

# Syntheses and reactivities of hydrosulfido- or sulfido-bridged heterobimetallic complexes containing Group 6 and Group 9 metals

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Reactions of  $[\text{Cp}_2\text{M}(\text{SH})_2]$  ( $\text{M} = \text{Mo}$  **1**,  $\text{W}$  **2**) with one equiv of  $[\text{IrH}_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})][\text{PF}_6]$  in acetone at room temperature under 1 atm of  $\text{H}_2$  afforded the hydrosulfido-hydrido complexes  $[\text{Cp}_2\text{M}(\mu\text{-SH})\text{IrH}_2(\text{PPh}_3)_2][\text{PF}_6]$  ( $\text{M} = \text{Mo}$  **4**,  $\text{W}$  **5**), whereas those of **1** and **2** with  $[\text{RhH}_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})(\text{EtOH})][\text{PF}_6]$  **6** resulted in the formation of  $[\text{Cp}_2\text{Mo}(\mu\text{-SH})\text{Rh}(\text{PPh}_3)_2][\text{PF}_6]$  **7** and  $[\text{Cp}_2\text{W}(\mu\text{-S})\text{Rh}(\text{PPh}_3)_2][\text{PF}_6]$  **8**. X-Ray analyses have been undertaken to clarify the detailed structure of  $[\text{Cp}_2\text{Mo}(\mu\text{-SH})\text{IrH}_2(\text{PPh}_3)_2][\text{BPh}_4]$  derived from **4** along with **7** and **8**. Bimetallic complexes **4**, **5**, **7**, and **8** catalysed the hydrogenation of alkynes such as 1-octyne and *tert*-butyl propiolate at room temperature under 1 atm of  $\text{H}_2$ , yielding 1-octene and *tert*-butyl acrylate as the major products, respectively. In both reactions, the Mo-Rh complex **7** showed the highest catalytic activity, although even the reactions using **7** are much slower than those catalyzed by the mononuclear Rh complex **6**.

## Introduction

Hydrosulfido complexes are currently attracting significant attention owing to their relevance to active sites in certain sulfur-containing industrial and biological catalysts.<sup>1</sup> Studies on the syntheses and reactivities of bimetallic hydrosulfido complexes are of particular interest, since these may provide useful information about the structures and functional mechanisms of the  $\text{MoS}_2$ -Co hydrodesulfurization (HDS) catalysts widely used in the hydrotreating process of crude oil and petroleum distillates.<sup>2</sup> It might also be noteworthy that in Dance's model for the reduction of  $\text{N}_2$  occurring on the  $\text{MoFe}_7\text{S}_9$  aggregate in the FeMo-cofactor of nitrogenase, proton transfer to coordinated  $\text{N}_2$  via a  $\mu\text{-SH}$  intermediate has been proposed.<sup>3</sup> However, when compared to the multinuclear heterometallic alkylthiolato and arylthiolato complexes ubiquitously known,<sup>4</sup> the corresponding hydrosulfido complexes are less well documented.<sup>1</sup>

Recent research in this laboratory has focused on the chemistry of noble metal-sulfur multinuclear complexes. As part of these studies, new dinuclear homometallic complexes with bridging hydrosulfido ligands such as  $[\text{Cp}^*\text{MCl}(\mu\text{-SH})_2\text{MCp}^*\text{Cl}]$  ( $\text{M} = \text{Ir}, \text{Rh}$ ,<sup>5</sup>  $\text{Ru}$ ,<sup>6</sup>  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ),  $[\text{Cp}^*\text{MCl}(\mu\text{-SH})_3\text{MCp}^*\text{Cl}]^+$  ( $\text{M} = \text{Ir}, \text{Rh}$ ),<sup>5</sup> and  $[(\text{Cym})\text{RuCl}(\mu\text{-SH})_2\text{Ru}(\text{Cym})\text{Cl}]$  ( $\text{Cym} = \eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i$ )<sup>7</sup> have been prepared and their intriguing reactivities forming tri- to penta-nuclear sulfido clusters have been demonstrated.<sup>8</sup> These findings have been extended more recently to the syntheses of hydrosulfido- and sulfido-bridged mixed metal complexes such as  $[\text{Cp}_2\text{Ti}(\mu\text{-SH})_2\text{RuCp}^*\text{Cl}]$ <sup>9</sup> and  $[\text{CpTiCl}(\mu\text{-S})_2\text{IrCp}^*(\text{PMe}_3)]$ <sup>10</sup> ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) along with exploitation of their selected reactivities.

In this paper, we wish to describe the reactions of mononuclear bis(hydrosulfido) complexes of Mo or W with mononuclear hydrido complexes of Ir or Rh, which have mostly resulted in the formation of the expected hydrosulfido-bridged Group 6 and Group 9 bimetallic complexes with or without hydride ligands on the noble metal center. These new complexes might represent one of the possible models for the active species generated on the HDS catalyst surface, on which hydrogen gas is dissociatively adsorbed to form the hydrosulfides and/or

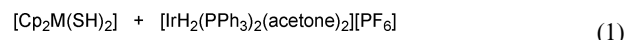
metal hydrides prior to the migration of these hydrogens presumably as protons and hydrides, respectively, to coordinated sulfur-containing substrates. Although the reactivities of the new complexes obtained here towards organo-sulfur compounds under  $\text{H}_2$  are still elusive, it has turned out that the hydrogenation reaction of certain alkynes is promoted by these new bimetallic complexes. However, their activities are lower than those exhibited by the parent mononuclear Rh and Ir complexes. Preliminary results on this catalysis are also reported here.

