

The reaction of triosmium and -ruthenium clusters with bifunctional ligands

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Abstract

The reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, **1**, or $[\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2]$, **2**, with bifunctional ligands carrying $-\text{OH}$, $-\text{SH}$ and $-\text{COOH}$ groups affords, as the major product, clusters of the general formula $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-E}^{\wedge}\text{E}'\text{H})]$ ($\text{E}, \text{E}' = \text{O}, \text{S}$ or COO). In some cases, a minor product with general formula $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu, \mu\text{-E}^{\wedge}\text{E}')\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]$ was also obtained. With $\text{Ru}_3(\text{CO})_{12}$, **3b**, only the first type of products is obtained. The structures of eight of the compounds have also been determined by single crystal X-ray crystallography. © 2008 Elsevier B.V. All rights reserved.

Keywords: Osmium; Ruthenium; Bifunctional ligand; Cluster

1. Introduction

Organometallic clusters are of interest as precursors for the deposition of molecular clusters [1] and size-controlled metallic particles [2]. A useful method for the deposition of molecular clusters onto surfaces is via a linking group between the surface and the cluster. We recently reported the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a means to examine such surface species [3], and in extending that study, we attempted to synthesise some clusters which have a ligand that can be used for anchoring onto various surfaces through the reaction of some precursor clusters with bifunctional ligands. The synthesis and characterisation of these clusters are described here.

2. Results and discussion

2.1. Reaction of triosmium and -ruthenium clusters with bifunctional ligands

The triosmium clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, **1**, or $[\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2]$, **2**, have been reported to react with

various alcohols to form hydridoalkoxy and dialkoxy-derivatives with the general formulae $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OR})]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OR})_2]$, respectively [4]; and with thiols and carboxylic acids to form hydridothiolato or hydridocarboxylato derivatives, respectively [5]. The reactions of **2** with thiolate–carboxylic acids and dicarboxylic acids have been reported to afford linked clusters with the general formula $[\{\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\}_2(\mu\text{-L}')] [6]$, while its reactions with $\text{HSCH}_2\text{CH}_2\text{SH}$ and diols afforded clusters with only one triosmium moiety, viz., $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SCH}_2\text{CH}_2\text{SH})]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\{\mu\text{-O}(\text{CH}_2)_n\text{-OH}\}]$, respectively. Interestingly though, the reaction of **2** with 1,3-propanedithiol afforded the linked cluster $[\{\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\}_2(\mu, \mu, \eta^2\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})]$ only [6e]. Similarly, the reaction of $[\text{Ru}_3(\text{CO})_{12}]$, **3b**, with $\text{HSCH}_2\text{-COOH}$ gave only $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SCH}_2\text{COOH})]$ [7].

We have found that the reaction of **1** in refluxing toluene, or **2** at ambient temperature in dichloromethane, with bifunctional ligands afforded two types of clusters (Scheme 1) [8]. The major product is of the general formula $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-E}^{\wedge}\text{E}'\text{H})]$ (type **A**). In some cases, a minor product with general formula $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu, \mu\text{-E}^{\wedge}\text{E}')\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]$ (type **B**) was also obtained. The reaction of **1** with 2,5-dimercapto-1,3,4-thiadiazol

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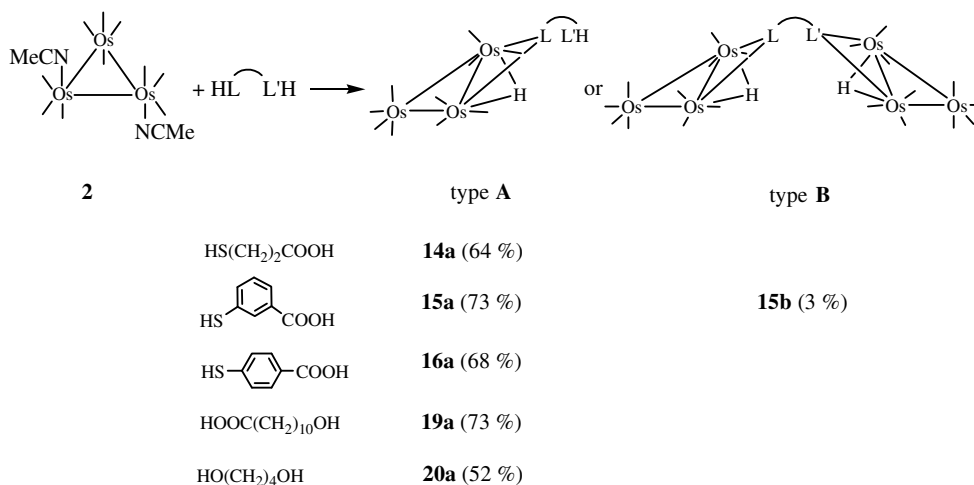
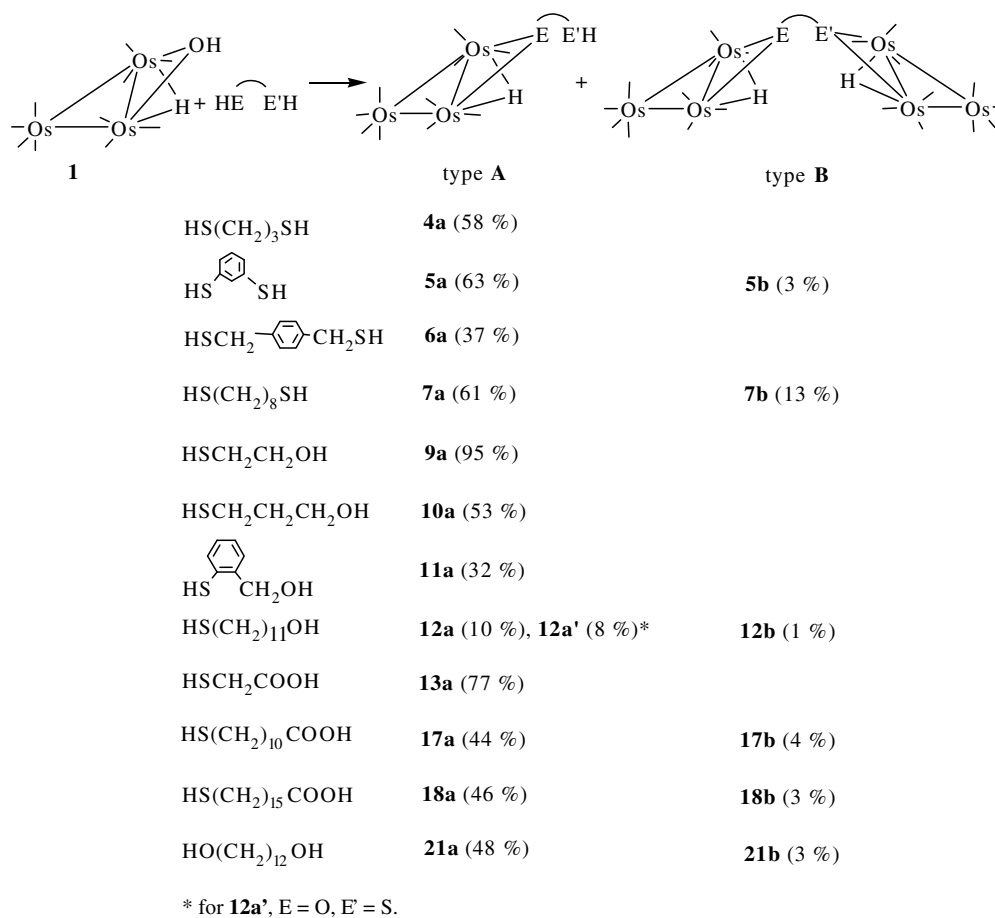
afforded a cluster with a more complex bonding mode, viz.



