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# Reaction of BH<sub>4</sub><sup>-</sup> with {Mo<sub>2</sub>Cp<sub>2</sub>(µ-SMe)<sub>n</sub>} species to give tetrahydroborato, hydrido or dimetallaborane compounds: control of product by ancillary ligands

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The reaction of mono- or dichloro-dimolybdenum(III) complexes  $[Mo_2Cp_2(\mu-SMe)_2(\mu-Cl)(\mu-Y)]$  ( $Cp = \eta^5-C_5H_5$ ; 1, Y = SMe; 2, Y = PPh\_2; 3, Y = Cl) with NaBH<sub>4</sub> at room temperature gave in high yields tetrahydroborato (8), hydrido (9) or metallaborane (12) complexes depending on the ancillary ligands. The correct formulation of derivatives 8 and 12 has been unambigously determined by X-ray diffraction methods. That of the hydrido compound 9 has been established in solution by NMR analysis and confirmed by an X-ray study of the  $\mu$ -azavinylidene derivative  $[Mo_2Cp_2(\mu-SMe)_2(\mu-PPh_2)(\mu-N=CHMe)]$  (10) obtained from the insertion of acetonitrile into the Mo–H bond of 9. Reaction of NaBH<sub>4</sub> with nitrile derivatives,  $[Mo_2Cp_2(\mu-SMe)_{4-n}(CH_3CN)_{2n}]^{n+}$  (5, n=1; 6 n=2), afforded the tetrahydroborato compound 8, together with a  $\mu$ -azavinylidene species  $[Mo_2Cp_2(\mu-SMe)_3(\mu-N=CHMe)]$  (14), when n=1, and the metallaborane complex 12, together with a mixed borohydrato-azavinylidene derivative  $[Mo_2Cp_2(\mu-SMe)_2(\mu-SMe)_3(\mu-N=CHMe)]$  (13), when n=2. The molecular structures of these complexes have been confirmed by X-ray analysis. Preparations of some of the starting complexes (3 and 4) are also described, as are the molecular structures of the precursors  $[Mo_2Cp_2(\mu-SMe)_2(\mu-X)-(\mu-Y)]$  (1, X/Y = Cl/SMe; 2, X/Y = Cl/PPh\_2; 4, X/Y = SMe/PPh\_2).

# 1. Introduction

The thermal stability of covalent f-element borohydrides allows them to be isolated and characterised easily.<sup>1</sup> In contrast, borohydride complexes [M(BH<sub>4</sub>)] of d-transition metals, with the exception of those of group 4, are less stable, decomposing readily to give either the corresponding hydride after elimination of borane<sup>2,3</sup> or a metallaborane after loss of dihydrogen.<sup>3,4</sup> Nevertheless, several stable borohydride complexes of d-transition elements have been isolated over the last fifteen years: examples are now known for the metals niobium,<sup>5</sup> chromium,<sup>6</sup> molybdenum,<sup>7</sup> manganese,<sup>8</sup> iron,<sup>9</sup> ruthenium,<sup>10</sup> osmium,<sup>106</sup> rhodium<sup>11</sup> and iridium.<sup>12</sup>

The usual synthetic route to a borohydride complex involves reaction of a metal halide with an alkali-metal borohydride.<sup>13</sup> Less common routes to borohydride compounds are based on either (i) insertion of a hydridoborane into a metal-hydride bond<sup>14</sup> or (ii) reaction of a borate salt with a cationic transition metal complex containing labile dative ligands in what is formally a substitution process.<sup>7,10c</sup> However, when an alkali-metal borohydride reacts with a metal halide which contains more than one chloro ligand, a metallaborane can be obtained *via* a stepwise process: initial formation of a transient polyborohydride is followed by elimination of dihydrogen.<sup>15</sup> It is also well established that replacement of Cl<sup>-</sup> by the pseudohalide BH<sub>4</sub><sup>-</sup> gives either a stable hydroborato complex or a metal hydride if the initial substitution reaction is followed by loss of BH<sub>3</sub>.<sup>2</sup>

At present it is impossible to state reliably which factors favour the formation of a borohydride rather than a hydrido complex in such reactions. We decided to approach this problem by reacting borate salts with bimetallic reagents in which the bridging units are systematically varied. Accordingly, we describe here the reactions of sodium borohydride with both the bimetallic halide and pseudohalide complexes  $[Mo_2Cp_2(\mu-SMe)_2(\mu-X)(\mu-Y)]$  $(Cp = \eta^5-C_5H_5; X/Y = Cl/SMe, Cl/PPh_2, Cl/Cl, and SMe/PPh_2)$ and the related cations  $[Mo_2Cp_2(\mu-SMe)_{4-n}(CH_3CN)_{2n}]^{n+}$  (n = 1 or 2) which contain labile nitrile ligands. One successful outcome of these reactions is the synthesis of borohydride and metallaborane derivatives of the dimolybdenum starting complexes. Some of the results demonstrate an understandable competition between borane or H<sub>2</sub> elimination and dimolybdenum polyborohydride disproportionation, giving rise to molybdenum hydrides or molybdoboranes. Furthermore, since the ancillary ligands condition the reactivity of the metal reagent toward BH<sub>4</sub><sup>-</sup>, we have determined, where it is appropriate, the molecular structures of the quadruply-bridged dimolybdenum precursors. Part of this work has been published in preliminary form.<sup>7</sup>

# 2. Results and discussion

# 2.1. Synthesis and characterisation of precursors 1–7. Molecular structures of 1, 2 and 4

The dinuclear complexes selected for reaction with sodium borohydride fall into two groups (see Fig. 1). Complexes 1-4 make up a series of quadruply-bridged bimetallic complexes  $[Mo_2Cp_2(\mu-SMe)_2(\mu-X)(\mu-Y)]$  in which the two halide or pseudohalide bridging ligands, X and Y, have been systematically varied in order to assess their influence on the reactivity of the complexes towards BH<sub>4</sub>; the respective X/Y combinations are Cl/SMe, Cl/PPh2, Cl/Cl, and SMe/PPh2. The second group consists of the thiolato-complexes 5 and 6 in which chloride ligands are absent but two or four labile nitrile ligands are present. These complexes were chosen in order to confirm that substrates which do not contain halide complexes can react with BH4- to give either borohydride compounds or metallaboranes. The tetrakis(nitrile) complex [Mo<sub>2</sub>Cp<sub>2</sub>(µ-SMe)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (5) and the bis(nitrile) derivative  $[Mo_2Cp_2(\mu-SMe)_3(MeCN)_2]$  (BF<sub>4</sub>) (6) have previously been synthesised and characterised by spectroscopy and elemental analysis; for (5) the structure has also been confirmed by X-ray diffraction.16,17

**2.1.1.** Molecular structures of 1 and 2. We earlier reported the synthesis of the hetero-quadruply-bridged complex  $[Mo_2Cp_2(\mu-SMe)_3(\mu-Cl)]$  (1) and its characterisation by spectroscopy and

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Fig. 1 Dimolybdenum precursors relevant to this work.

elemental analysis.<sup>18</sup> However, in the absence of suitable crystals, its molecular structure could not by confirmed by X-ray diffraction. We have also described the preparation of the quadruply-bridged compound  $[Mo_2Cp_2(\mu-SMe)_2(\mu-Cl)(\mu-PPh_2)]$  (2), which is obtained quantitatively by the addition of excess diphenylphosphine HPPH<sub>2</sub> to a tetrahydrofuran solution of **1**. **2** was also characterised by spectroscopy and elemental analysis but not by X-ray diffraction.<sup>19</sup>

Several attempts to get crystals of **2** of diffraction quality from a preparative sample of the complex in diethylether solution at -15 °C failed. Finally, a crystal of poor quality was obtained; it turned out to have an asymmetric unit which contained a molecule of **2** co-crystallized with a molecule of the parent species **1**. This result was unexpected, as the parent compound **1** was shown by NMR techniques to be only a minor impurity in the solution from which the crystal was obtained. The presence of molecules of  $[Mo_2Cp_2(\mu-SMe)_3(\mu-Cl)]$  (**1**) and  $[Mo_2Cp_2(\mu-SMe)_2(\mu-Cl)(\mu-PPh_2)]$ (**2**) in the same crystal has enabled us to complete a series of X-ray diffraction studies of quadruply-bridged dimolybdenum(III) derivatives with a variable number of thiolato ligands.