## Results and discussion

### Reactions of Mo and W bis(hydrosulfido) complexes with Ir and Rh hydrido complexes under $\text{H}_2$

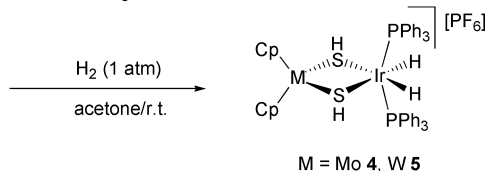
Bis(hydrosulfido) complexes  $\text{Cp}_2\text{M}(\text{SH})_2$  ( $\text{M} = \text{Mo}$  **1**,  $\text{M} = \text{W}$  **2**) reacted with an equimolar amount of an Ir hydrido complex  $[\text{IrH}_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})][\text{PF}_6]$  **3** in acetone at room temperature under  $\text{H}_2$  to form bimetallic hydrosulfido-hydrido complexes  $[\text{Cp}_2\text{M}(\mu\text{-SH})_2\text{IrH}_2(\text{PPh}_3)_2][\text{PF}_6]$  ( $\text{M} = \text{Mo}$  **4**,  $\text{M} = \text{W}$  **5**), which were isolated from the reaction mixtures as brown crystals in moderate yields (eqn. (1)). In the IR spectra, these products show both  $\nu(\text{S-H})$  bands (**4**, 2552; **5**, 2548  $\text{cm}^{-1}$ ) and  $\nu(\text{Ir-H})$  bands (**4**, 2116; **5**, 2120  $\text{cm}^{-1}$ ). The  $^1\text{H}$  NMR spectra are also consistent with these molecular formulae, which exhibit two triplets at high field, one being assignable to the SH protons (**4**,  $\delta -2.54$ ; **5**,  $\delta -1.54$ ) and the other, at much higher field, to the IrH protons (**4**,  $\delta -19.18$ ; **5**,  $\delta -18.13$ ). Treatment of **4** and **5** with  $\text{CD}_3\text{OD}$  in  $(\text{CD}_3)_2\text{CO}$  resulted in H/D exchange only for the SH protons, indicating unequivocally their protic nature, although the exchange reaction was quite slow and did not reach completion even after 24 h. The structures of **4** and **5** have been confirmed by single-crystal X-ray diffraction for  $[\text{Cp}_2\text{Mo}(\mu\text{-SH})_2\text{IrH}_2(\text{PPh}_3)_2][\text{BPh}_4]$  **4'** (*vide infra*) prepared in a similar manner from **1** and  $[\text{IrH}_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})][\text{BPh}_4]$  **3'**.

In contrast, reactions of **1** and **2** with a Rh hydrido complex  $[\text{RhH}_2(\text{PPh}_3)_2(\text{Me}_2\text{CO})(\text{EtOH})][\text{PF}_6]$  **6** under analogous conditions afforded bimetallic complexes without hydrido ligands

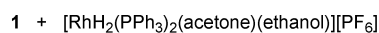


M = Mo 1, W 2

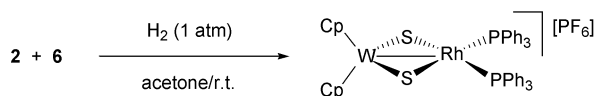
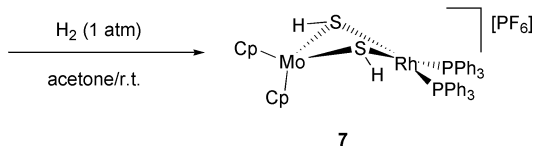
3



$[\text{Cp}_2\text{Mo}(\mu\text{-SH})_2\text{Rh}(\text{PPh}_3)_2][\text{PF}_6]$  **7** and  $[\text{Cp}_2\text{W}(\mu\text{-S})_2\text{Rh}(\text{PPh}_3)_2][\text{PF}_6]$  **8**, which were obtained in excellent yields as brown and black crystals, respectively (Scheme 1). Although the hydrido



6



Scheme 1

ligands of **6** are known to be highly dissociative as  $\text{H}_2$  gas in the absence of atmospheric  $\text{H}_2$ , it has been reported that the reactions of **6** with tertiary phosphines and arsines conducted under  $\text{H}_2$  result only in the replacement of coordinated solvent molecules by these ligands leaving the hydrides intact.<sup>11</sup> Noteworthy is that elimination of  $\text{H}_2$  from the Rh center occurred even when the above reactions were performed under a hydrogen atmosphere. The metal–hydride bonds are generally more stable in the 3rd transition series for the d-block metals than for those in the 2nd transition series of the same triad; the results observed here are consistent with this trend. Interestingly, concurrent loss of the hydrosulfido hydrogens along with the Rh–H hydrides took place in the reaction of **2** with **6** to afford **8**.

Complexes **7** and **8** were characterized spectroscopically and by X-ray analyses (*vide infra*). In the IR spectrum of **7**, a characteristic  $\nu(\text{SH})$  band appeared at  $2522 \text{ cm}^{-1}$ , which is slightly lower than those of **4** and **5**, while the  $^1\text{H}$  NMR spectrum showed a singlet assignable to the SH protons at  $\delta -2.02$  with an intensity integrated to be 2H. These spectral data indicate the presence of hydrosulfido protons in **7**, which has been confirmed by X-ray analysis locating unequivocally the H atoms attached to the bridging S atoms. In contrast, the IR and  $^1\text{H}$  NMR spectra of **8** exhibited no signals arising from SH protons. In the  $^1\text{H}$  NMR spectra of both **7** and **8**, no signals due to hydride ligands appeared.