With the exception of **8**, **15b**, **17b** and **18b**, all the other clusters exhibit similar patterns in the carbonyl region of their IR spectra, which are comparable to those of other triosmium clusters of the type $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SR})]$, indicating that the metal core of these products are structurally similar [4–6]. In the case of products containing

two triosmium moieties bridged by thiolato-carboxylato ligands (**15b**, **17b** and **18b**), their IR spectra showed a more complicated pattern, which can be regarded as the overlap of a thiolato-bridged $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})$ moiety, which has the highest energy band at $2108\text{--}2110\text{ cm}^{-1}$, and a carboxylato-bridged $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})$ moiety, which has the highest energy band at $2113\text{--}2114\text{ cm}^{-1}$.

The hydride resonances in the ^1H NMR spectra are also characteristic – the thiolato-, carboxylato- and alkoxy-



Scheme 1.

bridged clusters exhibited hydride resonances at about -17 , -10 , and -12 ppm, respectively. The hydride resonances for those containing an aromatic ring are also shifted upfield by about 0.3 – 0.7 and 0.3 ppm, for the thiolato- and carboxylato-bridged clusters, respectively, compared to the alkyl analogues.

Although the relative yields of the type **B** clusters are low compared to the type **A** clusters, their formation appears to depend on the nature of the ligand. Formation of the type **B** clusters is less likely with a shorter methylene chain, presumably due to the steric problem associated with having two clusters connected via a short chain. More importantly perhaps, the propensity of the functional groups to bond to the cluster also shows a very clear trend in the order: $\text{SH} > \text{COOH} > \text{OH}$. This can be seen in that bifunctional ligands containing an SH and an OH or COOH group afforded almost exclusively type **A** clusters with the thiolate bridge (**9**–**11a** and **13**–**18a**), and the ligand $\text{HO}(\text{CH}_2)_{10}\text{COOH}$ afforded a type **A** cluster with the carboxylate bridge (**19a**). The type **B** clusters were presumably formed via the intermediacy of the type **A** clusters; the room temperature reaction of $\text{HSCH}_2\text{CH}_2\text{COOH}$ with two equivalents of **2** afforded **14a** (21%) and the previously reported linked cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu,\mu\text{-SCH}_2\text{CH}_2\text{COO})\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]$, **14b** (11%) [6]. In addition, the reaction of **14a** with **2** also afforded **14b**.

In a similar set of reactions with $[\text{Ru}_3(\text{CO})_{12}]$, **3b**, only clusters of type **A** were obtained (Scheme 2). The IR spectra of the products also showed patterns in the metal carbonyl region that are similar to the osmium analogues, and the metal hydride resonances are at about -15 ppm, which indicated that it is the SH moiety which has reacted with the triruthenium core [7].

2.2. Crystallographic studies

Five clusters of type **A** (**5a**, **9a**, **13a**, **14a**, and **15a**) and two of type **B** (**5b** and **15b**), together with **8**, were characterised crystallographically. The molecular structures of **5a**

and **5b** are shown in Figs. 1 and 2, respectively. The overall structure of **5b** is very similar to that of the methanedithiolato and propanedithiolato analogues $[\{\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\}_2(\mu,\mu,\eta^2\text{-SCH}_2\text{S})]$ and $[\{\text{M}_3(\text{CO})_{10}(\mu\text{-H})\}_2(\mu,\mu,\eta^2\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})]$ ($\text{M} = \text{Os}, \text{Ru}$) [6a,6e]. Structurally, **5b** is equivalent to two moieties of **5a**.

Selected bond parameters and a common atomic number scheme for **5a**, **5b**, **9a**, **13a**, **14a**, and **15a** are shown in Table 1. The bond parameters are unexceptional; there is no obvious trend observable for the Os–Os bond distances, even between the thiolato-bridged Os–Os bond and the others, and these Os–Os bond distances as well as the Os–S distances are similar to those in related clusters [9].

Compound **15b** is a type **B** cluster in which $E \neq E'$. The molecular structure of **15b** and selected bond parameters are given in Fig. 3. The Os(4)–Os(5) bond [2.9244(10) Å], which is bridged by the carboxylate group, is longer than the others; this effect is well-documented [6].

The structure of **8** is shown in Fig. 4, together with selected bond parameters. It is structurally similar to **5b**, except that an additional nitrogen atom has also coordinated to one of the triosmium moiety in place of a carbonyl. The Os(1)–Os(2) distance [2.8067 Å] in this particular unit is shorter compared to the others in the same cluster [2.8413(9)–2.8503(10) Å], while the thiolato-bridged Os–Os bond length is again similar to those of structurally

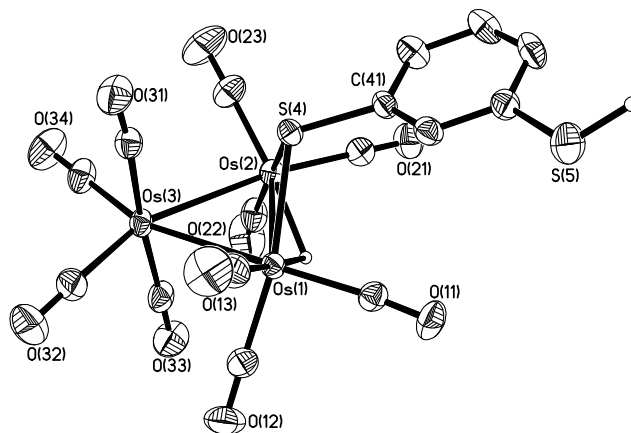


Fig. 1. ORTEP diagram for **5a**; thermal ellipsoids were drawn at the 50% probability level and aromatic hydrogens have been omitted.

