Vega, *Chem. Commun.*, 2005, 3956.

14 See, for example: (*a*) S. Kennedy, J. J. Alexander and S. G. Shore, *J. Organomet. Chem.*, 1981, **219**, 385; (*b*) E. D. Morrison, G. L. Geoffroy and A. L. Rheingold, *J. Am. Chem. Soc.*, 1985, **107**, 254.

15 See, for example: (*a*) A. M. Brodie, H. D. Holden, J. Lewis and M. J. Taylor, *J. Organomet. Chem.*, 1983, **253**, C1; (*b*) H. D. Holdon, B. F. G. Johnson, J. Lewis, P. R. Raithby and G. Uden, *Acta Crystallogr., Sect. C*, 1983, **39**, 1203; (*c*) A. J. Arce, P. Arrojo, Y. de Sanctis, A. J. Geeming and D. J. West, *Polyhedron*, 1992, **11**, 1013.

16 (*a*) R. D. Adams, H. S. Kim and S. Wang, *J. Am. Chem. Soc.*, 1985, **107**, 6107; (*b*) R. D. Adams and G. Chen, *J. Cluster Sci.*, 1991, **2**, 29; (*c*) R. D. Adams, J. E. Babin, H. S. Kim, J. T. Tanner and T. A. Wolfe, *J. Am. Chem. Soc.*, 1990, **112**, 3426, and references therein.

17 Examples of metal-mediated S–C bond cleavage processes: (*a*) K. Yu, H. Li, E. Watson, K. L. Virkaitis, G. B. Carpenter and D. A. Sweigart, *Organometallics*, 2001, **20**, 3550; (*b*) Y. J. Kim, S. C. Lee, M. H. Cho and S. W. Lee, *J. Organomet. Chem.*, 1999, **588**, 268; (*c*) A. Albéniz, P. Espinet and Y. S. Lin, *Organometallics*, 1996, **15**, 5010; (*d*) K. Osakada, T. Chiva, Y. Nakamura, T. Yamamoto and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1986, 1589; (*e*) J. Dehand and J. Jordanov, *J. Chem. Soc., Chem. Commun.*, 1975, 743; (*f*) J. A. Cabeza, M. A. Martínez-García, V. Riera, D. Ardura and S. García-Granda, *Eur. J. Inorg. Chem.*, 2000, 299; (*g*) K. Umakoshi, T. Yamashaki, A. Fukuoka, H. Kawano, M. Ichikawa and M. Onishi, *Inorg. Chem.*, 2002, **41**, 4093.

18 Reviews on the use of molecular compounds as models for HDS processes: (*a*) R. J. Angelici, *Acc. Chem. Res.*, 1988, **21**, 387; (*b*) R. J. Angelici, *Coord. Chem. Rev.*, 1990, **105**, 61; (*c*) T. B. Rauchfuss, *Prog. Inorg. Chem.*, 1990, **105**, 61; (*d*) R. Sánchez-Delgado, *J. Mol. Catal.*, 1994, **86**, 287; (*e*) C. Bianchini and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1996, 801; (*f*) R. J. Angelici, *Polyhedron*, 1997, **16**, 3073.

19 (*a*) T. B. Kovachev, P. N. Stamberov, D. S. Ivanov, M. K. Mitcheva, S. P. Marinova, H. A. Astroug and J. N. Stoychkov, *Pharmazie*, 1994, **49**, 25; (*b*) J. A. Cabeza, I. del Río, M. G. Sánchez-Vega and S. García-Granda, *Acta Crystallogr., Sect. E*, 2005, **61**, m1984.

20 A. M. Nijasure, V. N. Joshi and A. D. Savant, *J. Inorg. Biochem.*, 1999, **73**, 109.

21 G. M. Arvanitis, M. E. Bernardini, G. N. Parkinson and B. S. Schneider, *Acta Crystallogr., Sect. C*, 1993, **49**, 1246.

22 R. D. Adams, J. E. Babin and H. S. Kim, *J. Am. Chem. Soc.*, 1987, **109**, 1414.

23 B. F. G. Johnson, J. Lewis, P. R. Raithby and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, 1979, 1356.

24 K. Burgess and R. P. White, *Inorg. Synth.*, 1989, **25**, 193.

25 G. A. Foulds, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1985, **296**, 147.

26 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.

27 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould and J. M. M. Smits, *The DIRDIF96 Program System*, Crystallography Laboratory of the University of Nijmegen, Nijmegen, The Netherlands, 1996.

28 G. M. Sheldrick, *SHELXL97*, University of Göttingen, Göttingen, Germany, 1997.

29 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

30 A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, University of Utrecht, Utrecht, The Netherlands, 2003.

31 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.