Molecules of 1 and 2 (Figs. 2 and 3, Table 1) contain pairs of molybdenum atoms, in oxidation state III, directly bonded to each other and symmetrically bridged by four anionic ligands. In 1 the two molybdenum atoms are bridged by one chloro and three SMe ligands. Replacement by PPh<sub>2</sub> of the SMe trans to Cl converts 1 into 2. If the Mo-Mo bonds are ignored, the coordination of the metal atoms can be described in terms of a four-legged piano stool. Though many quadruply-bridged Mo(III)-Mo(III) complexes have been characterised by crystallography, in most cases the bridging ligands are either sulfur<sup>20</sup> or halogen<sup>21-23</sup> donors; of these only one,  $[Mo_2Cp'(\mu-Cl)_3(\mu-PPh_2)]$  (Cp' =  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et), also contains a bridging phosphido group.<sup>21b</sup> Complexes 1 and 2 therefore provide the first structural examples of quadruply-bridged dimolybdenum(III) thiolate derivatives in which there are bridging chloro and/or phosphido ligands. However, the molecular structure of a mixed thiolato-phosphido-sulfido-tetrabridged compound  $[Mo_2Cp(\mu-S^iPr)(\mu-S)_2(\mu-PPh_2)]$  has been described, but in this complex the Mo atoms are in oxidation state IV.24

For the two diamagnetic neutral species **1** and **2** a direct metal-metal bond is in accord with the short Mo–Mo distances of 2.601(1) and 2.627(1) Å, respectively, but is also compatible with acute Mo–Y–Mo (Y = S, Cl, P) bridging angles in the range 62.4(1)– $66.5(1)^{\circ.25}$  The metal-metal distances in **1** and **2** are in the range [2.580(2)–2.708(3) Å] found for related quadruply-bridged Mo(III)–Mo(III) compounds containing three-electron-donor halide



Fig. 2 A view of a molecule of 1. Here and elsewhere 20% probability ellipsoids are shown. Selected angles (°): Mo21–S21–Mo22 64.1(1), Mo21–S22–Mo22 64.0(1), Mo21–S23–Mo22 63.5(1), Mo21–Cl21–Mo22 63.2(1).



Fig. 3 A view of a molecule of 2. Selected angles (in °): Mo11–S11– Mo12 64.4(1), Mo11–S12–Mo12 64.5(1), Mo11–C111–Mo12 62.4(1), Mo11–P11–Mo12 66.5(1).

or pseudohalide (X) ligands (X = SR,<sup>20</sup> Cl,<sup>21</sup> Br,<sup>22</sup> I,<sup>23</sup> Cl/PPh<sub>2</sub>,<sup>21b</sup> Br/SR<sup>26</sup> and I/SR<sup>26</sup>). These Mo(III)-Mo(III) distances appear sensitive to the nature of the bridging ligands: shorter distances are found for tetrathiolato- and tetrachloro-bridged derivatives where the mean values are respectively 2.595 and 2.601 Å;20,21 the longest bonds occur in tetraiodo-bridged compounds [2.708(9) Å];<sup>23</sup> intermediate distances are present in tetrabromo- and mixed chlorophosphidoand tris(thiolato)bromo- or iodo-bridged complexes for which the respective means are 2.643(2),<sup>22</sup> 2.638(1)<sup>21b</sup> and 2.622(1) Å.<sup>26</sup> The Mo-S bonds distances (average 2.461 Å) and Mo-S-Mo angles (average 64.1°) in 1 and 2 are in the ranges (2.45-2.46 Å and 63-64°) generally observed for the tetra(µ-thiolato) compounds.<sup>20</sup> Evidently, replacement of one or more thiolates by a pseudohalide, such as chloride or phosphide, has little influence on these parameters. However, the most striking comparison is that between  $[Mo_2Cp_2(\mu-SMe)_2(\mu-Cl)(\mu-PPh_2)]$  (2) and the analogous compound  $[Mo_2Cp_2'(\mu-Cl)_3(\mu-PPh_2)]$  (Cp' = C<sub>5</sub>Me<sub>4</sub>Et).<sup>21b</sup> These compounds have the same trans arrangement of Cl and PPh2 ligands and differ only in the nature of the bridging ligands [X = Cl or SMe] cis to PPh<sub>2</sub> and in the substituents of the cyclopentadienyl groups. It is noteworthy that the Mo-Mo distances [2.627(1) Å in 2 and 2.639(1) Å in the Cp' complex] are nearly identical and that the mean Mo-Cl distance of 2.510(2) Å in the Cp' compound is only slightly [0.026(4) Å] shorter than the corresponding mean for 2,

Table 1 Selected distances (in Å) and angles (in °) in [Mo<sub>2</sub>Cp<sub>2</sub>(µ-SMe)<sub>2</sub>(µ-X)(µ-Y)] complexes<sup>a</sup>

	1		2		4		$10^{b}$	12a <sup>c</sup>	13	
X	Cl		Cl		SMe		N=CHMe	$B_2H_6$	N=CHMe	
Y	SMe		PPh <sub>2</sub>		PPh <sub>2</sub>		PPh <sub>2</sub>		$\mathrm{BH}_4$	
Мо-Мо	2.601(1)		2.627(1)		2.647(1)		2.612(1)	2.717(1)	2.630(1)	
Mo-S <sub>a</sub>	2.452(3)	2.458(3)	2.454(3)	2.475(3)	2.492(1)	2.472(1)	2.471(1)	2.428(1)	2.469(1)	2.469(1)
Mo-S <sub>6</sub>	2.465 (3)	2.476(3)	2.454(3)	2.471(3)	2.462(1)	2.469(1)	2.470(1)	2.435(1)	2.444(1)	2.436(1)
Mo-S	2.449(3)	2.455(3)	~ /		2.469(1)	2.477(1)				
Mo-PPh <sub>2</sub>	( )		2.398(3)	2.394(3)	2.415(1)	2.439(1)	2.414(1)			
Mo-Cl	2.481(3)	2.486(3)	2.548(3)	2.524(3)						
Mo–N	(-)						2.116(3)		2.083(2)	2.094(2)

whereas the mean Mo–P distance dramatically increases from 2.396(2) Å in **2** to 2.458(2) Å in the Cp' compound. Both the slight shortening of the Mo–Cl distances and the lengthening of the Mo–P distances probably result from the combined electronic effects of the cyclopentadienyl groups and the equatorial halide or pseudo-halide ligands.

Lastly, replacement of an SMe ligand in 1 by the sterically more demanding PPh<sub>2</sub> group in 2 has virtually no effect on the Mo–S(*cis* to Cl) distances [respective means 2.462(3) and 2.463(3) Å]. This contrasts with the lengthening of the mean Mo–Cl distance by 0.053(4) on going from 1 to 2 which suggests that the phosphido ligand exerts a stronger *trans*-influence than SMe.

**2.1.2.** Synthesis and characterisation of **3**. A solution of the salt  $[Mo_2Cp_2(\mu-SMe)_2(CH_3CN)_4](BF_4)_2$  (**5**)<sup>17</sup> in dichloromethane was treated with excess Et<sub>4</sub>NCl to afford the neutral bis( $\mu$ -chloro)-bimetallic complex **3** as a green solid in approximately 71% yield.



Compound **3** has been characterised from spectroscopic and analytical data (see Experimental section). It was shown by <sup>1</sup>H NMR spectroscopy that in solution the complex is present in two isomeric forms, **3a** and **3b**, which differ only in the orientations (*syn* and *anti*) of the bridging SMe groups. These isomers were inseparable by conventional chromatographic techniques and were obtained in 1:1 ratio.

**2.1.3.** Synthesis and characterisation of 4 and 7. Molecular structure of 4. Attempts to crystallize the hydride compound 9 (see section 2.2 below) in diethylether at 8 °C under nitrogen gave a mixture of crystals of two complexes 4 and 7 in about a 1:1 ratio according to a spectroscopic analysis (eqn. (2)). A redorange crystal of 4 was picked from the mixture and its structure determined by X-ray analysis.



The molecule of 4 (see Fig. 4 and Table 1) contains two CpMo fragments bridged almost symmetrically by one PPh2 and three SMe ligands, so that each Mo atom has a four-legged piano-stool coordination, as in 1 and 2. The Mo-Mo bond [2.647(1) Å] is a little longer than those in 1 and 2, as are corresponding Mo-S distances. A higher trans-influence for PPh2<sup>-</sup> relative to Cl<sup>-</sup> is consistent with the Mo-S distances trans to these ligands in 1 and 4 (see Table 1). Other structural parameters of 4 are unremarkable and agree with those in comparable structures, in particular 1, 2 and  $[Mo_2Cp'(\mu Cl_{3}(\mu-PPh_{2})](Cp' = \eta^{5}-C_{5}Me_{4}Et)^{21b}$  The spectroscopic (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}NMR) data for 4 (see Experimental section) show that the solution structure is consistent with that observed in the solid state. In particular, the <sup>31</sup>P NMR chemical shift of 4 ( $\delta$  88.6 ppm/H<sub>3</sub>PO<sub>4</sub>) confirms the presence of a metal-metal bond.<sup>27</sup> The <sup>1</sup>H NMR spectrum is typical for a complex with a  $\{Mo_2Cp_2(\mu-SMe)_3\}$  core: it exhibits a single resonance for the two cyclopentadienyl ligands and three peaks for the three SMe bridges.25 Moreover, the presence of two phenyl groups in 4 is shown by characteristic multiplets at 7.3-7.0 ppm.