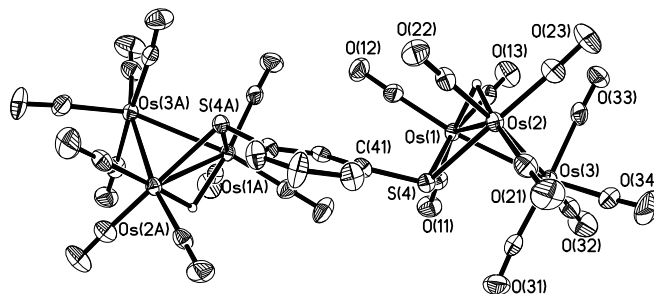
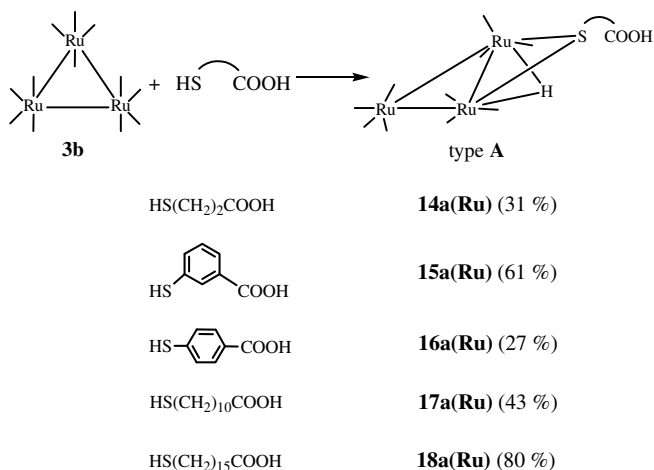
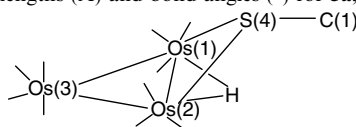


Fig. 2. ORTEP diagram for **5b**. Thermal ellipsoids were drawn at the 50% probability level and aromatic hydrogens have been omitted.

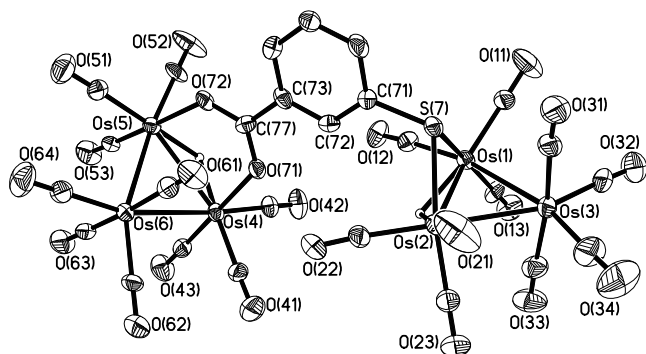
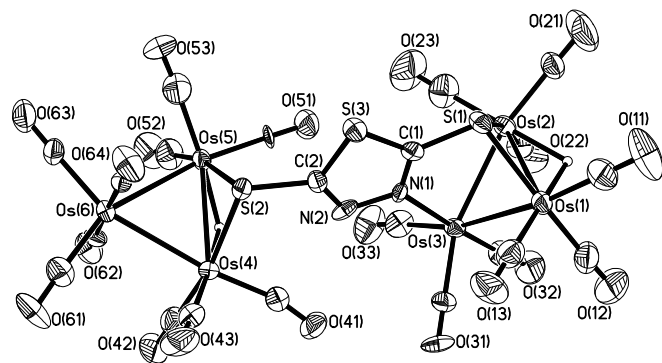


Scheme 2.

Table 1

Common atomic numbering scheme and selected bond lengths (Å) and bond angles (°) for **5a**, **5b**, **9a**, **13a**, **14a** and **15a**

	5a	5b	9a^a	13a	14a^b	15a
<i>Bond length (Å)</i>						
Os(1)–Os(2)	2.8628(2)	2.8571(4)	2.8841(4), 2.8576(4)	2.8546(4)	2.857(7)	2.8694(4)
Os(2)–Os(3)	2.8628(2)	2.8565(4)	2.8347(4), 2.8516(4)	2.8563(4)	2.851(6)	2.8418(4)
Os(3)–Os(1)	2.8462(2)	2.8658(5)	2.8349(4), 2.8467(4)	2.8483(4)	2.848(5)	2.8544(4)
Os(1)–S(4)	2.4171(10)	2.4185(18)	2.4102(16), 2.4123(17)	2.4059(18)	2.403(5)	2.4119(16)
Os(2)–S(4)	2.4171(10)	2.4153(18)	2.4124(16), 2.4061(16)	2.4063(19)	2.406(9)	2.4123(16)
S(4)–C(1)	1.793(4)	1.779(8)	1.828(6), 1.835(7)	1.836(8)	1.835(13)	1.788(6)
<i>Bond angle (°)</i>						
Os(1)–S(4)–Os(2)	72.63(3)	72.47(5)	73.46(4), 72.75(5)	72.77(5)	72.9(3)	73.00(5)

