

# Heterodinuclear complexes of rhenium and molybdenum with bridging $S_2CPR_3$ ligands

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## Abstract

Mononuclear complexes *fac*-[Re(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (R = cyclohexyl (Cy) (**1a**) or isopropyl (<sup>i</sup>Pr) (**1b**)) react with [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] to afford dinuclear complexes of formula [ReMo(CO)<sub>6</sub>(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)] (R = Cy (**2a**) or <sup>i</sup>Pr (**2b**)). Treatment of complexes **2** with monodentate phosphorus donors such as PEt<sub>3</sub> or P(OMe)<sub>3</sub> displaces one carbonyl ligand from the molybdenum atom, to afford pentacarbonyls [ReMo(CO)<sub>5</sub>(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)(L)] (**3a–3d**). Reactions of **2** with bidentate phosphorus donors displace one CO group from molybdenum and cleave one Re–S bond to give pentacarbonyls [ReMo(CO)<sub>5</sub>(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)(μ-L–L)] (**4a–4d**) (L–L = tetraethylpyrophosphite or bis(dimethylphosphino)methane), in which the S<sub>2</sub>CPR<sub>3</sub> bridges have changed their coordination mode from η<sup>2</sup>(S,S')η<sup>3</sup>(S,C,S') to η<sup>1</sup>(S)η<sup>3</sup>(S,C,S').

*Key words:* Molybdenum; Rhenium; Heterobimetallics

## 1. Introduction

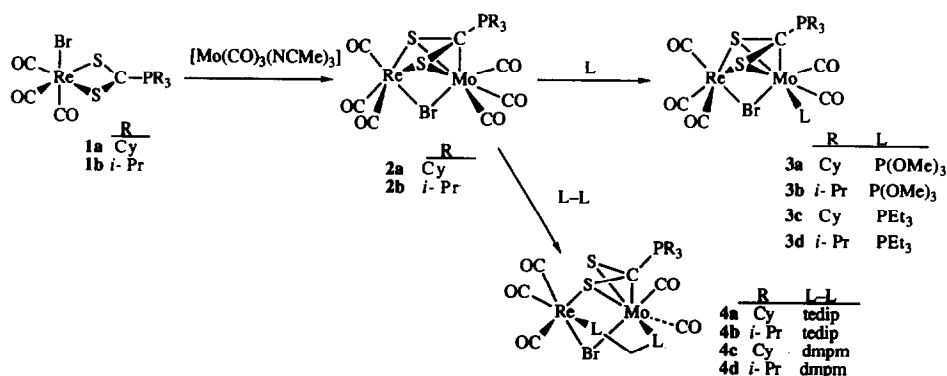
In recent studies we have found that complexes containing S<sub>2</sub>CPR<sub>3</sub> groups acting as η<sup>2</sup>(S,S')η<sup>3</sup>(S,C,S') bridges [1–4] are markedly more stable than the previously known complexes in which the S<sub>2</sub>CPR<sub>3</sub> bridges η<sup>1</sup>(S)η<sup>1</sup>(S') [5–7], η<sup>1</sup>(S)η<sup>2</sup>(C,S') [8] or η<sup>1</sup>(S)η<sup>3</sup>(S,C,S') [9]. This allowed us to undertake a systematic study of the reactivity of complexes with S<sub>2</sub>CPR<sub>3</sub> bridges, which had not been possible before. We found that complexes containing η<sup>2</sup>(S,S')η<sup>3</sup>(S,C,S') S<sub>2</sub>CPR<sub>3</sub> bridges across an Mn–Mn or an Re–Mn bond undergo nucleophilic addition reactions which are qualitatively different from those previously known for mononuclear complexes containing chelating S<sub>2</sub>CPR<sub>3</sub> ligands [10]. All this prompted us to design a rational synthesis of stable binuclear complexes with S<sub>2</sub>CPR<sub>3</sub> bridges which could serve as substrates to explore the chemistry of coordinated S<sub>2</sub>CPR<sub>3</sub> ligands. We have recently published a facile high yield synthesis of heterodinuclear carbonyl complexes containing one bridging bromide and one S<sub>2</sub>CPR<sub>3</sub> bridge between Mn<sup>I</sup> and Mo<sup>0</sup> other-

wise not directly bonded, using the (S,C,S',Br) donor set of [Mn(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] as a polydentate ligand donating six electrons to an Mo<sup>0</sup>(CO)<sub>3</sub> fragment [2,3]. We have also given a preliminary account of the use of the same method to obtain heterodinuclear complexes containing Ru and Mo, or Ru and W [4]. Here we wish to report the application of the synthetic procedure to the preparation of heterodinuclear hexacarbonyl complexes containing rhenium and molybdenum, and also the preparation of pentacarbonyl derivatives by replacement of CO.