### Description of the X-ray structures for **4'**, **7**, and **8**

To determine the detailed structures of the heterobimetallic complexes obtained here, X-ray analyses have been undertaken using single crystals of  $4' \cdot \text{Me}_2\text{CO}$ ,  $7 \cdot 0.5\text{Me}_2\text{CO}$ , and  $8 \cdot 0.75\text{Me}_2\text{CO}$ . Figs. 1, 2, and 3 depict the ORTEP<sup>12</sup> drawings of the cations in **4'**, **7**, and **8**, while Tables 1, 2, and 3 list the selected bond lengths and angles.

As shown in Fig. 1, **4'** containing formal Mo(IV) and Ir(III) centers has a nearly planar MoIrS<sub>2</sub> core. The deviations of these four atoms from their least-square plane are less than 0.053 Å. The geometry around the Mo center is distorted tetrahedral with respect to the two Cp centroids and the two SH ligands, while the Ir atom has an octahedral structure with two SH and

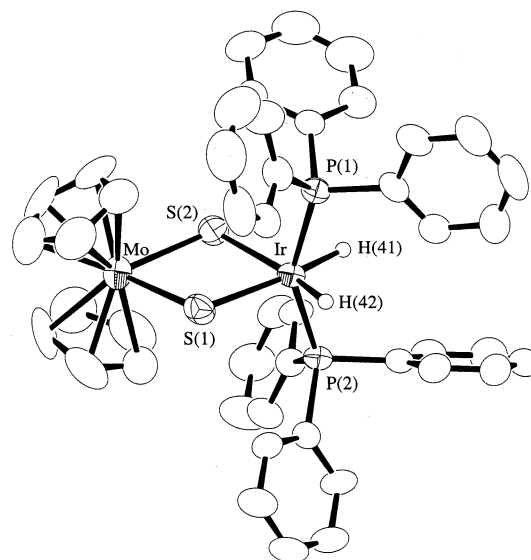


Fig. 1 Structure of the cation in **4'**. Hydrogen atoms are omitted for clarity except for the hydrides.

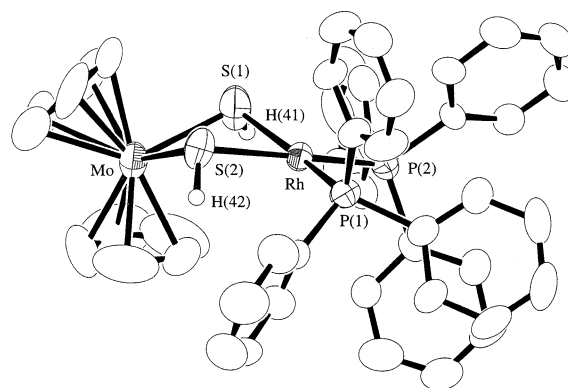


Fig. 2 Structure of the cation in **7**. Hydrogen atoms are omitted for clarity except for the hydrosulfido protons.

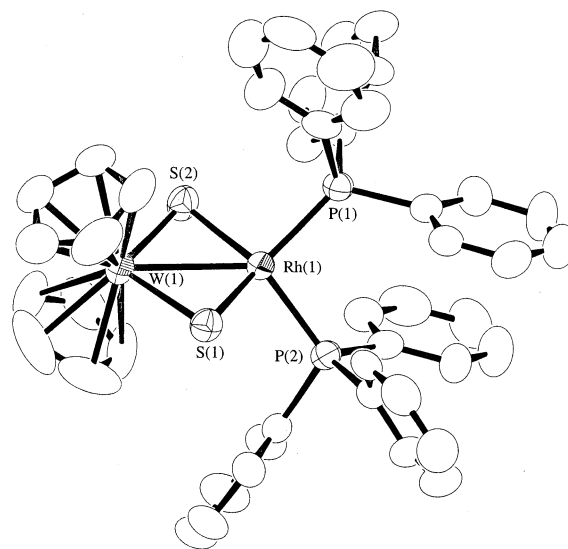


Fig. 3 Structure of the cation in one of the two independent molecules of **8** (molecule 1). Hydrogen atoms are omitted for clarity.

two hydride ligands on the basal plane. Two PPh<sub>3</sub> ligands occupying the remaining apical positions are considerably tilted towards the direction opposite to the Cp<sub>2</sub>Mo(μ-SH)<sub>2</sub> moiety with a P(1)–Ir–P(2) angle of 151.12(8)°. Such distortion is commonly observed for Ir complexes of the type *cis,trans,cis*-[IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>], where the P–Ir–P angles are in the range

**Table 1** Selected interatomic distances (Å) and angles (°) in 4'·Me<sub>2</sub>CO

Ir–S(1)	2.462(2)	Ir–S(2)	2.474(2)
Ir–P(1)	2.300(2)	Ir–P(2)	2.306(2)
Ir–H(41)	1.56(8)	Ir–H(42)	1.44(8)
Mo–S(1)	2.523(3)	Mo–S(2)	2.546(3)
Mo–C(Cp)	2.25(1)–2.37(1)	Ir ⋯ Mo	3.8894(9)
S(1)–Ir–S(2)	78.97(8)	S(1)–Ir–P(1)	103.76(8)
S(1)–Ir–P(2)	101.34(8)	S(2)–Ir–P(1)	96.66(8)
S(2)–Ir–P(2)	101.98(8)	P(1)–Ir–P(2)	151.12(8)
S(1)–Ir–H(42)	90(3)	S(2)–Ir–H(41)	94(2)
H(41)–Ir–H(42)	95(4)	S(1)–Mo–S(2)	76.50(8)
Ir–S(1)–Mo	102.55(8)	Ir–S(2)–Mo	101.57(8)