**Fig. 4** A view of a molecule of **4**. Selected angles (in °): Mo1–S1–Mo2 64.5(1), Mo1–S3–Mo2 65.0(1), Mo1–S2–Mo2 64.7(1), Mo1–P1–Mo2 66.1(1).

The formulation of compound 7 can be tentatively deduced from the spectroscopic data (see Experimental section). The <sup>31</sup>P{<sup>1</sup>H} spectrum of 7 exhibits just one signal in the region expected for bridging phosphido ligands ( $\delta$  88.7 ppm/H<sub>3</sub>PO<sub>4</sub>).<sup>28</sup> The observed shift is typical for a phosphido group bridging two directly-bonded metal atoms.<sup>27</sup> The <sup>1</sup>H NMR spectrum of 7 exhibits two different sets of signals for the phenyl groups: an AB pattern at 8.23 ppm is present in the region usual for aryl groups and eight-proton multiplets are observed between 7.0 and 7.3 ppm. These data suggest strongly that one phenyl group is bonded to a Mo atom through a carbon–carbon double bond so that the environment at each Mo atom is different, thereby explaining the non-equivalence of the cyclopentadienyl ligands (two resonances at 5.57 and 5.42 ppm). The presence of one signal (3 <sup>1</sup>H) in the range expected for a SMe group ( $\delta$  2.82 ppm) is also consistent with the structure proposed for 7.

#### 2.2. Reactions of dimolybdenum complexes with NaBH<sub>4</sub>

**2.2.1.** Reaction of 1 with NaBH<sub>4</sub>.  $[Mo_2Cp_2(\mu-SMe)_3(\mu-Cl)]$  (1) reacted with a large excess of sodium borohydride in tetrahydrofuran at room temperature to afford in high yield (88%) the borohydride compound **8** as a moderately air-sensitive orange solid.



The characterisation of **8** was accomplished by NMR spectroscopy, which showed that it was identical to the tetrahydroboride  $[Mo_2Cp_2(\mu-SMe)_3(\mu-BH_4)]$  we had previously obtained in moderate yields, together with an azavinylidene product, from the reaction of  $[Mo_2Cp_2(\mu-SMe)_3(CH_3CN)_2](BF_4)$  with NaBH<sub>4</sub> in either tetrahydrofuran or acetonitrile.<sup>7</sup> The synthesis of **8** from the metal chloride **1** is significantly more convenient than our previous method, which is based on the lability of CH<sub>3</sub>CN ligands.

**2.2.2.** Reaction of 2 with NaBH<sub>4</sub> and of 9 with CH<sub>3</sub>CN and t-BuNC. Since 2, like 1, is a  $\mu$ -chloro-complex, it also seemed a suitable candidate for reaction with BH<sub>4</sub><sup>-</sup> to give the corresponding  $\mu$ -BH<sub>4</sub> derivative. However, though the reaction of 2 with NaBH<sub>4</sub> proceeded with good selectivity, the targeted tetrahydroboride derivative was not obtained. Instead, reaction of excess NaBH<sub>4</sub> with 2 in tetrahydrofuran at room temperature led first to a violet solution; this rapidly turned green and from it there was extracted in high yield (74%) after evaporation of solvent the hydrido compound [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -SMe)<sub>2</sub>( $\mu$ -H)( $\mu$ -PPh<sub>2</sub>)] (9) as a very air-sensitive green solid.



Compound 9 is also somewhat unstable in organic solvents; it is transformed in a few hours into complexes 4 and 7, as mentioned above. However, in the solid state its decomposition took a few days. Nevertheless, 9 can be confidently characterised by elemental analysis and  $^1H$  and  $^{31}P$  NMR spectroscopy. Thus, its  $^{31}P\{^1H\}$  NMR spectrum shows a single resonance at 154.3 ppm corresponding to the µ-phosphido ligand.28 Moreover, the low-field chemical shift of the phosphorus atom is consistent with the presence of a Mo-Mo bond.<sup>27</sup> Comparing this chemical shift with that of the parent complex 2 ( $\delta$  120.3),<sup>19</sup> a valuable deshielding effect (*ca* 35 ppm) is observed on the phosphido resonance when chloride is replaced by hydride. The <sup>1</sup>H NMR spectrum of 9 displays only one cyclopentadienyl resonance ( $\delta$  5.32), typical for a symmetrical molecule and thus suggesting a bridging position for the hydride ligand. This is confirmed by the high-field chemical shift ( $\delta$  –8.9) of the resonance due to the hydrido ligand.29

Since we were unable to get suitable crystals of **9** for X-ray analysis (see section 2.1.3), we decided to react this hydrido compound with nitrile and isonitrile in order to confirm its proposed structure. It is well known that the interaction of nitriles or isonitriles with bimetallic hydrido compounds can lead to partial hydrogenation of these ligands, with the respective formation of  $\mu$ -alkylidenimido and  $\mu$ -formimidoyl ligands.<sup>30</sup> As expected, reaction of **9** with aceto-

nitrile in tetrahydrofuran under mild conditions gave quantitatively the targeted  $\mu$ -azavinylidene product **10**; similarly, **9** reacted with t-BuNC in tetrahydrofuran at room temperature, affording the  $\mu$ -formimidoyl derivative **11** in good yield (66%).



The structure of compound 10 was determined by X-ray analysis (Fig. 5). The complex is structurally related to the µ-phosphido species 2 and 4 (see Table 1). It consists of two CpMo fragments which are directly connected by a Mo-Mo bond of 2.612(1) Å in addition to being bridged by two thiolates, one phosphide and the nitrogen atom of the azavinylidene ligand. A crystallographic dyad axis passes through the atoms P1, N1 and C2, so that the  $PPh_2$  and N=C(H)Me ligands are disordered. All the bridges are symmetrical, even when not constrained to be so, as is the case for the single SMe ligand. The azavinylidene N1-C2 bond distance [1.234(7) Å] accords with a bond order of two.<sup>31</sup> The closest structural comparison to 10 is provided by the quadruply-bridged Mo(III)–Mo(III) compound  $[Mo_2Cp_2(\mu-SMe)_3(\mu-NC(H)Me)]$  (14),<sup>7</sup> which differs from 10 by having a µ-thiolato instead of a µ-phosphido ligand trans to the azavinylidene group. The mean Mo-N distances in 14 and 10 [2.078(8) and 2.116(3) Å] demonstrate yet again that phosphide exerts a high trans-influence (see sections 2.1.1 and 2.1.3 above). <sup>1</sup>H NMR data for 10 are in accord with the formulation proposed from the X-ray study. In particular, the proton attached to the C2 atom of the azavinylidene ligand appears at low-field ( $\delta$  8.08) as a quartet ( $J_{\text{H-H}} = 4.6 \text{ Hz}$ ) by coupling with the methyl group also attached to C2. Formation of **10** involves insertion of  $N \equiv C - CH_3$  into the Mo-H bonds of 9, followed by a shift of the hydride onto the nitrile carbon atom to form a threeelectron-donor µ-N=C(H)Me azavinylidene ligand. Similar reactions have been reported previously.32 Finally, the molecular structure of 10 supports that proposed from spectroscopic data for its parent complex 9.

Additional confirmation of the structure of 9 comes from formation of the µ-formimidoyl derivative 11 when 9 reacts with isonitrile (eqn. (5)). This requires insertion of isonitrile into an Mo-H bond, behaviour previously demonstrated by similar hydrido derivatives.33 Although we could not get crystals of 11 which were suitable for a diffraction study, the characterisation of 11 can be carried out on the basis of the analytical, IR and NMR data. The IR spectrum shows a v(CN) band (1651 cm<sup>-1</sup>) in the range typical of C=N double bonds, viz., 1470–1690 cm<sup>-1.34</sup> The <sup>1</sup>H NMR spectrum exhibits the sets of resonances expected for the  $\{Mo_2Cp_2(\mu-SMe)_2\}$ core and for the t-Bu and Ph groups. The presence of two resonances at 5.30 and 5.24 ppm assigned to the two cyclopentadienyl ligands accords with the unsymmetrical geometry proposed for 11. Moreover, a doublet ( $J_{P-H} = 4.4 \text{ Hz}$ ) detected at low field ( $\delta$  11.18) is typical of a formimidoyl proton.33 The formimidoyl bridge µ-HC=N(t-Bu) is also characterised in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum by the observation of one resonance ( $\delta$  232.5), at low field in the carbene range. Finally, the <sup>31</sup>P shift (92.6 ppm) is in accordance with the maintenance of the phosphido group in a bridging position<sup>28</sup> on transforming 9 to 11.