## 2. Results and discussion

Complexes *fac*-[Re(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (R = cyclohexyl (Cy) (**1a**) or isopropyl (<sup>i</sup>Pr) [11] readily react with [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] in dichloromethane to give purple–red solutions from which air-stable, deep-red crystalline solids [ReMo(CO)<sub>6</sub>(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)] (**2a** and **2b**) (Scheme 1) can be isolated with high yields. Comparable with Mn–Mo analogues [3], the spectroscopic data of the reaction mixtures showed the formation of **2**, with the central carbon atom of the S<sub>2</sub>CPR<sub>3</sub> bonded to Mo, as the only products. No significant amount of the corresponding isomers with a C–Re bond where

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Scheme 1.

detected. This indicates a stronger preference of the central carbon atom of S<sub>2</sub>CPR<sub>3</sub> to bind Mo rather than Re. No isomerization was observed upon heating solutions of **2** in tetrahydrofuran (THF) for several days; so this preference cannot be a kinetic effect. As proposed for Mn–Mo analogues [3], this can be rationalized by assuming that the S<sub>2</sub>CPR<sub>3</sub> ligand prefers low oxidation state centres when the central carbon atom is involved in the coordination.

The analytical (see Section 3) and spectroscopic data (Tables 1 and 2) indicate that **2a** and **2b** are isostructural with their analogues containing Mn and Mo [3]. The IR spectra of **2** contain six bands, one more than their Mn–Mo counterparts. This may be due to the accidental degeneracies for the Mn compounds of two normal modes which occur as two separate bands for the Re species. In the <sup>13</sup>C{<sup>1</sup>H}

NMR spectrum, the signals attributable to the carbonyl groups bonded to molybdenum fall within a range of ± 1.5 ppm in both series of complexes (Mn–Mo and Re–Mo), whereas the signals assigned to carbonyl groups bonded to rhenium are shifted upfield by 15–20 ppm from those bonded to manganese.

The reactivity of the hexacarbonyls **2a** and **2b** towards phosphorus donors closely parallels that previously found for their Mn–Mo analogues [3]. Thus, the reaction of hexacarbonyls **2** with monodentate P donors causes substitution of one carbonyl ligand on the molybdenum atom, yielding pentacarbonyls [ReMo(CO)<sub>5</sub>(L)(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)] (**3a–3d**) (Scheme 1), while reactions with potential bidentate ligands such as tetraethylpyrophosphite (tedip) or bis(dimethylphosphino)methane (dmpm) afford pentacarbonyls [ReMo(CO)<sub>5</sub>(μ-Br)(μ-S<sub>2</sub>CPR<sub>3</sub>)(μ-L-L)] (**4a–4d**) (Scheme 1)

TABLE 1. IR and <sup>31</sup>P{<sup>1</sup>H} nuclear magnetic resonance data for the new complexes