**Table 2** Selected interatomic distances (Å) and angles (°) in 7·0.5Me<sub>2</sub>CO

Rh–S(1)	2.362(3)	Rh–S(2)	2.390(3)
Rh–P(1)	2.266(3)	Rh–P(2)	2.234(3)
Mo–S(1)	2.510(3)	Mo–S(2)	2.521(3)
Mo–C(Cp)	2.24(2)–2.32(2)	Mo ⋯ Rh	3.671(1)
S(1)–Rh–S(2)	75.9(1)	S(1)–Rh–P(1)	166.5(1)
S(1)–Rh–P(2)	96.1(1)	S(2)–Rh–P(1)	91.95(10)
S(2)–Rh–P(2)	171.0(1)	P(1)–Rh–P(2)	96.39(10)
S(1)–Mo–S(2)	71.0(1)	Rh–S(1)–Mo	97.7(1)
Rh–S(2)–Mo	96.7(1)		

**Table 3** Selected interatomic distances (Å) and angles (°) in 8·0.75Me<sub>2</sub>CO

Molecule 1			
W(1)–Rh(1)	2.8699(9)	W(1)–S(1)	2.370(3)
W(1)–S(2)	2.372(3)	W(1)–C(Cp)	2.31(2)–2.37(2)
Rh(1)–S(1)	2.269(3)	Rh(1)–S(2)	2.273(3)
Rh(1)–P(1)	2.277(3)	Rh(1)–P(2)	2.262(3)
S(1)–W(1)–S(2)	100.39(9)	S(1)–Rh(1)–S(2)	106.65(10)
S(1)–Rh(1)–P(1)	142.2(1)	S(1)–Rh(1)–P(2)	87.06(10)
S(2)–Rh(1)–P(1)	91.13(10)	S(2)–Rh(1)–P(2)	142.4(1)
P(1)–Rh(1)–P(2)	98.94(10)	W(1)–S(1)–Rh(1)	76.40(8)
W(1)–S(2)–Rh(1)	76.28(8)		
Molecule 2			
W(2)–Rh(2)	2.885(1)	W(2)–S(3)	2.376(3)
W(2)–S(4)	2.382(3)	W(2)–C(Cp)	2.30(1)–2.39(2)
Rh(2)–S(3)	2.267(3)	Rh(2)–S(4)	2.274(3)
Rh(2)–P(3)	2.262(3)	Rh(2)–P(4)	2.262(3)
S(3)–W(2)–S(4)	99.97(9)	S(3)–Rh(2)–S(4)	106.7(1)
S(3)–Rh(2)–P(3)	138.8(1)	S(3)–Rh(2)–P(4)	92.76(10)
S(4)–Rh(2)–P(3)	90.1(1)	S(4)–Rh(2)–P(4)	138.8(1)
P(3)–Rh(2)–P(4)	98.61(10)	W(2)–S(3)–Rh(2)	76.77(8)
W(2)–S(4)–Rh(2)	76.52(8)		

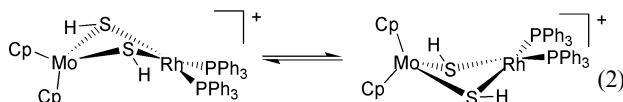
153–168° for the S-donor ligands L including thiophene, tetrahydrothiophene,<sup>13</sup> and dihydrobenzothiophene.<sup>14</sup>

The Mo ⋯ Ir distance at 3.8894(9) indicates the lack of any metal–metal bonding interaction, which is consistent with the 18-electron count satisfied for the Mo(IV) and Ir(III) centers in the absence of a metal–metal bond. The Mo–S bonds at 2.523(3) and 2.546(3) Å are longer than the Ir–S bonds at 2.462(2) and 2.474(2) Å, but only slightly. Since the hydrosulfido hydrogens were not located, the *syn* or *anti* configuration with respect to the two S–H groups is not clear.

Fig. 2 shows that the formal Mo(IV)–Rh(I) complex **7** contains a distorted tetrahedral Mo center as observed in **4'** along with a square-planar Rh center surrounded by two SH and two PPh<sub>3</sub> ligands. The MoRhS<sub>2</sub> core is puckered with dihedral angles of 138.8° and 129.5° around the S–S and Mo–Rh vectors, respectively. The Mo ⋯ Rh distance at 3.671(1) Å indicates the absence of any bonding interactions between the formal 18-electron Mo and 16-electron Rh centers. As a related Mo/Rh complex with bridging thiolato ligands, [Cp<sub>2</sub>Mo(μ-S-Me)<sub>2</sub>Rh(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] has been reported,<sup>15</sup> in which the dihedral

angle of 171° between the MoS<sub>2</sub> and RhS<sub>2</sub> planes is much larger than that in **7**, affording a nearly planar MoRhS<sub>2</sub> core, although the Mo ⋯ Rh separation of 3.813(3) Å is almost comparable.

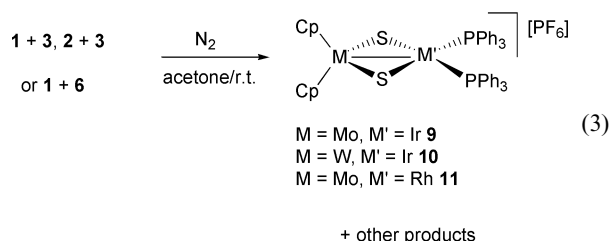
The Mo–S bond lengths of 2.510(3) and 2.521(3) Å are slightly longer than the Rh–S bond distances at 2.362(3) and 2.390(3) Å. Two SH protons could be found in the Fourier map; as depicted in Fig. 2, two SH ligands mutually have a *syn*-equatorial orientation with respect to the MoRhS<sub>2</sub> ring. The X-ray structure indicates that the two Cp groups are not equivalent in the solid state. However, the Cp protons are observed as one singlet in the <sup>1</sup>H NMR spectrum at room temperature. This finding presumably suggests that rapid inversion of the MoRhS<sub>2</sub> core is occurring in solution (eqn. (2)).