^a Two crystallographically independent molecules.^b Values for **14a** are averaged over the five crystallographically independent molecules; e.s.d.s are over the sample size of five molecules.Fig. 3. ORTEP diagram for **15b**. Thermal ellipsoids drawn at the 50% probability level and organic hydrogens have been omitted. Selected bond lengths (Å) and bond angles (°): Os(1)–Os(2) 2.8708(7), Os(2)–Os(3) 2.8746(8), Os(3)–Os(1) 2.8450(7), Os(4)–Os(5) 2.9244(10), Os(5)–Os(6) 2.8659(7), Os(6)–Os(4) 2.8758(8), Os(1)–S(1) 2.418(3), Os(2)–S(1) 2.426(3), Os(4)–O(71) 2.131(7), Os(5)–O(72) 2.150(7), S(1)–C(1) 1.807(10), Os(1)–S(1)–Os(2) 72.69(8).Fig. 4. ORTEP diagram and selected bond lengths (Å) and angles (°) for **8**. Thermal ellipsoids were drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Os(1)–Os(2) 2.8067(10), Os(2)–Os(3) 2.8318(10), Os(3)–Os(1) 2.8083(10), Os(4)–Os(5) 2.8464(9), Os(5)–Os(6) 2.8413(9), Os(6)–Os(4) 2.8503(10), Os(1)–S(1) 2.426(5), Os(2)–S(1) 2.453(4), Os(4)–S(2) 2.413(4), Os(5)–S(2) 2.417(2), S(1)–C(1) 1.733(17), S(2)–C(2) 1.791(17), Os(1)–S(1)–Os(2) 70.23(12), Os(4)–S(2)–Os(5) 72.11(11).

similar clusters such as $[\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-pyS})]$ and $[\{\text{Os}_3(\text{CO})_9(\mu\text{-H})\}(\mu\text{-SC}_5\text{H}_3\text{NCO}_2)\{\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\}]$ [10,9b].

3. Conclusion

In conclusion, we have found that the reaction of the clusters $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})$ or $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with bifunctional ligands $\text{HE}^{\wedge}\text{E}'\text{H}$ gave as the major products, clusters with the general formula $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-E}^{\wedge}\text{E}'\text{H})]$. The propensity towards binding of the functional group E with the cluster follows the order: $\text{SH} > \text{COOH} > \text{OH}$. When the ligand contains an aromatic ring or a long methylene chain spacer, the formation of clusters containing two triosmium moieties linked by the ligand, viz., $[\{\text{Os}_3(\text{CO})_{10}(\mu\text{-H})\}_2(\mu\text{-L}^{\wedge}\text{L}')]]$, increased. In contrast, the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with mercaptocarboxylic acids

afforded only triruthenium clusters of the type $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-L}^{\wedge}\text{COOH})]$.

4. Experimental

4.1. General procedure

All reactions were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere. Solvents that were used for reactions were distilled over the appropriate drying agents under nitrogen and kept in flasks provided with Teflon valves before use. Reaction mixtures were separated by TLC. ^1H NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer. The solvent used was deuterated chloroform. FAB-MS were obtained with a HP6890 GC system. Elemental analyses were carried out on a Perkin–Elmer PE 2400 CHN or CHNS Elemental