Compound	IR (CH <sub>2</sub> Cl <sub>2</sub> ), ν(CO) (cm <sup>-1</sup> )	<sup>31</sup> P{ <sup>1</sup> H}(CD <sub>2</sub> Cl <sub>2</sub> ), δ (ppm)		
		(S <sub>2</sub> CP)	Mo-P	Re-P
<b>2a</b> [ReMo(CO) <sub>6</sub> (μ-Br)(μ-S <sub>2</sub> CPCy <sub>3</sub> )]	2037m, 2018vs, 1953s, 1928m, 1895m, 1869w	38.48		
<b>2b</b> [ReMo(CO) <sub>6</sub> (μ-Br)(μ-S <sub>2</sub> CP <sup><i>i</i></sup> Pr <sub>3</sub> )]	2038m, 2019vs, 1956s, 1929m, 1897m, 1870w	50.43		
<b>3a</b> [ReMo(CO) <sub>5</sub> (P(OMe) <sub>3</sub> )(μ-Br)(μ-S <sub>2</sub> CPCy <sub>3</sub> )]	2022s, 1924vs, 1891m, 1830m	37.79	163.35	
<b>3b</b> [ReMo(CO) <sub>5</sub> (P(OMe) <sub>3</sub> )(μ-Br)(μ-S <sub>2</sub> CP <sup><i>i</i></sup> Pr <sub>3</sub> )]	2023s, 1923vs, 1892m, 1832m	49.61	163.11	
<b>3c</b> [ReMo(CO) <sub>5</sub> (PEt <sub>3</sub> )(μ-Br)(μ-S <sub>2</sub> CPCy <sub>3</sub> )]	2021s, 1920vs, 1888m, 1805m	37.53	29.76	
<b>3d</b> [ReMo(CO) <sub>5</sub> (PEt <sub>3</sub> )(μ-Br)(μ-S <sub>2</sub> CP <sup><i>i</i></sup> Pr <sub>3</sub> )]	2021s, 1920vs, 1889m, 1807m	49.16	30.00	
<b>4a</b> [ReMo(CO) <sub>5</sub> (μ-Br)(μ-S <sub>2</sub> CPCy <sub>3</sub> )(μ-tedip)]	2038s, 1954s, 1918sh, 1909s, 1798m	38.22	164.44 <sup>a</sup>	105.43 <sup>a</sup>
<b>4b</b> [ReMo(CO) <sub>5</sub> (μ-Br)(μ-S <sub>2</sub> CP <sup><i>i</i></sup> Pr <sub>3</sub> )(μ-tedip)]	2039s, 1955s, 1920sh, 1910s, 1797m	47.67	165.10 <sup>b</sup>	105.76 <sup>b</sup>
<b>4c</b> [ReMo(CO) <sub>5</sub> (μ-Br)(μ-S <sub>2</sub> CPCy <sub>3</sub> )(μ-dmpm)]	2027s, 1937s, 1908sh, 1895s, 1771m	37.57 <sup>c</sup>	12.96 <sup>d</sup>	-25.71 <sup>e</sup>
<b>4d</b> [ReMo(CO) <sub>5</sub> (μ-Br)(μ-S <sub>2</sub> CP <sup><i>i</i></sup> Pr <sub>3</sub> )(μ-dmpm)]	2028s, 1938s, 1911sh, 1896s, 1773m	47.19 <sup>f</sup>	12.43 <sup>g</sup>	-25.80 <sup>h</sup>

<sup>a</sup> d, J(P–P) = 38 Hz.

<sup>b</sup> d, J(P–P) = 37 Hz.

<sup>c</sup> d, J(P–P) = 3 Hz.

<sup>d</sup> d, J(P–P) = 11 Hz.

<sup>e</sup> dd, J(P–P) = 11 and 3 Hz.

<sup>f</sup> d, J(P–P) = 4 Hz.

<sup>g</sup> d, J(P–P) = 11 Hz.

<sup>h</sup> dd, J(P–P) = 11 and 4 Hz.

through CO replacement on the molybdenum atom and the cleavage of an S–Re bond.

The <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts of the phosphorus ligand in **3a–3d** are very close to those observed for Mn–Mo analogues, as expected after the substitution of one Mo-bonded CO in both cases. No further substitution was observed when an excess of donor or a higher reaction temperature was used. In contrast, in the <sup>31</sup>P NMR spectra of **4a–4d**, which contain bidentate ligands, the chemical shifts of the bands corresponding to P bonded to Mo are not significantly different from those of the Mn–Mo, while the signals of P bonded to Re (narrower peaks) are shifted upfield

to more than 40 ppm compared with those of the Mo–Mn compounds (broader bands).

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the pentacarbonyl compounds **3** and **4**, the signals of Mo-bonded CO are nearly unchanged compared with those of the Mn–Mo analogues, whereas the bands attributed to carbonyl groups bonded to rhenium are shifted upfield, by 15–20 ppm, from those of carbonyl groups bonded to Mn. The hexacarbonyl complexes **2** show a similar phenomenon.