In an asymmetric unit of the crystal of 8·0.75Me<sub>2</sub>CO, there exist two crystallographically independent molecules whose structures are essentially identical. For one of the two solvating Me<sub>2</sub>CO molecules in the crystal used for this X-ray analysis, the occupancy was calculated to be only *ca.* 50%. The structure of the cation in one of these two molecules (molecule 1) is shown in Fig. 3. Complex **8** has an almost planar WRhS<sub>2</sub> core, with the deviations of the atom positions from this least-square plane being less than 0.09 and 0.01 Å for molecules 1 and 2, respectively. The formal W(IV) and Rh(III) centers are separated by 2.8699(9) and 2.885(1) Å, which presumably indicates the presence of a metal–metal single bond. Donation of two electrons from W to Rh results in the formal 18- and 16-electron counts with respect to the W and Rh centers. It is to be noted that the geometry around Rh is severely distorted from a square planar structure; the dihedral angles between the RhP<sub>2</sub> and RhWS<sub>2</sub> planes are 48.7° (molecule 1) and 53.2° (molecule 2). This might suggest that the oxidation states of the two metals could be assigned as W(V) and Rh(II). The W–S distances varying from 2.370(3) to 2.382(3) Å are slightly longer than the Rh–S distances in the range 2.267(3)–2.274(3) Å.

### Reactions of Mo and W bis(hydrosulfido) complexes with Ir and Rh hydrido complexes under N<sub>2</sub>

When the reactions of the hydrosulfido complexes **1** and **2** with the hydrido complex **3** and the reaction of **1** with **6** were performed under N<sub>2</sub>, sulfido-bridged bimetallic complexes were obtained in low yields together with the above mentioned hydrosulfido-bridged complexes (eqn. (3)). These sulfido-bridged complexes have been characterized as being [Cp<sub>2</sub>M(μ-S)<sub>2</sub>M'(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (M = Mo, M' = Ir **9**; M = W, M' = Ir **10**; M = Mo, M' = Rh **11**) based on spectral and microanalytical data. For **10**, the X-ray analysis was also carried out. This has revealed that the structure of **10** is essentially the same as that of **8**, details of which can be found in the CIF data (see <http://www.rsc.org/suppdata/dt/b1/b108227m/>). From the IR and <sup>1</sup>H NMR criteria, the structures of **9** and **11** are presumed to be similar.



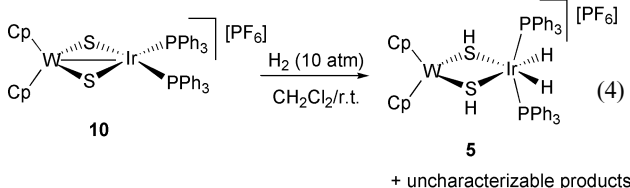
Interestingly, when **10** dissolved in CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature under pressurized H<sub>2</sub> (10 atm), the hydro-

**Table 4** Hydrogenation of *tert*-butyl propiolate using sulfur-bridged heterobimetallic complexes<sup>a</sup>

Catalyst	Reaction time	Conversion(%)	Yield of CH <sub>2</sub> =CHCOOBut <sup>b</sup> (%)
<b>7</b>	5 h	100	99
<b>8</b>	5 h	23	22
	2 days	100	85
<b>4</b>	7 days	68	39
<b>5</b>	7 days	59	30
<i>cf.</i> monomeric complexes			
<b>6</b>	1 h	100	82
<b>3</b>	1 h	100	93

<sup>a</sup> Catalyst, 10 mol%; room temperature; H<sub>2</sub>, 1 atm; solvent, acetone. <sup>b</sup> GLC yield.

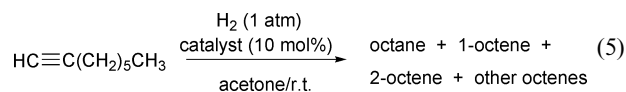
sulfido-hydrido complex **5** was obtained as one of the three products detectable by <sup>31</sup>P NMR spectroscopy of the reaction mixture (eqn. (4)). Although the other two products were not identified, these complexes probably contain hydrosulfido and hydrido ligands since the <sup>1</sup>H NMR spectrum of the reaction mixture shows several resonances in the SH and hydrido regions along with those of **5**. It should be noted that the precedented reactions of sulfido complexes with H<sub>2</sub> gas forming hydro-sulfido complexes are quite limited, *e.g.* [(CpMo)<sub>2</sub>(μ-SH)<sub>2</sub>(μ-S)<sub>2</sub>] from [(CpMo)<sub>2</sub>(μ-S)<sub>2</sub>](μ-S)<sub>2</sub>,<sup>16</sup> [{RhH(triphos)}<sub>2</sub>(μ-SH)<sub>2</sub>]<sup>2+</sup> from [{Rh(triphos)}<sub>2</sub>(μ-S)<sub>2</sub>]<sup>2+</sup> (triphos = tris(diphenylphosphino-methyl)ethane),<sup>17</sup> and a mononuclear example [Cp\*<sub>2</sub>TiH(SH)] from [Cp\*<sub>2</sub>TiS(py)],<sup>18</sup>



### Hydrogenation reactions of alkynes

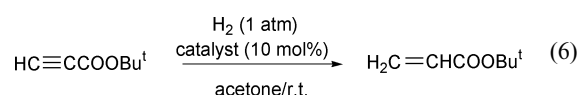
It has been found that the catalytic hydrogenation of alkynes such as 1-octyne and *tert*-butyl propiolate proceeds in the presence of **4**, **5**, **7**, and **8**. Hydrosulfido- or sulfido-bridged bimetallic complexes **4**, **5**, **7**–**11** are recovered from all of the reaction mixtures, suggesting that the hydrogenations are taking place with retention of the dinuclear catalyst cores.