**2.2.3.** Reactions of 3 and 4 with NaBH<sub>4</sub>. The reaction of the bis-chloro compound 3,  $[Mo_2Cp_2(\mu-SMe)_2(\mu-Cl)_2]$ , with excess NaBH<sub>4</sub> at room temperature resulted in the formation of a single metallaborane 12, which was isolated in high yield.



**Fig. 5** A view of a molecule of **10**. Atoms P1, N1 and C2 lie on a two-fold axis. Disorder of the phosphido phenyl rings and of the azavinylidene ligand is not show. Selected distances and angles (in Å and °): N1–C2 1.234(7), C2–C3 1.484(9), Mo1–S1–Mo1<sup>i</sup> 63.8(1), Mo1–P1–Mo1<sup>i</sup> 65.5(1), Mo(1)–N(1)–Mo(1)<sup>i</sup> 76.2(1), Mo(1)–N(1)–C(2) 141.9(1). Symmetry code: (i) -x, y, -z+1/2.



The new compound was identified as a molybdenum dimer bridged by an ethane-like  $B_2H_6$  ligand on the basis of its spectroscopic data and solid-state structure. It was shown by NMR spectroscopy that 12 was obtained as a mixture of two isomers which differ only in the orientations *syn* (12a) or *anti* (12b) of the bridging SMe groups, as discussed below. These isomers could not be separated by conventional chromatographic techniques and were obtained in a 4:1 ratio. However, only the *syn*-isomer 12a was formed in a reaction described in the next section, and crystals of 12a so obtained were used for spectroscopic and X-ray studies of 12.

The <sup>11</sup>B NMR spectrum of **12a** contains only one resonance, suggesting a single boron environment, and the chemical shift  $(\delta - 44.1)$  accords with hydrogen-bridged rather than direct Mo–B linkages. The <sup>1</sup>H NMR spectrum shows a single Cp resonance (relative intensity 10) at 4.47 ppm, one SMe signal (intensity 6) at 1.84 ppm, one B-H resonance (intensity 2) at 1.11 ppm, and a single Mo-H-B signal (intensity 4) at -12.40 ppm. All these NMR data are consistent with both a syn orientation of the SMe groups and an ethane-like B<sub>2</sub>H<sub>6</sub><sup>2-</sup> ligand which symmetrically bridges the two {CpMo} cores, as shown in eqn. (6). As formulated, 12 is derived from  $[M_2Cp_2^*(\mu-Cl)_2(\mu-B_2H_6)]$  (M = Mo, W; Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>),<sup>4c,4d</sup> with SMe<sup>-</sup> and Cp respectively replacing Cl<sup>-</sup> and Cp\*. 12 also resembles  $[Ta_2Cp_2^*(\mu-X)_2(\mu-B_2H_6)]$  (X = Cl, Br); however, the tantalum complexes exist in solution as a mixture of isomers: the predominant component in solution and in the solid contains an unsymmetrical B<sub>2</sub>H<sub>6</sub> ligand but at least one of the minor components in solution may have a symmetrical B<sub>2</sub>H<sub>6</sub>.<sup>4a</sup>

This formulation of **12** as a  $\mu$ -hexahydrodiborato complex was confirmed by X-ray analysis of a single crystal of **12a**, obtained from a cooled diethylether solution (see Fig. 6 and Tables 1 and 2). The structure contains a fairly long Mo–Mo bond [2.717(1) Å] which is bridged both by two thiolates in a *syn* orientation and by a symmetrical B<sub>2</sub>H<sub>6</sub> group with a B(1)–B(1)<sup>i</sup> separation [1.700(7) Å] consistent with boron–boron bonding. A crystallographic mirror plane contains the metal atoms and bisects the B–B bond. The Mo…B distances [2.406(3) and 2.402(3) Å] are equal to within experimental error and indicate the presence of four equivalent

Table 2 Selected bond lengths (in Å) and angles (in °) for  $[Mo_2Cp4_2(\mu-SMe)_2(\mu-B_2H_6)]$  (12a)

Mo1-Mo2 Mo1-S1 Mo1-B1 Mo1-H2 B1-H1 B1-H3	2.717(1) 2.428(1) 2.406(3) 1.88(3) 1.17(3) 1.10(3)	Mo2–S1 Mo2–B1 Mo2–H1 B1–H2 B1–B1 <sup>a</sup>	2.435(1) 2.402(3) 1.90(3) 1.17(3) 1.700(7)
Mo1–S1–Mo2 H1–B1–H3 B1 <sup><i>a</i></sup> –B1–H1 B1 <sup><i>a</i></sup> –B1–H3	69.9(1) 103(2) 117(1) 118(2)	H1–B1–H2 H2–B1–H3 B1 <sup><i>a</i></sup> –B1–H2	101(2) 103(2) 114(2)

MoHB bridges. The length of a direct Mo<sup>III</sup>-B bond was found to be 2.21 Å in [Cp\*2Mo2(Cl)2(µ-B3H7)].4c The B-B bond distance in 12a is close to the corresponding distances in the related complexes  $[Ta_2(p-tolNCHNtol-p)_4(\mu-B_2H_6)]$  [1.68(2) Å]<sup>35</sup> and  $[Mo_2Cp_2*(\mu-D_2)^{-1}(\mu-D_2)^{$ Cl)<sub>2</sub>( $\mu$ -B<sub>2</sub>F<sub>6</sub>)] (Cp\* =  $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>) [1.63(3) Å],<sup>4c</sup> but is significantly shorter than that found in  $[Ta_2Cp_2^*(\mu-Br)_2(\mu-B_2H_6)] [1.88(3) Å].^{4a}$ These results indicate that 12a is stabilised by covalent interaction of the  $\{Mo_2Cp_2(\mu-SMe)_2\}^{2+}$  moiety with the  $B_2H_6^{2-}$  anion through four bent Mo-H-B bonds, only two being independent [Mo-H 1.88(3) and 1.90(3); B-H 1.17(3) Å (both)]; the bridging B-H bonds are somewhat longer than the terminal B-H bonds [1.10(3) Å]. **12a** can also be viewed as a metallaborane cluster since it has the expected electron count (40 cve) for a M<sub>2</sub>B<sub>2</sub> tetrahedron, with two thiolates bridging the Mo-Mo bond and four hydrogen atoms connecting the two boron atoms to the two molybdenum atoms. Three related µ-hexahydrodiborato complexes have been structurally characterised:  $[Ta_2(p-tolNCHNtol-p)_4(\mu-B_2H_6)]^{35}$  $[Ta_2Cp_2^*(\mu-Br)_2(\mu-B_2H_6)]^{4a}$  and  $[Mo_2Cp_2^*(\mu-Cl)_2(\mu-B_2H_6)]^{4c}$  The structure of 12 differs significantly from the latter two of these complexes which have direct metal-boron bonds. Moreover, in the MoCp\* complex an unsymmetrical arrangement of the B<sub>2</sub>H<sub>6</sub> group is observed.



Fig. 6 A view of a molecule of 12a.

As pointed out earlier, when **12** is formed by reaction of **3** with NaBH<sub>4</sub> (eqn. (6)), the <sup>1</sup>H NMR spectrum indicates the presence in solution of two inseparable isomers **12a** and **12b**. Since a *syn* orientation of the SMe groups has been demonstrated for **12a**, two geometries are mainly possible for **12b** (see Scheme 1): (i) an *anti*-isomer with the hexahydrodiborato ligand symmetrically-bridged (**A**), and (ii) a *syn*- or *anti*-isomer with the hexahydrodiborato ligand unsymmetrically-bridged (**B**).