The preparation of the hexacarbonyls **2a** and **2b** demonstrates the applicability of the synthetic method, and the reactions to produce the derivatives with mon-

TABLE 2. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} nuclear magnetic resonance data for the new complexes <sup>a</sup>

Compound	<sup>1</sup> H NMR, δ ppm	<sup>13</sup> C{ <sup>1</sup> H} NMR, δ (ppm)
<b>2a</b>	2.56 (m, 3H, CH of Cy); 1.95–1.33 (m, br, 30H, CH <sub>2</sub> of Cy)	242.5 (d (6), 2xMoCO); 217.3 (s, MoCO); 191.3 (s, ReCO); 190.0 (s, 2x ReCO); 101.7 (d (38), S <sub>2</sub> CP); 33.3 (d(40), C <sup>(1)</sup> of Cy); 27.3 (s, C <sup>(2)</sup> and C <sup>(6)</sup> of Cy); 26.7 (d(12), C <sup>(3)</sup> and C <sup>(5)</sup> of Cy); 25.1 (s, C <sup>(4)</sup> of Cy)
<b>2b</b>	2.86 (m, 3H, CH of <sup>i</sup> Pr); 1.50 (m, 18H, CH <sub>3</sub> of <sup>i</sup> Pr)	242.2 (d (6), 2xMoCO); 218.1 (s, MoCO); 191.5 (s, ReCO); 190.7 (s, 2x ReCO); 102.0 (d (39), S <sub>2</sub> CP); 23.7 (d(41), CH of <sup>i</sup> Pr); 18.0 (s, CH <sub>3</sub> of <sup>i</sup> Pr)
<b>3a</b>	3.79 (d(11), 9H, POCH <sub>3</sub> ); 2.52 (m, 3H, CH of Cy); 2.16–1.33 (m, br, 30H, CH <sub>2</sub> of Cy)	249.0 (dd (32 and 6), MoCO); 227.6 (d(8), MoCO); 191.1 (s, ReCO); 189.8 (s, ReCO); 189.3 (s, ReCO); 96.3 (dd (41 and 6), S <sub>2</sub> CP); 51.4 (d(3), POCH <sub>3</sub> ); 32.2 (d(37), C <sup>(1)</sup> of Cy); 26.3 (s, C <sup>(2)</sup> and C <sup>(6)</sup> of Cy); 25.8 (d(11), C <sup>(3)</sup> and C <sup>(5)</sup> of Cy); 24.3 (s, C <sup>(4)</sup> of Cy)
<b>3b</b>	3.80 (d(11), 3H, POCH <sub>3</sub> ); 2.84 (m, 3H, CH of <sup>i</sup> Pr); 1.49 (m, 18H, CH <sub>3</sub> of <sup>i</sup> Pr)	249.8 (dd (32 and 6), MoCO); 228.1 (d (8), MoCO); 192.0 (s, ReCO); 190.7 (s, ReCO); 190.3 (s, ReCO); 96.8 (dd (42 and 8), S <sub>2</sub> CP); 52.4 (d(3), POCH <sub>3</sub> ); 23.3 (d(41), CH of <sup>i</sup> Pr); 17.9 (s, CH <sub>3</sub> of <sup>i</sup> Pr)
<b>3c</b>	2.51–1.14 (m, br, Et and Cy)	254.9 (dd (28 and 5), MoCO); 231.3 (d(6), MoCO); 192.3 (s, ReCO); 191.0 (s, ReCO); 190.5 (s, ReCO); 95.4 (dd (42 and 4), S <sub>2</sub> CP); 33.4 (d(35), C <sup>(1)</sup> of Cy); 27.4 (s, C <sup>(2)</sup> and C <sup>(6)</sup> of Cy); 26.8 (d(11), C <sup>(3)</sup> and C <sup>(5)</sup> of Cy); 25.3 (s, C <sup>(4)</sup> of Cy); 17.9 (d(23), CH <sub>2</sub> of PEt <sub>3</sub> ); 7.8 (s, CH <sub>3</sub> of PEt <sub>3</sub> )