The reactions of 1-octyne in acetone at room temperature under 1 atm of H<sub>2</sub> in the presence of 10 mol% catalyst resulted in the formation of mixtures of 1-octene and its isomers together with *n*-octane, which are confirmed by mass spectroscopy (eqn. (5)). Among the four complex catalysts, the Mo–Rh complex **7** displayed the highest catalytic activity. Thus, all of the 1-octyne was consumed in 15 h, whereby the yields of octane, 1-octene, and 2-octene including the *cis* and *trans* isomers were 32, 22, and 28%, respectively. The formation of small amounts of 3- and 4-octenes were also observed, the combined yield of which was *ca.* 3%. On the other hand, it took 2–4 days to convert all of the 1-octyne into hydrogenated products in the reactions catalyzed by the other three complexes. However, even the reaction using **7** is much slower than that catalyzed by mononuclear Rh complex **6**, which terminated in 1 h under analogous conditions, affording 1-octene and some C<sub>16</sub> compounds by alkyne dimerization.



Hydrogenation of *tert*-butyl propiolate also proceeded catalytically under similar conditions in the presence of **4**, **5**, **7**, and **8** (eqn. (6)). As observed in the above reaction, **7** exhibited much higher activity than the other three complexes, which is shown in Table 4. After 5 h, the alkyne was converted into the

acrylate almost quantitatively. However, this reaction also proceeded more rapidly in the presence of mononuclear complex **6**, although the reaction using **6** is so fast that the further hydrogenated product, the propionate, forms in addition to the acrylate even after 1 h. In the reactions using **4**, **5**, and **8**, the selectivity of the acrylate is less than that catalyzed by **7** due to the formation of alkyne oligomers.



In conclusion, it has been demonstrated that the sulfur-bridged bimetallic complexes obtained in this study catalyze the hydrogenation of certain alkynes and the catalytic activity significantly depends upon the nature of the combined metals. Although even the highest activity observed here for the Mo–Rh complex **7** is inferior to that of the mononuclear Rh complex **6**, it may be emphasized that, if compared with complexes containing P-, N-, and O-donor ligands, those with S-donor ligands have been poorly exploited in their use in catalytic reactions.<sup>19,20</sup> Especially, employment of heterobimetallic complexes with thiolato or sulfido ligands has been investigated quite rarely: as the precedented example, [Pt<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>(μ-S)<sub>2</sub>Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> is known to catalyze the hydrogenation of cyclohexene, but the reaction is much slower than that using [RhCl(PPh<sub>3</sub>)<sub>3</sub>].<sup>21</sup> It might also be noteworthy that a monomeric thiolate complex [RhH<sub>2</sub>(SR)(PPh<sub>3</sub>)<sub>3</sub>] shows much higher catalytic activity in the hydrogenation of cyclohexene than the corresponding thiolato-bridged dimer [Rh<sub>2</sub>(μ-SR)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>].<sup>22</sup>

## Experimental

### General

All manipulations were carried out *under an atmosphere of hydrogen* using Schlenk techniques except for those stated otherwise. IR and NMR spectra were recorded on JASCO FT/IR-420 and JEOL LA-400 spectrometers, respectively, while elemental analyses were conducted with a Perkin-Elmer 2400 series II CHN analyzer. The GLC and GC-MS studies were carried out using a Shimadzu GC-14B chromatograph equipped with a CBP10 capillary column and a Shimadzu GCMS-QP5050 spectrometer. Compounds **1**,<sup>23</sup> **2**,<sup>24</sup> **3**,<sup>25</sup> and **6**<sup>26</sup> were prepared by the literature methods, while **3'** was obtained from **3** by anion metathesis using NaBPh<sub>4</sub>.

### Synthesis

**[Cp<sub>2</sub>Mo(μ-SH)<sub>2</sub>IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]** **4**. Complexes **1** (292 mg, 1.00 mmol) and **3** (980 mg, 1.00 mmol) were dissolved in acetone (30 cm<sup>3</sup>) and the solution was stirred overnight at room temperature. Addition of diethyl ether to the resultant dark brown solution afforded **4**·Me<sub>2</sub>CO as brown crystals (862 mg, 75%). Found: C, 48.80; H, 4.43. C<sub>49</sub>H<sub>50</sub>OP<sub>3</sub>S<sub>2</sub>F<sub>6</sub>IrMo requires C, 48.47; H, 4.15%. IR (KBr): ν(SH), 2552; ν(IrH), 2116 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -19.18 (t, J<sub>H-P</sub> = 20.0 Hz, 2H, IrH), -2.54