Table 2
 Spectroscopic and analytical data for the type A osmium clusters

Compound	IR (hexane) ν_{CO} (cm^{-1})	FAB (m/z) [M^+]: Calc. (Found)	^1H δ (ppm in CDCl_3)	Elemental Anal. (%) Calc. (Found)
4a	2109w, 2067vs, 2058s, 2021vs, 1996m, 1987w	959 (960)	2.62 (q, $^3J_{\text{HH}} = 8.3$ Hz, 2H, CH_2SH), 2.47 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H, SCH_2), 1.94 (quintet, 2H, SCH_2CH_2), 1.39 (t, $^3J_{\text{HH}} = 8.3$ Hz, SH), -17.40 (s, 1H, OsHO s)	C, 16.28 (16.75); H, 0.84 (0.85); S, 6.69 (6.98)
5a	2110w, 2071s, 2059m, 2023s, 2000m, 1998w ^a	993 (994)	7.23–7.01 (m, 4H, Ph), 3.47 (s, 1H, SH), -17.05 (s, 1H, OsHO s)	C, 19.35 (19.80); H, 0.61 (0.63); S, 6.46 (6.13)
6a	2109w, 2067s, 2058m, 2022s, 1997w, 1981w ^a	1021 (1020)	7.27 (d, $^3J_{\text{HH}} = 10.7$ Hz, 4H, Ph), 3.71 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, CH_2SH), 3.58 (s, 2H, SCH_2), 1.73 (t, 1H, SH), -17.38 (s, 1H, OsHO s)	C, 21.01 (21.28); H, 1.76 (2.03); S, 6.23 (6.04)
7a	2109m, 2067vs, 2058s, 2026vs, 2019s, 1999m, 1989m, 1983w	1029 (1028)	2.50 (q, $^3J_{\text{HH}} = 7.4$ Hz, 2H, CH_2SH), 2.35 (t, 2H, SCH_2), 1.63 (m, 5H, SCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{SH}$, SH), 1.30–1.47 (m, 8H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{CH}_2\text{SH}$), -17.40 (s, 1H, OsHO s)	C, 21.01 (21.28); H, 1.76 (2.03); S, 6.23 (6.04)
8	2114w, 2088m, 2075vs, 2067s, 2030vs, 2003s, 1958w	1823 (1824)	-16.93 (s, H, OsHO s), -11.70 (s, 1H, OsHO s)	
9a	2109w, 2068s, 2059m, 2025s, 2020sh, 2001w, 1990w, 1984w	929 (930)	3.85 (t, $^3J_{\text{HH}} = 5.8$ Hz, 2H, CH_2OH), 2.62 (t, 2H, SCH_2), 1.74 (t, 1H, OH), -17.36 (s, 1H, OsHO s)	C, 15.52 (15.51); H, 0.65 (0.79); S, 3.45 (3.01)
10a	2108w, 2067vs, 2057m, 2021s, 1995w, 1980w	945 (944)	3.77 (q, $^3J_{\text{HH}} = 2.8$ Hz, 2H, CH_2OH), 2.49 (t, $^3J_{\text{HH}} = 5.0$ Hz, 2H, SCH_2), 1.87 (quintet, 2H, SCH_2CH_2), 1.34 (t, 1H, OH), -17.38 (s, 1H, OsHO s)	C, 16.56 (16.44); H, 0.86 (0.89); S, 3.57 (3.40)
11a	2110w, 2069vs, 2057vs, 2024s, 1999m, 1967w	991 (992)	7.32–7.40 (m, 3H, Ph), 6.82 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ph), 5.09 (s, 2H, CH_2) -16.92 (s, 1H, OsHO s)	C, 20.60 (20.32); H, 0.81 (0.78); S, 3.24 (2.91)
12a	2109w, 2069vs, 2058m, 2020s, 1998w, 1980w	1054 (1055)	3.63 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, CH_2OH), 2.35 (t, $^3J_{\text{HH}} = 8.2$ Hz, 2H, SCH_2), 1.54 (m, 4H, SCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{OH}$), 1.27 (m, 14H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{OH}$), -17.40 (s, 1H, OsHO s)	C, 23.90 (24.32); H, 2.29 (2.14); S, 3.04 (2.84)
12a'	2108w, 2066vs, 2057m, 2021s, 1997w, 1983w	1054 (1057)	3.52 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, CH_2O), 2.67 (t, 7.4 Hz, 2H, HSCH_2), 1.54 (m, 4H, SCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{OH}$), 1.27 (m, 14H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{OH}$), -12.53 (s, 1H, OsHO s)	
13a	2111w, 2070s, 2060m, 2023s, 1999w ^a	942 (941)	3.21 (s, 2H, CH_2), -17.36 (s, 1H, OsHO s)	C, 15.29 (15.63); H, 0.43 (0.78); S, 3.40 (3.29)
14a	2112w, 2071s, 2061m, 2026vs, 2021 m (sh), 2001m, 1989w, 1984w	957 (958)	2.74–2.87 (m, 4H, CH_2CH_2), -17.30 (s, 1H, OsHO s)	C, 16.32 (16.54); H, 0.63 (0.62); S, 3.35 (3.49)
15a	2110w, 2069s, 2060m, 2024vs, 2001m, 1982w	1005 (1005)	8.0 (s, 1H, Ph), 7.96 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H, Ph), 7.56 (d, $^3J_{\text{HH}} = 9.1$ Hz, 1H, Ph), 7.41 (t, 1H, Ph), -16.98 (s, 1H, OsHO s)	C, 20.32 (20.18); H, 0.60 (0.65); S, 3.19 (3.12)
16a	2110w, 2070s, 2060m, 2024vs, 2001m, 1982w ^a	1005 (1006)	8.04 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H, Ph), 7.39 (d, 2H, Ph), -7.06 (s, 1H, OsHO s)	
17a	2108w, 2066vs, 2057m, 2024s, 2020s, 1996m, 1989w, 1982w	1070 (1072)	2.35 (m, 4H, SCH_2 , CH_2COOH), 1.65 (m, 4H, SCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{COOH}$), 1.27 (m, 12H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_6$), -17.41 (s, 1H, OsHO s)	C, 23.59 (23.56); H, 2.07 (1.70); S, 3.00 (3.07)
18a	2108w, 2066vs, 2057m, 2021vs, 1996w, 1982w ^a	1139 (1140)	3.63 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, SCH_2), 2.35 (t, $^3J_{\text{HH}} = 8.2$ Hz, 2H, CH_2COOH), 1.54 (m, 4H, SCH_2CH_2 , $\text{CH}_2\text{CH}_2\text{COOH}$), 1.24 (m, 22H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_{11}$), -17.41 (s, 1H, OsHO s)	C, 27.41 (27.40); H, 2.83 (2.25); S, 2.81 (2.87)
19a	2113w, 2074vs, 2062s, 2024vs, 2014s, 1981w	1067 (1068)	3.63 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, CH_2OH), 2.18 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H, CH_2COO), 1.54 (m, 4H, HOCH_2CH_2 , $\text{OOCCH}_2\text{CH}_2$), 1.22 (m, 14H, $\text{HOCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{CH}_2\text{COOH}$), -10.51 (s, 1H, OsHO s)	C, 24.76 (25.22); H, 2.27 (2.49)
20a	2109w, 2067vs, 2058s, 2025vs, 1988w	941 (942)	3.57 (m, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 1.53 (m, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$)	C, 17.87 (18.26); H, 1.07 (1.14)
21a	2109w, 2069vs, 2058s, 2020vs, 1997m, 1977w	1053 (1054)	3.63 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, CH_2OH), 3.51 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, OCH_2), 1.45 (m, 4H, HOCH_2CH_2 , OCH_2CH_2), 1.23 (m, 16H, $\text{HOCH}_2\text{CH}_2(\text{CH}_2)_8$), -12.53 (s, 1H, OsHO s)	C, 25.09 (24.67); H, 2.49 (2.53)

^a IR spectrum was recorded in dichloromethane.

Table 3
Spectroscopic and analytical data for the type **B** osmium clusters

Compound	IR (CH ₂ Cl ₂) ν _{CO} (cm ⁻¹)	FAB (<i>m/z</i>) [M ⁺]: Calc. (Found)	¹ H δ (ppm in CDCl ₃)
5b	2109w, 2071s, 2061m, 2027vs, 2021sh, 2004w	1844 (1843)	7.42 (s, 1H, <i>Ph</i>), 7.32 (t, ³ J _{HH} = 8.3 Hz, 1H, <i>Ph</i>), 7.03 (d, 2H, <i>Ph</i>), -17.05 (s, 1H, OsHOs)
7b	2108w, 2066vs, 2057m, 2020vs, 1998m	2056 (2056)	2.67 (t, ³ J _{HH} = 6.6 Hz, 2H, CH ₂ S), 2.35 (t, ³ J _{HH} = 7.4 Hz, 2H, SCH ₂), 1.66 (quintet, 4H, SCH ₂ CH ₂), 1.32 (m, 8H, SCH ₂ CH ₂ (CH ₂) ₄ CH ₂ CH ₂ SH), -17.40 (s, 1H, OsHOs)
12b	2108w, 2068vs, 2058m, 2020s, 1996w, 1982w	1906 (1905)	3.52 (t, ³ J _{HH} = 7.4 Hz, 2H, CH ₂ O), 2.35 (t, ³ J _{HH} = 7.4 Hz, 2H, SCH ₂), 1.54 (m, 4H, SCH ₂ CH ₂ , CH ₂ CH ₂ OH), 1.27 (m, 14H, SCH ₂ CH ₂ (CH ₂) ₇ CH ₂ CH ₂ OH), -12.53 (s, 1H, OsHOs), -17.40 (s, 1H, OsHOs)
15b	2114w, 2110w, 2076m, 2070s, 2066m, 2061m, 2027vs, 2017m, 2003w, 1991w, 1986w	1856 (1857)	7.58 (d, 1H, <i>Ph</i>), 7.56 (s, 1H, <i>Ph</i>), 7.47 (d, 1H, <i>Ph</i>), 7.21 (m, 1H, <i>Ph</i>), -10.28 (s, 1H, OsHOs), -17.08 (s, 1H, OsHOs)
17b	2112w, 2109w, 2072s, 2067vs, 2063s, 2058m, 2029vs, 2023vs, 2014s, 2000m, 1989m, 1985w	1919 (1920)	2.35 (t, ³ J _{HH} = 8.3 Hz, 2H, SCH ₂), 2.18 (t, ³ J _{HH} = 7.4 Hz, 2H, CH ₂ COOH), 1.61 (m, 4H, SCH ₂ CH ₂ , CH ₂ CH ₂ COOH), 1.24 (m, 22H, SCH ₂ CH ₂ (CH ₂) ₁₁), -10.51 (s, 1H, OsHOs), -17.41 (s, 1H, OsHOs)
18b	2113w, 2109w, 2075s, 2067vs, 2063s, 2058m, 2028vs, 2024vs, 2014s, 1999m, 1989m, 1984w	1990 (1990)	2.35 (t, ³ J _{HH} = 6.6 Hz, 2H, SCH ₂), 2.18 (t, ³ J _{HH} = 8.3 Hz, 2H, CH ₂ COOH), 1.54 (m, 4H, SCH ₂ CH ₂ , CH ₂ CH ₂ COOH), 1.24 (m, 22H, SCH ₂ CH ₂ (CH ₂) ₁₁), -10.51 (s, 1H, OsHOs), -17.41 (s, 1H, OsHOs)
21b	2109w, 2069vs, 2059m, 2021s, 1997w	1904 (1902)	3.51 (t, ³ J _{HH} = 7.4 Hz, 4H, CH ₂ O), 1.47 (m, 4H, HOCH ₂ CH ₂), 1.22 (m, 16H, HOCH ₂ CH ₂ (CH ₂) ₈), -12.53 (s, 1H, OsHOs)