<b>3d</b>	2.85 (m, 3H, CH of <sup>i</sup> Pr); 1.93 (m, 6H, CH <sub>2</sub> of Et); 1.49 (m, 18H, CH <sub>3</sub> of <sup>i</sup> Pr); 1.19 (m, 9H, CH <sub>3</sub> of Et)	254.4 (dd (22 and 6), MoCO); 231.0 (s, MoCO); 192.2 (s, ReCO); 190.9 (s, ReCO); 190.5 (s, ReCO); 95.2 (dd (43 and 4), S <sub>2</sub> CP); 23.4 (d(42), CH of <sup>i</sup> Pr); 18.0 (d (3), CH <sub>3</sub> of <sup>i</sup> Pr); 17.9 (d(23), CH <sub>2</sub> of PEt <sub>3</sub> ); 7.8 (s, CH <sub>3</sub> of PEt <sub>3</sub> )
<b>4a</b>	4.28 (m, 8H, CH <sub>2</sub> of tedip); 2.60 (m, 3H, CH of Cy); 2.03–1.29 (m, br, 42H, CH <sub>2</sub> of Cy and CH <sub>3</sub> of tedip)	245.5 (dd (25 and 5), MoCO); 229.5 (d(9), MoCO); 194.1 (d(106), ReCO); 187.3 (d(12), ReCO); 185.9 (d(12), ReCO); 79.9 (ddd (58, 13 and 7), S <sub>2</sub> CP); 63.8–61.4 (m, CH <sub>2</sub> of tedip); 34.9 (d(40), C <sup>(1)</sup> of Cy); 28.2 (s, C <sup>(2)</sup> and C <sup>(6)</sup> of Cy); 27.3 (d(11), C <sup>(3)</sup> and C <sup>(5)</sup> of Cy); 26.1 (s, C <sup>(4)</sup> of Cy); 16.8–16.2 (m, CH <sub>3</sub> of tedip)
<b>4b</b>	4.24 (m, 8H, CH <sub>2</sub> of tedip); 2.89 (m, 3H, CH of <sup>i</sup> Pr); 1.56–1.33 (m, 30H, CH <sub>3</sub> of <sup>i</sup> Pr and tedip)	245.8 (dd (26 and 5), MoCO); 229.4 (d(9), MoCO); 193.9 (d(106), ReCO); 187.9 (d(13), ReCO); 185.8 (d(13), ReCO); 78.9 (ddd (59, 12 and 7), S <sub>2</sub> CP); 63.4– 61.6 (m, CH <sub>2</sub> of tedip); 25.1 (d(42), CH of <sup>i</sup> Pr); 18.4 (s, CH <sub>3</sub> of <sup>i</sup> Pr); 16.2 (m, CH <sub>3</sub> of tedip)
<b>4c</b>	3.37 (m, 1H, PCH <sub>2</sub> P of dmpm); 2.63 (m, 4H, CH of Cy, and PCH <sub>2</sub> P of dmpm); 2.18–1.18 (m, br, 42H, CH <sub>2</sub> of Cy and CH <sub>3</sub> of dmpm)	248.9 (dd (18 and 5), MoCO); 232.5 (d(7), MoCO); 194.6 (d(68), ReCO); 189.5 (d(7), ReCO); 187.9 (d(7), ReCO); 77.1 (ddd (60, 11 and 5), S <sub>2</sub> CP); 37.9 (dd (21 and 10), CH <sub>2</sub> of dmpm); 34.8 (d(40), C <sup>(1)</sup> of Cy); 28.2 (s, C <sup>(2)</sup> and C <sup>(6)</sup> of Cy); 27.3 (d(11), C <sup>(3)</sup> and C <sup>(5)</sup> of Cy); 26.1 (s, C <sup>(4)</sup> of Cy); 20.5–16.2 (m, CH <sub>3</sub> of dmpm)
<b>4d</b>	3.35 (m, 1H, PCH <sub>2</sub> P of dmpm); 2.89 (m, 1H, PCH <sub>2</sub> P of dmpm); 1.93–1.36 (m, 30H, CH <sub>3</sub> of dmpm and <sup>i</sup> Pr)	249.0 (dd (18 and 5), MoCO); 232.3 (d(7), MoCO); 194.5 (d(67), ReCO); 189.4 (d(7), ReCO); 187.9 (d(7), ReCO); 76.6 (ddd (62, 12 and 4), S <sub>2</sub> CP); 37.8 (dd (21 and 10), CH <sub>2</sub> of dmpm); 25.1 (d(42), CH of <sup>i</sup> Pr); 18.4 (s, CH <sub>3</sub> of <sup>i</sup> Pr); 20.7–16.3 (m, CH <sub>3</sub> of dmpm)