The <sup>1</sup>H NMR spectrum of a pure sample of **12a** and that of a mixture of **12a** and **12b** are unchanged over the temperature range 223–293 K. This indicates that interconversion or fluxional processes do not occur in solutions of **12**. Subtracting the <sup>1</sup>H NMR spectrum of **12a** from that of **12** yields the spectral pattern of **12b**. It shows only one resonance in the region expected for Cp ( $\delta$  4.95;



relative intensity 10), suggesting that the Cp groups are equivalent in solution. The remaining pattern reveals two signals at 1.94 and 1.42 ppm (both of intensity 3) assigned to two SMe groups, and also two kinds of MoHB bridges ( $\delta$  –12.02 and –15.45; both; intensity 2). Signals for terminal BH are not detected. Another interesting feature is that the <sup>11</sup>B NMR spectrum of **12b** indicates the presence of a single boron environment, and the chemical shift ( $\delta$  –44.9) is more consistent with hydrogen-bridged rather than direct Mo–B bonding. These observations eliminate structure (**B**) in which the B<sub>2</sub>H<sub>6</sub><sup>2-</sup> ligand bridges the CpMo–MoCp core unsymmetrically. On the other hand, (**A**) in Scheme 1 has two types of MoHB protons, two types of SMe hydrogens, equivalent Cp groups, and equivalent borons: all these features are consistent with the <sup>1</sup>H and <sup>11</sup>B NMR data, since no atom exchanges have been detected on the NMR time scale from 223 to 293 K.

Complex 12 has been obtained here in high yield and as a single product from the reaction of the dichloro compound 3 with NaBH<sub>4</sub> under mild conditions. In contrast, with a single exception,<sup>4e</sup> previously reported syntheses of dimetallaboranes containing an ethane-like B<sub>2</sub>H<sub>6</sub> ligand have required harsh conditions or given low-to-moderate vields.<sup>4a-4d,5a,35,36</sup> Another interesting feature is that 12 is the first stable example of an  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>-metallaborane with a  $B_2H_6$  ligand; in all other known derivatives the cyclopentadienyl ligands has at least one non-hydrogen substituent.<sup>4a,4c-4e,5a</sup> It is well known that early transition metal monocyclopentadienyl halides react readily with nucleophiles or Lewis bases.<sup>37</sup> The high reactivity of BH<sub>4</sub><sup>-</sup> towards the dichlorodimolybdenum(III) compound **3** to give the metallaborane derivative 12 is consistent with this observation. Moreover,  $[Cp*_2M_2(\mu-Cl)_4]$  species (M = Mo<sup>III</sup>, W<sup>III</sup>) react readily with electrophilic reagents such as BH<sub>3</sub>.thf to afford ethanelike metallaborane products in low or moderate yields.<sup>4c,4d</sup> The use here of BH<sub>4</sub><sup>-</sup> instead of BH<sub>3</sub> as a reagent with metal halides avoids cluster expansion reactions. These lower selectivity by giving rise to a greater variety of metallaborane products.

The reaction of metal halides with borohydrides provides effective syntheses of metallaborane and hydride complexes. We were interested to see if a metal pseudohalide would react with  $BH_4^-$  in a similar way and therefore treated  $[Mo_2Cp_2(\mu-SMe)_3(\mu-PPh_2)]$  (4) with NaBH<sub>4</sub>. Regretably, no reaction (eqn. (7)) was observed under either the same or more forcing conditions than those employed for the corresponding reaction of (2) with NaBH<sub>4</sub> (section 2.2.2). Evidently, reactions involving pseudo-halide compounds are less straightforward than those using halide derivatives.

$$\begin{array}{c} Ph & Ph \\ SMe & SMe \\ Me & SMe \\ 4 \end{array} + NaBH_4, thf$$
(7)

**2.2.4.** Reactions of nitrile complexes 5 and 6 with NaBH<sub>4</sub> and of 8 with bases. We have previously shown that the borohydride compound 8 can be effectively synthesised by treating  $[Mo_2Cp_2(\mu-SMe)_3(MeCN_2)]^+$  (6) with NaBH<sub>4</sub> (eqn. (8)); competition between this reaction and formation of the azavinylidene 14 can be controlled by the solvent.<sup>7</sup> Here we describe the reaction of **8** with bases. Abstraction of BH<sub>3</sub> from **8** to give the hydrido compound  $[Mo_2Cp_2(\mu-SMe)_3(\mu-H)]$  proved to be very difficult: the usual BH<sub>3</sub> abstractors failed to transform **8** into the corresponding hydride. Thus, no reaction was observed when solutions of **8** and triethylamine in either tetrahydrofuran or dichloromethane were stirred overnight at room temperature; unchanged **8** was recovered quantitatively (eqn. (9)). Heating a dichloromethane solution of **8** and Et<sub>3</sub>N to 60 °C only achieved the thermal decomposition of **8**; after 24 h the borohydride was completely transformed into unidentified decay-products and no hydrido derivative was detected in the NMR spectrum. Similar reactions of the borohydride complex **8** with Lewis bases, such as acetonitrile and isonitrile (t-BuNC), also failed to transform **8** into the corresponding hydride.



As shown in eqn. (10),  $[Mo_2Cp_2(\mu-SMe)_2(CH_3CN)_4](BF_4)_2$  (5) reacted with 3 equivalents of NaBH<sub>4</sub> at room temperature in acetonitrile to give, after complete consumption of the starting material (about 4 h), the mixed  $\mu$ -borohydride- $\mu$ -azavinylidene derivative **13** as the major product. **13** (yield: 30%) was separated by column chromatography from a minor product, the dimetallaborane species **12a** (yield: 10%), and several other compounds. These were obtained in small amounts and could not be characterised.



Complex 12 had already been obtained (eqn. (6)) by reaction of the bis(chloro) complex 3 with  $BH_4^-$ . Its formation here from the tetrakis(nitrile) derivative is understandable. It has been identified by comparison of its NMR spectra with those of an authentic sample.

The new derivative **13** was identified as a molybdenum dimer bridged by both tetrahydroboride and azavinylidene ligands, on the basis of its spectroscopic data and solid-state structure. **13** combines the structural elements present in complexes **8** ( $\mu$ - $\eta^1$ : $\eta^1$ tetrahydroboride) and **14** ( $\mu$ -azavinylidene). Thus, several spectroscopic features of **13** are common to **8** or **14**. For example, in the <sup>1</sup>H NMR spectrum a quadruplet at  $\delta$  7.59 and a doublet at  $\delta$  1.61

 $(J_{\rm H-H} = 4.7 \text{ Hz})$  indicate that a hydride has been transferred to one of the acetonitrile ligands, and that an azavinylidene N=C(H)Me unit is present in the complex. The presence of the BH<sub>4</sub> fragment in 13 is also revealed by two typical broad BH<sub>b</sub> resonances at  $\delta$  -15.57 (intensity 1) and -15.97 (intensity 1), and one broad BH<sub>t</sub> band at  $\delta$ 1.60 (intensity 2). The results of 2D <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>11</sup>B correlation NMR experiments are in accord with these assignments. A <sup>11</sup>Bdecoupled <sup>1</sup>H-<sup>1</sup>H 2D-experiment showed that the two resonances at  $\delta$  -15.57 and -15.97 are coupled to each other and also to the peak at  $\delta$  1.60, and a <sup>1</sup>H–<sup>11</sup>B inverse-correlation experiment confirmed that the protons are bound to the boron atom. Moreover, the <sup>1</sup>H NMR spectrum is typical for a complex with a  $\{Mo_2Cp_2(\mu-SMe)_2\}$ core; it exhibits two signals at 5.13 and 4.93 ppm for the two cyclopentadienyl ligands indicating a chemically unsymmetrical molecule, and two peaks at 2.07 and 1.02 ppm for the two SMe bridges. Another interesting spectroscopic feature is that the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of 13 shows a broad resonance with a chemical shift  $(\delta - 27.5)$  very close to that  $(\delta - 27.0)^7$  of the borohydride derivative 8. The structure of 13 (Fig. 7 and Tables 1 and 3) was confirmed by X-ray analysis of a single crystal obtained from a diethylether solution at room temperature.