Table 4
Spectroscopic and analytical data for the ruthenium clusters

Compound	IR (CH ₂ Cl ₂) ν _{CO} (cm ⁻¹)	FAB (<i>m/z</i>) [M ⁺]: Calc. (Found)	¹ H δ (ppm in CDCl ₃)	Elemental Anal. (%) Calc. (Found)
14a(Ru)	2105w, 2066s, 2057m, 2024s, 2010w, 1992w	689 (685)	3.13 (t, ³ J _{HH} = 6.6 Hz, 2H, CH ₂), 2.95 (t, 2H, CH ₂), -15.42 (s, 1H, RuHRu)	
15a(Ru)	2107w, 2068s, 2058m, 2022vs, 1962w	738 (737)	8.0 (s, 1H, <i>Ph</i>), 7.94 (d, ³ J _{HH} = 7.4 Hz, 1H, <i>Ph</i>), 7.59 (d, ³ J _{HH} = 6.6 Hz, 1H, <i>Ph</i>), 7.35 (t, ³ J _{HH} = 7.4 Hz, 1H, <i>Ph</i>), -14.96 (s, 1H, RuHRu)	
16a(Ru)	2106w, 2067s, 2057m, 2024s, 2015w	738 (663)	8.08 (d, 2H, <i>Ph</i>), 7.47 (d, ³ J _{HH} = 8.1 Hz, 2H, <i>Ph</i>), -15.08 (s, 1H, RuHRu)	
17a(Ru)	2104w, 2064vs, 2053m, 2022s, 2005w	802 (799)	2.34 (t, ³ J _{HH} = 7.4 Hz, 2H, CH ₂ COOH), 2.14 (t, 2H, SCH ₂), 1.62 (m, 4H, SCH ₂ CH ₂ , CH ₂ CH ₂ COOH), 1.28 (m, 12H, SCH ₂ CH ₂ (CH ₂) ₆ CH ₂ CH ₂ COOH), -15.36 (s, 1H, RuHRu)	C, 31.46 (31.84); H, 2.77 (3.19); S, 4.00 (4.29)
18a(Ru)	2104w, 2063vs, 2055m, 2021s, 2006w, 1988w	872 (873)	2.34 (t, ³ J _{HH} = 7.4 Hz, 2H, CH ₂ COOH), 2.14 (t, ³ J _{HH} = 8.3 Hz, 2H, SCH ₂), 1.64 (m, 4H, SCH ₂ CH ₂ , CH ₂ CH ₂ COOH), 1.25 (m, 22H, SCH ₂ CH ₂ (CH ₂) ₁₁ CH ₂ CH ₂ COOH), -15.36 (s, 1H, RuHRu)	C, 35.82 (36.07); H, 3.70 (3.57); S, 3.68 (3.57)

Analyser. The clusters [Os₃(CO)₁₀(μ-H)(μ-OH)], **1**, and [Os₃(CO)₁₀(NCCH₃)₂], **2**, were prepared according to reported procedures [11,12]. [Os₃(CO)₁₂], **3a**, and [Ru₃(CO)₁₂], **3b**, were purchased from Oxkem Ltd., and all other reagents were purchased from other commercial sources, and used as supplied without further purification.

4.2. Synthesis of clusters

In a typical experiment, to a solution of **1** (30 mg, 0.035 mmol) in toluene (20 ml) was added the ligand in excess and HBF₄/ether (one drop) and the resulting mixture refluxed for 5 h. The reaction was monitored by

NMR spectroscopy. With cluster **2** (80 mg, 0.085 mmol), the mixture with excess ligand in dichloromethane (30 ml) was allowed to stir at ambient temperature overnight. After the reaction, the solvents were removed in vacuo and the products purified by column chromatography using hexane/DCM as the eluant; the type **B** clusters were eluted first. With cluster **3b** (30 mg), the mixture with a stoichiometric amount of ligand in toluene (10 ml) was heated at 60 °C for 1 h. After the reaction, the solvents were removed in vacuo and the products purified by column chromatography using dichloromethane as the eluant. Tables 2–4 contain the spectroscopic and analytical data of the products.