<sup>a</sup> From CD<sub>2</sub>Cl<sub>2</sub> solutions.

odentate (**3a–3d**) or bidentate (**4a–4d**) ligands are good proof of the stability of the  $S_2CPR_3$  bridges in these families of complexes.

### 3. Experimental details

All reactions were carried out in dry solvents under dinitrogen. Starting materials and donors were purchased and used without purification. IR spectra were recorded on a Perkin–Elmer FT 1720-X spectrometer.  $^1H$  NMR (300.1 MHz,  $\delta$  (ppm) from internal  $Si(Me)_4$ ), and  $^{31}P\{^1H\}$  NMR (121.5 MHz,  $\delta$ (ppm) to higher frequencies from external 85%  $H_3PO_4$ ) spectra were recorded on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin–Elmer 240 B analyser.

#### 3.1. $[ReMo(CO)_6(\mu-Br)(\mu-S_2CPCy_3)]$ (**2a**)

A solution of  $[Mo(CO)_3(NCMe)_3]$  was prepared by heating  $[Mo(CO)_6]$  (0.066 g, 0.25 mmol) in acetonitrile (15 ml) for 3 h at reflux temperature. The solvent was evaporated *in vacuo* and  $[Re(CO)_3(S_2CPCy_3)Br]$  [11] (0.177 g, 0.25 mmol) was added to the dry residue. The mixture of solids were dissolved in  $CH_2Cl_2$  (15 ml), and the resulting solution was stirred for 15 min and then filtered. The filtrate was concentrated *in vacuo* to about 5 ml. The addition of hexane (10 ml) and slow concentration gave **2a** as a red microcrystalline solid (yield, 0.19 g, (86%)). Anal. Found: C, 33.7; H, 3.6.  $C_{25}H_{33}BrMoO_6PReS_2$  calc.: C, 33.9; H, 3.7%.

#### 3.2. $[ReMo(CO)_6(\mu-Br)(\mu-S_2CP^iPr_3)]$ (**2b**)

Compound **2b** was prepared by a method similar to that described above, using  $[Mo(CO)_6]$  (0.066 g, 0.25 mmol), and  $[Re(CO)_3(S_2CP^iPr_3)Br]$  [11] (0.147 g, 0.25 mmol). The product **2b** was obtained as red microcrystals, (yield, 0.15 g, (78%)). Anal. Found: C, 25.6; H, 2.7.  $C_{16}H_{21}BrMoO_6PReS_2$  calc.: C, 25.1; H, 2.8%.

#### 3.3. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CPCy_3)\{P(OMe)_3\}]$ (**3a**)

To a solution of **2a** (0.177 g, 0.20 mmol) in  $CH_2Cl_2$  (15 ml) was added  $P(OMe)_3$  (24  $\mu$ l, 0.20 mmol). The mixture was stirred for 15 min, and then hexane (10 ml) was added. Slow evaporation *in vacuo* gave **3a** as deep-red microcrystals (yield, 0.17 g (85%)). Anal. Found: C, 32.9; H, 4.3.  $C_{27}H_{42}BrMoO_8P_2ReS_2$  calc.: C, 33.0; H, 4.3%.

#### 3.4. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CP^iPr_3)\{P(OMe)_3\}]$ (**3b**)

Compound **3b** was prepared by the method described for **3a**, using **2b** (0.153 g, 0.20 mmol) and  $P(OMe)_3$  (24  $\mu$ l, 0.32 mmol), (yield, 0.14 g (82%)). Anal. Found: C, 25.4; H, 3.4.  $C_{18}H_{30}BrMoO_8P_2ReS_2$  calc.: C, 25.1; H, 3.5%.

#### 3.5. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CPCy_3)(PEt_3)]$ (**3c**)

Compound **3c** was prepared by the method described for **3a**, using **2a** (0.177 g, 0.20 mmol) and  $PEt_3$  (30  $\mu$ l, 0.20 mmol), (yield, 0.16 g, (84%)). Anal. Found: C, 36.5; H, 5.1.  $C_{30}H_{48}BrMoO_5P_2ReS_2$  calc.: C, 36.9; H, 4.9%.