**Table 5** Details of the X-ray crystallography

	4'·Me <sub>2</sub> CO	7·0.5Me <sub>2</sub> CO	8·0.75Me <sub>2</sub> CO
Formula	C <sub>73</sub> H <sub>70</sub> OBP <sub>2</sub> S <sub>2</sub> MoIr	C <sub>47.5</sub> H <sub>45</sub> O <sub>0.5</sub> F <sub>6</sub> P <sub>3</sub> S <sub>2</sub> MoRh	C <sub>48.25</sub> H <sub>44.5</sub> O <sub>0.75</sub> F <sub>6</sub> P <sub>3</sub> S <sub>2</sub> RhW
<i>M</i>	1388.39	1093.76	1194.17
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> (no. 4)
Crystal size/mm	0.6 × 0.2 × 0.1	0.3 × 0.3 × 0.05	0.55 × 0.25 × 0.15
<i>a</i> /Å	12.467(3)	12.334(2)	11.005(2)
<i>b</i> /Å	13.079(5)	13.920(3)	12.920(2)
<i>c</i> /Å	21.467(2)	28.980(2)	12.020(2)
<i>a</i> °	92.13(2)	90	90
<i>β</i> °	101.12(1)	90.136(9)	98.06(1)
<i>γ</i> °	112.40(2)	90	90
<i>V</i> /Å <sup>3</sup>	3151(1)	4618(1)	4796(1)
<i>Z</i>	2	4	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.463	1.573	1.654
<i>μ</i> (Mo-Kα)/cm <sup>-1</sup>	24.75	8.81	28.88
Unique reflections	11072	10577	14172
Observed reflections [ <i>I</i> > 3σ( <i>I</i> )]	7887	3523	9159
<i>R</i> <sup>a</sup>	0.043	0.047	0.040
<i>R</i> <sub>w</sub> <sup>b</sup>	0.054	0.049	0.038
GOF <sup>c</sup>	1.88	1.22	1.41
Residuals/e Å <sup>-3</sup>	+1.04, -0.87	+0.48, -0.38	+1.10, -0.77

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$  ( $w = \{[\sigma(F_o)]^2 + (p^2/4)F_o^2\}^{-1}$ ). <sup>c</sup> GOF =  $[\sum w(|F_o| - |F_c|)^2 / \{(\text{no. observed}) - (\text{no. variables})\}]^{1/2}$ .

(*t*, *J*<sub>H-P</sub> = 7.8 Hz, 2H, SH), 2.17 (s, 6H, Me<sub>2</sub>CO), 4.89 (s, 10H, Cp), 7.4–7.7 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 11.8 (s).

**[Cp<sub>2</sub>Mo(μ-SH)<sub>2</sub>IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>] 4'**. Brown crystals of 4' were obtained by analogous treatment of 1 (13 mg, 0.045 mmol) with 3' (52 mg, 0.045 mmol) in 5 cm<sup>3</sup> of acetone (16 mg, 25%). Found: C, 63.18; H, 4.97. C<sub>70</sub>H<sub>64</sub>P<sub>2</sub>S<sub>2</sub>BIrMo requires C, 63.20; H, 4.85%. IR (KBr): ν(SH), 2547; ν(IrH), 2116, 2098 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -19.22 (*t*, *J*<sub>H-P</sub> = 20.0 Hz, 2H, IrH), -2.67 (*t*, *J*<sub>H-P</sub> = 8.1 Hz, 2H, SH), 4.17 (s, 10H, Cp), 6.8–7.6 (m, 50H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 11.9 (s). A single crystal collected for the X-ray analysis contained one solvating Me<sub>2</sub>CO molecule per molecule of 4'.

**[Cp<sub>2</sub>W(μ-SH)<sub>2</sub>IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] 5**. Analogous treatment of 2 (224 mg, 0.590 mmol) with 3 (578 mg, 0.590 mmol) in 30 cm<sup>3</sup> of acetone afforded 5·Me<sub>2</sub>CO as brown crystals (539 mg, 69%). Found: C, 45.41; H, 4.15. C<sub>49</sub>H<sub>50</sub>OP<sub>3</sub>S<sub>2</sub>F<sub>6</sub>IrW requires C, 45.20; H, 3.87%. IR (KBr): ν(SH), 2548; ν(IrH), 2120 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -18.13 (*t*, *J*<sub>H-P</sub> = 19.8 Hz, 2H, IrH), -1.54 (*t*, *J*<sub>H-P</sub> = 7.6 Hz, 2H, SH), 2.17 (s, 6H, Me<sub>2</sub>CO), 4.82 (s, 10H, Cp), 7.4–7.7 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 11.7 (s).

**[Cp<sub>2</sub>Mo(μ-SH)<sub>2</sub>Rh(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] 7**. Analogous treatment of the reaction mixture of 1 (206 mg, 0.705 mmol) and 6 (611 mg, 0.705 mmol) in acetone (10 cm<sup>3</sup>) gave 7·0.5Me<sub>2</sub>CO as brown crystals (635 mg, 82%). Found: C, 52.18; H, 4.31. C<sub>47.5</sub>H<sub>45</sub>O<sub>0.5</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>MoRh requires C, 52.16; H, 4.15%. IR (KBr): ν(SH), 2522 cm<sup>-1</sup>. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: δ -2.20 (s, 2H, SH), 2.08 (s, Me<sub>2</sub>CO), 5.62 (s, 10H, Cp), 7.2–7.6 (m, 30H, Ph). The quantity of solvating Me<sub>2</sub>CO was confirmed by X-ray analysis. <sup>31</sup>P{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: δ 44.2 (d, *J*<sub>Rh-P</sub> = 169 Hz).