The molecule contains two CpMo fragments which are almost symmetrically bridged by two thiolates, a nitrogen atom of the azavinylidene group and a BH4 unit. There is covalent interaction between the  $\{Mo_2Cp_2(\mu-SMe)_2(\mu-NCHMe)\}^+$  moiety and the BH<sub>4</sub>anion through two 3c-2e Mo-H-B bonds [Mo-H 1.81(3) and 1.83(3), B-H 1.25(3) and 1.24(3) Å]. There are several structural parallels with  $[Mo_2Cp_2(\mu-SMe)_3(\mu-BH_4)]$  (8): thus, the bridging B-H bonds in 13 are longer than the terminal B-H bonds [1.12(4) and 1.17(3) Å]; both 13 and 8 contain distorted tetrahedral  $\mu$ - $\eta^1$ :  $\eta^1$ -BH<sub>4</sub> ligands; the Mo–B distances in 13 [2.726(2) and 2.752(2) Å]are nearly equal and somewhat longer than those in 8 [2.681(6) and 2.711(6) Å] where direct Mo-B bonding was excluded.<sup>7</sup> The bridging Mo-H bonds in 13 are comparable to those in 8 [1.87(5) and 1.84(5) Å] but seem somewhat longer than the corresponding values in  $[Ir_2(C_5Me_5)_2H_3(\mu-BH_4)]$  [1.61(8) Å],<sup>12</sup>  $[Mn_2(CO)_6(\mu-H_2)_6(\mu-H_2)]$ H)( $\mu$ -BH<sub>4</sub>)( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] [1.65(4) and 1.68(4) Å],<sup>14a</sup> and  $[Ru_2(C_5Me_5)_2H_3(\mu-BH_4)]$  [1.69(3) Å].<sup>10c</sup> These may indicate that there is less transfer of hydrogen from boron to the metal atoms in 13 and 8 than there is in the Ir, Mn and Ru complexes, though the large standard errors on the M-H distances render this conclusion very tentative. The Mo-Mo distance in 13 [2.630(1) Å] reveals a bond of unit order (see Table 1).25 It is, however, appreciably longer than the value of 2.564(1) Å found in the  $\mu$ -azavinylidene derivative  $[Mo_2Cp_2(\mu-SMe)_3(\mu-N=CHMe)]$  (14),<sup>7</sup> a difference which seems to reflect the replacement of one thiolate group in 14 by a  $BH_4^-$  ligand. In contrast, the µ-azavinylidene unit has a similar effect to µ-thiolate on the Mo–Mo distance, since the value found in 8 [2.653 Å]<sup>7</sup>

Table 3 Selected bond lengths (in Å) and angles (in °) for  $[Mo_2Cp_2(\mu-SMe)_2(\mu-BH_4)(\mu-N=CHMe)]$  (13)

Mo1–Mo2	2.630(1)		
Mo1-S1	2.469(1)	Mo2-S1	2.469(1)
Mo1-S2	2.444(1)	Mo2-S2	2.436(1)
Mo1–N1	2.083(2)	Mo2-N1	2.094(2)
Mo1····B1	2.726(2)	Mo2&B1	2.752(2)
Mo1–H1×	1.81(3)	Mo2–H3×	1.83(3)
B1–H1×	1.25(3)	B1–H2×	1.12(4)
B1–H3×	1.24(3)	B1–H4×	1.17(3)
N1-C3	1.274(3)	C3–C4	1.502(3)
Mo1-N1-Mo2	78.1(1)		
Mo1-S1-Mo2	64.4(1)	Mo1-S2-Mo2	65.2(1)
C3-N1-Mo1	138.2(2)	C3-N1-Mo2	143.8(2)
H1×–B1–H2×	113(2)	H2×–B1–H3×	109(2)
H1×–B1–H3×	109(2)	H2×–B1–H4×	118(2)
H1×–B1–H4×	103(2)	H3×–B1–H4×	100(2)

is close to that in **13**. The azavinylidene ligand spans the Mo–Mo axis in **13** almost symmetrically [Mo–N 2.083(2) and 2.094(2) Å] and the N(1)–C(13) distance [1.274(3) Å] accords with bond order of 2;<sup>31</sup> similar features occur in **10**,  $[Mo_2Cp_2(\mu-SMe)_2(\mu-PPh_2)(\mu-N=CHMe)]$  (section 2.2.2), where the Mo–N distance (Table 1, Fig. 4) is *ca* 0.03 Å longer than in **13**.

#### 2.2. Discussion and mechanistic considerations

The reaction of a metal chloride with a group 13 hydride, e.g. BH<sub>4</sub><sup>-</sup> and AlH<sub>4</sub><sup>-</sup>, constitutes one of the standard methods for preparing molecular hydrides.38 Recently, Fehlner et al. proposed that this reaction proceeds initially by replacement of Cl- by a pseudohalide.39 For example, if the first step involves substitution of chloride by BH<sub>4</sub><sup>-</sup>, subsequent loss of the Lewis acid BH<sub>3</sub>, either by displacement or hydrolysis, would generate the hydride. The reactions reported here show clearly that this mechanism operates only in some cases and is strongly dependent on the ancillary ligands. Thus, Fehlner's mechanism provides a plausible rationalisation of the reaction of 2,  $[Mo_2Cp_2(\mu-SMe)_2)(\mu-Cl)(\mu-PPh_2)]$ , with NaBH<sub>4</sub> in tetrahydrofuran (Scheme 2): the BH<sub>4</sub><sup>-</sup> ligand formed by the initial replacement of Cl<sup>-</sup> could generate hydride by loss of BH<sub>3</sub> in a second step, initiated by the solvent, which is a Lewis base, and almost certainly helped by the good donor properties of PPh2. This last conclusion is supported by consideration of the reaction of 1,  $[Mo_2Cp_2(\mu-SMe)_3(\mu-Cl)]$ , with BH<sub>4</sub><sup>-</sup>: the product is the stable borohydride compound 8. Under similar conditions 2 gives the hydride complex 9, the presence of PPh<sub>2</sub> rather than SMe trans to the substitution site evidently facilitating displacement of BH<sub>3</sub>. Furthermore, no displacement of BH<sub>3</sub> is observed, even when 8 is exposed to CH<sub>3</sub>CN or bases stronger than tetrahydrofuran, such as Et<sub>3</sub>N (see eqn. (9)). Indeed, the  $\mu$ -hydrido-tris( $\mu$ -thiolato) analogue of 9 has never been detected in reactions of 8 with bases, the starting complex being always fully recovered.

The kinetics of the reaction in which Cl<sup>-</sup> is replaced by a BH<sub>4</sub><sup>-</sup> when **1** or **2** is treated with NaBH<sub>4</sub> depend strongly on the donor strength of the bridging ligand *trans* to Cl: thus complete reaction of **1**, with SMe *trans* to Cl, took 60 h at room temperature, whereas for **2**, where the stronger donor PPh<sub>2</sub> is *trans* to Cl, the reaction was complete in 1 h under the same conditions. This accords with the observed structural *trans*-influence on Mo–Cl bonds: the mean Mo–Cl(*trans* to SMe) bond length [2.483(3) Å] in **1**.

It is well established that a metal polyhalide can be transformed into a polyborohydride which can then eliminate  $H_2$  to yield a metallaborane; this reaction in some circumstances competes advantageously with the alternative elimination of a Lewis acid to form a metal hydride.<sup>15</sup> The  $H_2$  elimination mechanism has been invoked to explain the formation of  $[Cp^*_2Rh_2(\mu-B_2H_6)]$ , *via*  $[Cp^*_2Rh_2(BH_4)_2]$ , from Li(BH<sub>4</sub>) and  $[Cp^*_2Rh_2Cl_4]$ .<sup>4e</sup> By analogy, we suggest that the formation of metallaborane  $[Mo_2Cp_2(\mu-SMe)_2(\mu-B_2H_6)]$  (12) by reaction of the dichloro compound **3** with NaBH<sub>4</sub> proceeds through the bis-( $\mu$ -BH<sub>4</sub>) derivative **C** (Scheme 3) although no direct evidence for the presence of **C** during the reaction has been obtained.



Scheme 2 Proposed pathways for the reaction of compound 2 with sodium borohydride.  $[Mo-Mo]=CpMo(\mu-SMe)_2MoCp. B=thf.$ 



Scheme 3 Proposed route for the formation of 12.  $[Mo-Mo]=CpMo(\mu-SMe)_2MoCp$ .

A more unusual synthetic approach to borohydrides and metallaboranes than the treatment of metal halides or hydrides with either monoboranes or BH<sub>4</sub><sup>-</sup> salts of alkali metals<sup>15</sup> involves the substitution of dative ligands by either BH<sub>4</sub><sup>-</sup> or a polyborane. Only a few examples of this reaction have been reported:7,10c,40 they include (a) formal substitution of carbonyl by BH<sub>4</sub><sup>-</sup> when Fe(CO)<sub>5</sub> reacts with a mixture of LiBHEt<sub>3</sub> and BH<sub>3</sub>.thf, to give [Fe<sub>2</sub>(CO)<sub>6</sub>(B<sub>2</sub>H<sub>6</sub>)]<sup>40</sup> and (b) formation of borohydride compounds by substituting the aqua ligands of the dicationic complex  $[Ru(\eta^6-C_6Me_6)(H_2O)_3]^{2+}$ by BH4<sup>-.10c</sup> More recently, we have shown<sup>7</sup> that BH4<sup>-</sup> reacts with the bis-nitrile complex  $[Mo_2Cp_2(\mu-SMe)_3(\mu-MeCN)_2]^+$  to generate the stable  $[Mo_2Cp_2(\mu-SMe)_3(\mu-BH_4)]$  compound (8). However, metal azavinylidene formation competes with formation of 8 and the tetrahydroboride (8): azavinylidene (14) ratios depend upon the solvent. Acetonitrile favours the formation of the tetrahydroboride (8: 14 = 80: 20), whereas tetrahydrofuran promotes that of the azavinylidene product (8:14 = 20:80).<sup>7</sup> Here we have shown that a mixture of 8 and acetonitrile (excess) at room temperature in tetrahydrofuran does not generate 14 (Scheme 4). Moreover, no trace of the  $\mu$ -hydrido compound [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -SMe)<sub>3</sub>( $\mu$ -H)] has been detected when 8 is stirred in thf for 24 h. This excludes all possibility that 14 results from 8 by displacement of BH<sub>3</sub> to give a  $\mu$ -hydrido species which subsequently adds acetonitrile (Scheme 4).