Table 5
Crystal and refinement data for **5a**, **5b**, **9a**, **13a**

Compound	5a	5b	9a	13a
Empirical formula	C ₁₆ H ₆ O ₁₀ Os ₃ S ₂	C ₂₆ H ₆ O ₂₀ Os ₆ S ₂	C ₁₂ H ₆ O ₁₁ Os ₃ S	C ₁₂ H ₄ O ₁₂ Os ₃ S
Formula weight	992.93	1843.63	928.83	942.81
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.1515(3)	33.388(2)	8.7589(7)	9.4313(3)
<i>b</i> (Å)	9.3399(3)	8.9768(6)	13.3493(11)	17.0659(5)
<i>c</i> (Å)	14.6987(5)	13.1874(9)	32.146(3)	11.9575(4)
α (°)	80.5880(10)	90	90	90
β (°)	86.0230(10)	110.932(2)	95.157(2)	105.544(2)
γ (°)	63.6290(10)	90	90	90
Volume (Å ³)	1110.46(6)	3691.7(4)	3743.4(5)	1854.21(10)
<i>Z</i>	2	4	8	4
<i>D</i> _{calc} (Mg/m ³)	2.970	3.317	3.296	3.377
Absorption coefficient (mm ⁻¹)	17.358	20.762	20.480	20.680
<i>F</i> (000)	884	3240	3280	1664
Crystal size (mm)	0.32 × 0.20 × 0.06	0.20 × 0.12 × 0.02	0.36 × 0.24 × 0.16	0.36 × 0.22 × 0.12
θ Range for data collection (°)	2.46–30.50	2.36–29.97	2.36–29.99	2.13–28.27
Reflections collected	16,621	16,837	24,188	17,223
Independent reflections [<i>R</i> _{int}]	6254 [0.0263]	5224 [0.0421]	10,408 [0.0367]	4594 [0.0455]
Maximum and minimum transmission	0.4223 and 0.0720	0.6815 and 0.1035	0.1381 and 0.0508	0.1904 and 0.0502
Data/restraints/parameters	6254/0/281	5224/0/249	10,408/0/493	4594/0/265
Goodness-of-fit on <i>F</i> ²	1.070	1.134	1.021	1.043
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0239, <i>wR</i> ₂ = 0.0589	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.0802	<i>R</i> ₁ = 0.0327, <i>wR</i> ₂ = 0.0651	<i>R</i> ₁ = 0.0319, <i>wR</i> ₂ = 0.0707
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0601	<i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.0842	<i>R</i> ₁ = 0.0458, <i>wR</i> ₂ = 0.0686	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.0738
Largest difference in peak and hole (e Å ⁻³)	2.036 and -1.300	2.050 and -1.453	1.263 and -2.209	1.490 and -1.574

Table 6
Crystal and refinement data for **14a**, **15a**, **15b** and **8**

Compound	14a	15a	15b	8
Empirical formula	C ₁₃ H ₆ O ₁₂ Os ₃ S	C ₁₇ H ₆ O ₁₂ Os ₃ S	C ₂₇ H ₆ O ₂₂ Os ₆ S	C ₂₁ H ₂ N ₂ O ₁₉ Os ₆ S ₃
Formula weight	956.84	1004.88	1855.58	1823.63
Crystal system	Triclinic	Orthorhombic	Tetragonal	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.0749(3)	12.3476(5)	23.727(3)	10.8843(6)
<i>b</i> (Å)	14.6717(5)	12.9906(5)	23.727(3)	11.6681(7)
<i>c</i> (Å)	39.0412(12)	28.1609(12)	26.730(8)	27.8651(16)
α (°)	91.9960(10)	90	90	90
β (°)	90.9060(10)	90	90	90
γ (°)	91.3260(10)	90	90	90
Volume (Å ³)	5192.8(3)	4517.1(3)	15049(6)	3538.8(4)
<i>Z</i>	10	8	16	4
<i>D</i> _{calc} (Mg/m ³)	3.060	2.955	3.276	3.423
Absorption coefficient (mm ⁻¹)	18.463	16.988	20.324	21.713
<i>F</i> (000)	4240	3584	13,056	3192
Crystal size (mm)	0.22 × 0.10 × 0.05	0.36 × 0.30 × 0.14	0.22 × 0.12 × 0.07	0.18 × 0.08 × 0.06
θ Range for data collection (°)	2.06–26.37	2.19–26.3	2.06–26.37	2.01–26.02
Reflections collected	71,185	41,930	72,144	49,350
Independent reflections [<i>R</i> _{int}]	21,250 [0.0642]	4619 [0.0638]	7688 [0.0927]	6981 [0.0768]
Maximum and minimum transmission	0.4587 and 0.1063	0.1995 and 0.0639	0.3304 and 0.0944	0.3558 and 0.1115
Data/restraints/parameters	21250/0/1306	4619/0/321	7688/0/508	6981/126/460
Goodness-of-fit on <i>F</i> ²	1.031	1.040	1.121	1.133
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.0885	<i>R</i> ₁ = 0.0274, <i>wR</i> ₂ = 0.0625	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.0878	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.1004
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0666, <i>wR</i> ₂ = 0.0967	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0649	<i>R</i> ₁ = 0.0512, <i>wR</i> ₂ = 0.0915	<i>R</i> ₁ = 0.0532, <i>wR</i> ₂ = 0.1027
Absolute structure parameter	–	–	–	0.000(19)
Largest difference in peak and hole (e Å ⁻³)	1.792 and -1.217	2.017 and -0.803	2.330 and -1.155	2.947 and -1.261

4.3. Reaction of **14a** with **2**

A mixture of **14a** (30 mg, 0.031 mmol) and **2** (29 mg, 0.031 mmol) in CHCl_3 was stirred overnight at room temperature. The solvent was then removed in vacuo and separation of the residue by column chromatography using hexane/ CHCl_3 as the eluant afforded $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})-(\mu,\mu\text{-SCH}_2\text{CH}_2\text{COO})\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]$, **14b** (10.2 mg, 18.2%) and unreacted **14a** (19.4 mg).

14b: $^1\text{H NMR}$ (CDCl_3) δ 2.49 (t, 2H, CH_2O), 2.37 (t, 2H, CH_2S), -10.47 (s, OsHOs), -17.50 (s, OsHOs) ppm. Lit. [6a]: δ 2.47 (t), 2.34 (t), -10.50 (s), -17.50 (s) ppm.

4.4. Reaction of $\text{HSCH}_2\text{CH}_2\text{COOH}$ with 2 equiv. of **2**

A mixture of $\text{HSCH}_2\text{CH}_2\text{COOH}$ (2.84 mg, 0.027 mmol) and **2** (50 mg, 0.054 mmol) in CHCl_3 was stirred overnight at room temperature. Subsequent workup as above afforded **14b** (10.7 mg, 11.0%) and **14a** (10.5 mg, 20.5%).