**[Cp<sub>2</sub>W(μ-S)<sub>2</sub>Rh(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] 8**. Analogous treatment of 2 (242 mg, 0.639 mmol) with 6 (554 mg, 0.639 mmol) afforded 8·0.5Me<sub>2</sub>CO as black crystals (676 mg, 90%). Found: C, 48.23; H, 3.81. C<sub>47.5</sub>H<sub>43</sub>O<sub>0.5</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>WRh requires C, 48.36; H, 3.67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.17 (s, 3H, Me<sub>2</sub>CO), 5.18 (s, 10H, Cp), 7.1–7.7 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 52.3 (d, *J*<sub>Rh-P</sub> = 166 Hz). Single crystals suitable for X-ray analysis were obtained from acetone/hexane and contained 0.75 equiv of solvating acetone.

**[Cp<sub>2</sub>M(μ-S)<sub>2</sub>M'(PPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] (M = Mo, M' = Ir 9; M = W, M' = Ir 10; M = Mo, M' = Rh 11)**. Similar treatment of 1 or 2

with 3 and that of 1 with 6 under N<sub>2</sub> afforded the title compounds 9, 10, and 11 together with other products including 4, 5, and 7, respectively. Products 9, 10, and 11 deposited as dark brown crystals and were separated manually from the other products, recrystallized from acetone/diethyl ether, and characterized as follows. Yields of these compounds were not determined.

**9**. Found: C, 48.17; H, 3.87. C<sub>46</sub>H<sub>40</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>MoIr requires C, 47.90; H, 3.50%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.03 (s, 10H, Cp), 7.1–7.7 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 35.1 (s).

**10**. Found: C, 44.78; H, 3.60. C<sub>46</sub>H<sub>40</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>WIr requires C, 44.56; H, 3.25%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.09 (s, 10H, Cp), 7.1–7.5 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 33.6 (s).

**11·0.5Me<sub>2</sub>CO**. Found: C, 52.52; H, 4.20. C<sub>47.5</sub>H<sub>43</sub>O<sub>0.5</sub>P<sub>3</sub>S<sub>2</sub>F<sub>6</sub>MoRh requires C, 52.26; H, 3.97%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.17 (s, 3H, Me<sub>2</sub>CO), 5.13 (s, 10H, Cp), 7.2–7.6 (m, 30H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 52.0 (d, *J*<sub>Rh-P</sub> = 165 Hz).

### Reaction of 10 with H<sub>2</sub>

A stainless steel autoclave was charged with a CH<sub>2</sub>Cl<sub>2</sub> solution (5 cm<sup>3</sup>) of 10 (0.050 mmol) and stirred at room temperature under 10 atm of H<sub>2</sub>. The <sup>31</sup>P NMR spectrum of the resulting dark brown solution showed a singlet at δ 11.7 assignable to 5 together with two singlets at δ 7.0 and 18.4, whose intensity ratio is *ca.* 1 : 2 : 1.3. Attempts to isolate and characterize the two products exhibiting the latter two resonances were unsuccessful.

### Hydrogenation of alkynes

Under 1 atm of H<sub>2</sub>, 0.2 mmol of the alkyne was added to an acetone solution (5 cm<sup>3</sup>) of the complex catalyst (0.02 mmol) and the mixture was stirred at room temperature. Then, the product solution was subjected to GC-MS analysis (in order to characterize the organic products) and GLC analysis (for determining the yield of each compound). Qualitative analysis of octane and octenes were carried out by analyzing the GC-MS spectra of the reaction mixture and the authenticated compounds.

### X-Ray crystallography

Single crystal X-ray analyses of complexes 4', 7, and 8 were carried out at room temperature on a Rigaku AFC7R diffractometer equipped with a Mo-Kα source. Details of crystal and

data collection parameters are summarized in Table 5. For **8**, space group  $P2_1$  with  $Z = 4$  was chosen, because additional centers of symmetry could not be found. The correctness of this choice has been suggested by the Flack parameter of  $-0.017(10)$ .

Structure solution and refinements were conducted using the TEXSAN program package.<sup>27</sup> The positions of the non-hydrogen atoms were determined by DIRDIF PATTY<sup>28</sup> and were refined anisotropically. Hydrogen atoms were placed at calculated positions and included at the final stages of refinements with fixed parameters. For  $4 \cdot \text{Me}_2\text{CO}$ , the  $\text{BPh}_4$  anion occupies two disordered positions with the same occupancies. The carbon atoms in the solvating  $\text{Me}_2\text{CO}$  as well as the hydride hydrogens found in the Fourier map were refined isotropically. However, the hydrosulfido protons could not be located at reasonable positions and were not included in the refinements. The hydrosulfido hydrogens in **7** were located from the Fourier map and refined isotropically, while the carbon atoms in the solvating  $\text{Me}_2\text{CO}$  with 50% occupancy for  $8 \cdot 0.75\text{Me}_2\text{CO}$  were refined using isotropic parameters.

Crystal data for  $10 \cdot 0.5\text{CH}_2\text{Cl}_2$  are as follows.  $\text{C}_{46.5}\text{H}_{41}\text{F}_6\text{P}_3\text{S}_2\text{ClWIr}$ ,  $M = 1282.39$ , monoclinic, space group  $P2_1/a$  (no. 14),  $a = 15.155(4)$ ,  $b = 19.601(4)$ ,  $c = 17.635(4)$  Å,  $\beta = 112.51(2)^\circ$ ,  $V = 4839.2(2)$  Å<sup>3</sup>, room temperature,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 54.28 \text{ cm}^{-1}$ , SHELX-97,<sup>29</sup>  $R1 = 0.053$ ,  $wR2 = 0.170$  for 7311 reflections with  $I > 3.00\sigma(I)$  and 601 variables.

CCDC reference numbers 170943–170946.

See <http://www.rsc.org/suppdata/dt/b1/b108227m/> for crystallographic data in CIF or other electronic format.

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