Instead, we suggest that 14 is formed from 6 by formal addition of H<sup>-</sup> onto the C atom of coordinated acetonitrile. Using thf as solvent favours production of 14.7 Transition metal-assisted reduction of nitriles by BH<sub>4</sub><sup>-</sup> has been the subject of previous



**Scheme 4** Mechanisms of formation of **8** and **14**. [Mo–Mo]=CpMo(μ-SMe)<sub>2</sub>MoCp.

studies.<sup>41,42</sup> Two possible pathways have been proposed: coordination of the nitrile to a metal activates the C=N group toward hydride addition, either from solvated BH<sub>4</sub><sup>-</sup> (Scheme 5a) or from a hydrido intermediate which can undergo a 1,3-hydride shift (Scheme 5b). The latter pathway is a less likely route to **14** since initial formation of the hydrido compound [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -SMe)<sub>3</sub>( $\mu$ -H)] cannot be proved. More plausible is the two step process shown in Scheme 6: initial nucleophilic attack at the CN carbon atom by H<sup>-</sup> leads to intermediate **D**; subsequent transfer of an N lone pair to the electron-deficient Mo(III) centre and loss of nitrile gives **14**. In contrast BH<sub>4</sub><sup>-</sup> and [ReCl<sub>2</sub>(NCMe)(NO)(PMe<sub>3</sub>)<sub>2</sub>] react to give a chelating iminoborane, presumably by BH<sub>3</sub> attack on an N lone pair.<sup>42</sup> These results suggest that the molybdenum(III) center in **D** (Scheme 6) is a stronger Lewis acid than BH<sub>3</sub>.

Scheme 5 Possible pathways of nitrile reduction.

The reaction of  $[Mo_2Cp_2(\mu-SMe)_2(\mu-MeCN)_4]^{2+}$  (5) with NaBH<sub>4</sub> also shows the generation of borohydride and metallaborane complexes through BH<sub>4</sub><sup>-</sup> or polyborane substitution of dative ligands (eqn. (10)). Interestingly, both borohydride (13) and polyborane (12) are probably produced *via* a polyborohydride intermediate C and subsequent H<sub>2</sub> elimination (Scheme 7). Formation of 12 competes with that of 13. Since 13 combines structural elements present in 8 ( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>1</sup>-tetrahydroboride) and 14 ( $\mu$ -azavinylidene) its formation logically occurs by consecutive generation of tetrahydroboride (E) and  $\mu$ -azavinylidene (F) intermediates (Scheme 7). The order in which this happens is unclear and no intermediate has been detected



Scheme 6 Proposed route for the formation of 14. [Mo–Mo]=CpMo( $\mu$ -SMe)<sub>2</sub>MoCp.

in the <sup>1</sup>H NMR spectra. Complexes containing both borohydride and azavinylidene functions resulting from the displacement of two pairs of dative ligands appear to be without precedent.

# 3. Conclusions

Some general features of the reactions of thiolato-dimolybdenum(III) complexes with NaBH<sub>4</sub> have been established. Chloro-bridged compounds give rise to hydroborato or hydride complexes. A bridging ligand with strong donor properties *trans* to the leaving chloro unit favors formation of hydrides. Dichloro-dimolybdenum derivatives similarly give rise to metallaboranes. We have also shown that hydroborato or metallaborane complexes can be formed if dative ligands, instead of chlorides, are initially displaced by borohydride groups. Bis(nitrile) species give rise to either  $\mu$ -hydroborato or  $\mu$ -azavinylidene products, while tetrakis(nitrile) derivatives yield compounds simultaneously containing both of these ligands or, alternatively, metallaboranes.

# 4. Experimental

# 4.1 General procedures and materials

All reactions were performed under an atmosphere of argon or dinitrogen using conventional Schlenk techniques. Solvents were deoxygenated and dried by standard methods. Some of the starting materials  $[Mo_2Cp_2(\mu-SMe)_3(\mu-Cl)]$  (1),<sup>18</sup>  $[Mo_2Cp_2(\mu-SMe)_$ Cl)( $\mu$ -PPh<sub>2</sub>)] (2),<sup>19</sup> [Mo<sub>2</sub>Cp<sub>2</sub>( $\mu$ -SMe)<sub>2</sub>(MeCN)<sub>4</sub>] (BF<sub>4</sub>)<sub>2</sub> (5)<sup>17</sup> and  $[Mo_2Cp_2(\mu$ -SMe)<sub>3</sub>(MeCN)<sub>2</sub>] (BF<sub>4</sub>) (6)<sup>16</sup> were prepared as described previously. All other reagents were purchased commercially. Yields of all products are relative to the starting dimolybdenum complexes. Column chromatography was carried out with either silica gel or florisil purchased from SDS. Chemical analyses were performed either by the Service de Microanalyse I.C.S.N., Gif sur Yvette (France), or by the Centre de Microanalyses du CNRS, Vernaison (France). IR spectra were recorded on a Nicolet-Nexus FT IR spectrometer from KBr pellets. The NMR spectra (1H, 31P, <sup>11</sup>B) were recorded at room temperature in CDCl<sub>3</sub> or toluene-d<sub>8</sub> solutions, unless stated otherwise, with Bruker AC 300 or AMX 400 spectrometers and were referenced to SiMe<sub>4</sub> (<sup>1</sup>H), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), and BF<sub>3</sub>.Et<sub>2</sub>0 (<sup>11</sup>B). <sup>1</sup>H-<sup>1</sup>H 2D and <sup>1</sup>H-<sup>11</sup>B 2D experiments were carried out on a Bruker DRX 500 spectrometer.

# 4.2 Preparation of 3

A solution of complex  $5^{17}$  (700 mg, 0.93 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was stirred in the presence of 4 equiv. of Et<sub>4</sub>NCl (616 mg) for 4 h



Scheme 7 Proposed pathways for the reaction of 5 with NaBH<sub>4</sub>. [Mo-Mo]=CpMo( $\mu$ -SMe)<sub>2</sub>MoCp.

at room temperature. The colour of the solution readily turned from red to green. The solvent was then removed under vacuum and the organometallic products were extracted from the residue with diethylether ( $2 \times 50$  ml). After evaporation of the diethylether, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and chromatographed on silica gel. Elution with a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) removed a green band. Evaporation of the volatiles afforded compound **3** as an analytically pure green powder (320 mg, 71% yield). This complex **3** was obtained as a mixture of two inseparable *anti* (**3a**) and *syn* (**3b**) isomers in. 1:1 ratio. Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>Cl<sub>2</sub>Mo<sub>2</sub>S<sub>2</sub>: C, 29.6; H, 3.3; S, 13.5; Cl, 14.5. Found C, 30.1; H, 3.3; S, 13.6; Cl, 14.1%. <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K), **3a** : 5.66 (s,10H,C<sub>5</sub>H<sub>5</sub>), 1.60 (s,3H,SMe), 1.54 (s,3H,SMe); **3b** : 5.66 (s,10H,C<sub>5</sub>H<sub>5</sub>), 1.58 (sS,6H,SMe).

#### 4.3 Preparation of 4 and 7

On standing overnight in ether at 281 K, complex **9** was converted into compounds **4** and **7**. Spectroscopic (<sup>1</sup>H NMR) analysis of the

crop of crystals showed that the two species were each formed in about 45% yield. 4 and 7 have been characterised by their spectroscopic data and the structure of 4 was confirmed by a X-ray diffraction study. 4: <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 7.3–7.0 (m,10H,Ph), 5.47 (s,10H,C<sub>5</sub>H<sub>5</sub>), 1.57 (s,3H,SMe), 1.49 (s,3H,SMe), 0.82 (s,3H,SMe). <sup>31</sup>P{<sup>1</sup>H} NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 88.7 (s,  $\mu$ -PPh<sub>2</sub>). 7 : <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 88.7 (s,  $\mu$ -PPh<sub>2</sub>). 7 : <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 8.23 (AB,2H,Ph), 7.3–7.0 (m,8H,Ph), 5.57 (s,5H,C<sub>5</sub>H<sub>5</sub>), 5.42 (s,5H,C<sub>5</sub>H<sub>5</sub>), 2.82 (s,3H,SMe). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>; 298 K): 167.4 (s,  $\mu$ -PPh<sub>2</sub>).