4.5. Crystallographic studies

Crystals of diffraction quality were grown either by cooling or slow evaporation. X-ray crystallographic data were collected on a Bruker APEX diffractometer equipped with a CCD detector, employing $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), at 223 K with the SMART suite of programs [13]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [14], and for absorption effects with SADABS [15]. Structural solution and refinement were carried out with the SHELXTL suite of programs [16]. Crystal and refinement data are summarised in Tables 5 and 6.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. Organic hydrogen atoms were placed in calculated positions and refined with a riding model, except for **13a** (refined on coordinates with isotropic thermal parameter fixed at 0.04 \AA^2) and **15a** (refined freely). The metal hydrides were either located from low angle difference electron density maps, or placed in calculated positions using XHYDEX [17]. They were refined freely (**5b** and **9a**), refined on coordinates with isotropic thermal parameter fixed at 0.04 \AA^2 (**13a** and **15a**) or with a riding model.

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Appendix A. Supplementary material

CCDC 662214, 662215, 662216, 662217, 662218, 662219, 662220 and 662221 contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.01.025](https://doi.org/10.1016/j.jorganchem.2008.01.025).

References

- [1] For examples, see: (a) M. Abe, T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K. Uosaki, Y. Sasaki, *Angew. Chem., Int. Ed.* 42 (2003) 2912; (b) A. Morneau, A. Manivannan, C.R. Cabrera, *Langmuir* 10 (1994) 3940; (c) D. Li, L.W. Moore, B.L. Swanson, *Langmuir* 10 (1994) 1177; (d) S.E. Deutsch, J.R. Chang, B.C. Gates, *Langmuir* 9 (1993) 1284; (e) S. Yamamoto, R.M. Lewis, Y. Nabata, H. Hotta, H. Kuroda, *Inorg. Chem.* 20 (1990) 4342; (f) S. Yamamoto, R.M. Lewis, H. Hotta, H. Kuroda, *Vacuum* 41 (1990) 65; (g) J.J. Venter, M.A. Jeremy, *J. Mol. Catal.* 56 (1989) 117; (h) C. Dossi, A. Fusi, E. Grilli, R. Psaro, R. Ugo, R. Zaroni, *Catal. Today* 2 (1988) 585; (i) B.M. Choudary, K.R. Kumar, *Appl. Catal.* 35 (1987) 177; (j) S.C. Brown, J. Evans, *J. Chem. Soc., Chem. Commun.* (1978) 1063.
- [2] For examples, see (a) R. Ugo, C. Dossi, R. Psaro, *J. Mol. Catal. A* 107 (1996) 13; (b) Y. Chi, H.-L. Yu, W.-L. Ching, C.-S. Liu, Y.-L. Chen, T.-Y. Chou, S.-M. Peng, G.-H. Lee, *J. Mater. Chem.* 12 (2002) 1363.
- [3] C. Li, M.Y.D. Lai, W.K. Leong, *J. Organomet. Chem.* 690 (2005) 3861.
- [4] (a) B.F.G. Johnson, J. Lewis, T.I. Odiaka, P.R. Raithby, *J. Organomet. Chem.* 216 (1981) C51; (b) A.J. Arce, Y.D. Danctics, A.J. Deeming, *J. Organomet. Chem.* 311 (1986) 371.
- [5] (a) S.E. Kabir, C.A. Johns, K.M.A. Malik, M.A. Mottalib, E. Rosenberg, *J. Organomet. Chem.* 625 (2001) 112; (b) G.R. Fraunhoff, *Coord. Chem. Rev.* 121 (1992) 131.
- [6] (a) R.D. Adams, N.M. Golembeski, J.P. Selegue, *J. Am. Chem. Soc.* 103 (1981) 546; (b) E.W. Ainscough, A.M. Brodie, R.K. Coll, A.J.K. Mair, J.M. Waters, *J. Organomet. Chem.* 509 (1996) 259; (c) E.W. Ainscough, A.M. Brodie, R.K. Coll, B.A. Coombridge, J.M. Waters, *J. Organomet. Chem.* 556 (1998) 197; (d) E.W. Ainscough, A.M. Brodie, R.K. Coll, J.M. Waters, *Aust. J. Chem.* 52 (1999) 801; (e) K.M. Hanif, E.K. Shariff, M.A. Mottalib, M.B. Hursthouse, K.M.A. Malik, E. Rosenberg, *Polyhedron* 19 (2000) 1073.
- [7] S. Jeannin, Y. Jeannin, G. Lavigne, *Inorg. Chem.* 17 (1978) 2103.
- [8] We have earlier reported the syntheses of **9a** and **17a**: (a) K.H. Chan, W.K. Leong, G. Jaouen, L. Leclercq, S. Top, A. Vessières, *J. Organomet. Chem.* 691 (2006) 9; (b) M.O.E. Ahmed, W.K. Leong, *J. Organomet. Chem.* 691 (2006) 1055.
- [9] (a) E.W. Ainscough, A.M. Brodie, R.K. Coll, A.J.K. Mair, J.M. Waters, *Inorg. Chim. Acta* 214 (1993) 21; (b) E.W. Ainscough, A.M. Brodie, R.K. Coll, T.G. Kotch, A.J. Lees, A.J.A. Mair, J.M. Waters, *J. Organomet. Chem.* 517 (1996) 173; (c) E.W. Ainscough, A.M. Brodie, S.L. Ingham, T.G. Kotch, A.J. Lees, J. Lewis, J.M. Waters, *J. Chem. Soc., Dalton Trans.* (1994) 1.
- [10] A.J. Deeming, R. Vassh, *Polyhedron* 13 (1994) 3285.

- [11] D. Roberto, E. Lucenti, C. Roveda, R. Ugo, *Organometallics* 16 (1997) 5974.
- [12] J.N. Nicholls, M.D. Vargas, *Inorg. Synth.* 28 (1990) 232.
- [13] SMART Version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- [14] SAINT+ Version 6.22a, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- [15] G.M. Sheldrick, SADABS, 1996.
- [16] SHELXTL Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
- [17] A.G. Orpen, XHYDEX: A Program for Locating Hydrides in Metal Complexes, School of Chemistry, University of Bristol, UK, 1997.