#### 3.6. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CP^iPr_3)(PEt_3)]$ (**3d**)

Compound **3d** was prepared by the method described for **3a**, using **2b** (0.153 g, 0.20 mmol) and  $PEt_3$  (30  $\mu$ l, 0.20 mmol), (yield, 0.17 g (85%)). Anal. Found: C, 29.9; H, 4.2.  $C_{21}H_{36}BrMoO_5P_2ReS_2$  calc.: C, 29.4; H, 4.2%.

#### 3.7. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CPCy_3)(\mu-tedip)]$ (**4a**)

A mixture of **2a** (0.177 g, 0.20 mmol) and *tedip* (49  $\mu$ l, 0.20 mmol) in  $CH_2Cl_2$  (15 ml) was stirred at room temperature for 20 min. The solvent was evaporated under reduced pressure to about 5 ml. The addition of hexane (10 ml) gave **4a** as a red solid which was recrystallized from  $CH_2Cl_2$ –hexane (yield, 0.17 g, (78%)). Anal.  $C_{32}H_{53}BrMoO_{10}P_3ReS_2$  calc.: C, 34.4; H, 4.8. Found: C, 34.4; H, 4.8%.

#### 3.8. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CP^iPr_3)(\mu-tedip)]$ (**4b**)

Compound **4b** was prepared as described above for **4a**, using **2b** (0.15 g, 0.20 mmol) and *tedip* (49  $\mu$ l, 0.20 mmol) (yield, 0.14 g (72%)). Anal. Found: C, 28.0; H, 4.1.  $C_{23}H_{41}BrMoO_{10}P_3ReS_2$  calc.: C, 27.7; H, 4.1%.

#### 3.9. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CPCy_3)(\mu-dmpm)]$ (**4c**)

To a cooled ( $-78^\circ C$ ) solution of **2a** (0.177 g, 0.20 mmol) in THF (20 ml), was added *dmpm* (30  $\mu$ l, 0.19 mmol). After stirring at  $-78^\circ C$  for 5 min, the mixture was allowed to warm slowly to room temperature (about 20 min). The solvent was evaporated *in vacuo*, and the residue was taken in  $CH_2Cl_2$  (5 ml), and filtered. The addition of hexane (15 ml) to the filtrate produced **4c** as a red solid (yield, 0.15 g (75%)). Anal. Found: C, 34.6; H, 4.8.  $C_{29}H_{47}BrMoO_5P_3ReS_2$  calc.: C, 35.0; H, 4.8%.

#### 3.10. $[ReMo(CO)_5(\mu-Br)(\mu-S_2CP^iPr_3)(\mu-dmpm)]$ (**4d**)

Compound **4d** was prepared as described for **4c**, using **2b** (0.153 g, 0.20 mmol), and *dmpm* (30  $\mu$ l, 0.19 mmol), (yield, 0.12 g (71%)). Anal. Found: C, 27.9; H, 4.1.  $C_{20}H_{35}BrMoO_5P_3ReS_2$  calc.: C, 27.5; H, 4.0%.

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**References**

- 1 D. Miguel, V. Riera, J.A. Miguel, M. Gómez and X. Soláns, *Organometallics*, **10** (1991) 1683.
- 2 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem.*, **420** (1991) C12.
- 3 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Organometallics*, **12** (1993) 1394.
- 4 J. Cuyás, D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *Polyhedron*, **11** (1992) 2713.
- 5 C. Bianchini, C.A. Ghilardi, A. Meli, A. Orlandini and G. Scapacci, *J. Chem. Soc., Dalton Trans.*, (1983) 1969.
- 6 R. Usón, A. Laguna, M. Laguna, P.G. Jones and C. Fittschen, *J. Chem. Soc., Dalton Trans.*, (1987) 3017.
- 7 D. Miguel, V. Riera and J.A. Miguel, *J. Organomet. Chem.*, **412** (1991) 127.
- 8 (a) H. Werner, *Coord. Chem. Rev.*, **43** (1982) 165; (b) H. Otto, M. Ebner and H. Werner, *J. Organomet. Chem.*, **311** (1986) 63.
- 9 C. Bianchini, C.A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *Organometallics*, **1** (1982) 778.
- 10 B. Alvarez, S. García-Granda, Y. Jeannin, D. Miguel, J.A. Miguel and V. Riera, *Organometallics*, **10** (1991) 3005.
- 11 B. Alvarez, D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Granda, *J. Organomet. Chem.*, **427** (1992) C33.