#### 4.4 Reaction of 1 with NaBH<sub>4</sub>

A solution of compound 1 (500 mg, 1.0 mmol) in tetrahydrofuran (50 ml) was stirred in the presence of 4 equiv. of  $NaBH_4$  (151 mg) for 60 h at room temperature. The colour of the solution turned from green to orange. The solvent was then removed under vacuum and the organometallic derivative was extracted from the residue with diethylether (2 × 50 ml). Evaporation of the volatiles gave compound **8** as an orange solid (420 mg, 88% yield). **8** was identified by comparison of its NMR data with those of an authentic sample.<sup>7</sup>

### 4.5 Reaction of 2 with NaBH<sub>4</sub>

A solution of complex **2** (150 mg, 0.23 mmol) in tetrahydrofuran (30 ml) was stirred in the presence of 4 equiv. of NaBH<sub>4</sub> (35 mg, 0.92 mmol) for 1 h at room temperature. The colour of the solution readily turned from violet to green. The solvent was then removed under vacuum and the organometallic product was extracted with diethylether (2 × 50 ml). Evaporation of the volatiles afforded complex **9** as an analytically pure, green solid (106 mg, 75% yield). Anal. Calcd. for C<sub>24</sub>H<sub>27</sub>Mo<sub>2</sub>PS<sub>2</sub>: C, 47.8; H, 4.5; P, 5.1. Found C, 47.3; H, 4.2; P, 4.9%. <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 7.3–7.0 (m,10H,Ph), 5.32 (s,10H,C<sub>5</sub>H<sub>5</sub>), 1.78 (s,6H,SMe), -8.9 (d, *J*<sub>P-H</sub> = 14.4 Hz, 1H,µ-H). <sup>31</sup>P {<sup>1</sup>H} NMR  $\delta$ /ppm (CDCl<sub>3</sub>;298 K): 154.3 (s,µ-PPh<sub>2</sub>).

#### 4.6 Reaction of 9 with CH<sub>3</sub>CN and t-BuNC

Compound **9** (50 mg, 0.083 mmol) was dissolved in a mixture of CH<sub>3</sub> CN/thf (1:1) (20 ml). On standing at room temperature overnight, the colour of the solution turned from green to orange. Evaporation of the volatiles gave quantitatively compound **10** as a spectroscopically pure orange powder (53 mg, 0.083 mmol). Orange X-ray quality crystals of **10** were obtained by cooling a concentrated diethylether solution of **10** to -10 °C overnight. <sup>1</sup>H NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 8.08 (q,  $J_{H-H}$  = 4.6 Hz, 1H, *CH*CH<sub>3</sub>), 7.36–7.11 (m,10H,Ph), 5.44 (s,5H,C<sub>5</sub>H<sub>5</sub>), 5.28 (s,5H;C<sub>5</sub>H<sub>5</sub>), 1.91 (d,  $J_{H-H}$  = 4.6 Hz, 3H, CHCH<sub>3</sub>), 1.24 (s,6H,SMe). <sup>31</sup>P {1H} NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K): 76.7 (s,PPh<sub>2</sub>).

To a solution of complex 9 (70 mg, 0.116 mmol) in tetrahydrofuran (10 ml) was added 1 equiv. of t-BuNC (13 µl) at room temperature. The colour of the solution instantaneously turned from green to orange. The solvent was then removed under vacuum and the products were extracted from the residue with diethylether  $(2 \times 20 \text{ ml})$ . Evaporation of the volatiles gave a solid, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) and chromatographed on florisil. Elution with CH<sub>2</sub>Cl<sub>2</sub> removed an orange band. Evaporation of the solvent afforded compound 11 as an orange powder (70 mg, 85% yield). Anal. Calc. for C<sub>29</sub>H<sub>36</sub>Mo<sub>2</sub>NPS<sub>2</sub>, 0.25 CH<sub>2</sub>Cl<sub>2</sub>: C, 49.7; H, 5.2; N, 2.0; P, 4.4. Found C, 49.9; H, 5.4, N, 1.9; P, 3.6%. <sup>1</sup>H NMR δ/ppm  $(CDCl_3; 298 \text{ K}): 11.18 \text{ (d, } J_{P-H} = 4.4 \text{ Hz}, 1\text{H}, CH\text{Nt}-Bu), 7.10 \text{ (d, } J_{P-H} = 4.4 \text{ Hz}, 1000 \text$  $J_{P-H} = 5.9 \text{ Hz}, 10\text{H}, \text{Ph}), 5.30 (s, 5\text{H}, C_5\text{H}_5), 5.24 (s, 5\text{H}, C_5\text{H}_5), 1.48$ (s,6H,SMe), 1.10 (s,9H,t-Bu).  ${}^{13}C{}^{1}H{}NMR \delta/ppm$  (CDCl<sub>3</sub>;298 K): 232.5 (CHNt–Bu), 141.0 (d, J<sub>P-C</sub> = 36 Hz, Cipso(Ph)), 135.5 (d  $J_{P-C} = 7.5$  Hz,Ph), 125.1 (s,Cpara(Ph)), 124.8 (d,  $J_{P-C} = 9$  Hz,Ph), 89.3 (Cp), 88.2 (Cp), 53.5 (C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 17.5 (d,  $J_{P-C} = 18$  Hz,SMe). <sup>31</sup>P{1H} NMR  $\delta$ /ppm (CDCl<sub>3</sub>; 298 K):92.6  $(s, PPh_2)$ . IR (KBr pellet, cm<sup>-1</sup>): v(CN): 1651 m.

#### 4.7 Reactions of 3 and 4 with NaBH<sub>4</sub>

A solution of complex 3 (300 mg, 0.62 mmol) in tetrahydrofuran (50 ml) was stirred in the presence of 3 equiv. of NaBH<sub>4</sub> (70 mg) at

room temperature. The green colour of the solution did not change after 4 h of stirring. The solvent was then removed under vacuum, and the organometallic products were extracted from the residue with diethylether ( $2 \times 30$  ml). After evaporation of the diethylether, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and chromatographed on silica gel. Elution with a mixture of CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:1) removed a green band. Evaporation of volatiles afforded compound 12 as a green powder (210 mg, 77% yield). 12 was obtained as a mixture of two inseparable syn (12a) and anti (12b) isomers (in 4:1 ratio) by chromatography. Dark green X-ray quality crystals of 12a were obtained by cooling a diethylether solution of the complex to -10 °C for two days. Anal. Calcd. for C<sub>12</sub>H<sub>22</sub>B<sub>2</sub>Mo<sub>2</sub>S<sub>2</sub>: C, 32.5; H, 5.0; B, 4.9. Found C, 32.4; H, 4.9; B, 4.9%. <sup>1</sup>H {<sup>11</sup>B}NMR δ/ppm (Tol-d8; 223 K), 12a:4.77 (s,10H,C5H5), 1.84 (s,6H,SMe), 1.11  $(m, 2H, Mo_2(\mu-H)_4B-H_t)$ , -12.40 (d,  ${}^2J_{H-H} = 16.5$  Hz, 4H, Mo-H-B); 12b : 4.95 (s,10H,C<sub>5</sub>H<sub>5</sub>), 1.94 (s,3H,SMe), 1.42 (s,3H,SMe), undetected peaks (2H,B-Ht), -12.02 (d,  ${}^{2}J_{H-H} = 17.1$  Hz, 2H, Mo–*H*–B), -15.45 (d,  ${}^{2}J_{H-H} = 17.1$  Hz, 2H, Mo–*H*–B).  ${}^{11}B$  NMR δ/ppm (CDCl<sub>3</sub>;223 K), **12**:44.3. IR (KBr pellet, cm<sup>-1</sup>), **12**:ν(B-H<sub>t</sub>): 2427 m, 2293 f.

Similarly, a solution of compound 4 (250 mg, 0.38 mmol) in tetrahydrofuran (40 ml) was stirred in the presence of 3 equiv. of NaBH<sub>4</sub> (43 mg) at room temperature. As monitored by <sup>1</sup>H NMR spectroscopy no reaction was observed, all the starting complex 4 was recovered after 24 hours stirring.

#### 4.8 Reactions of 8 with Et<sub>3</sub>N, CH<sub>3</sub>CN and t-BuNC

A solution of compound **8** (200 mg, 0.42 mmol) in either tetrahydrofuran (30 ml) or dichloromethane (30 ml) was stirred in the presence of 1.5 equiv. of  $Et_3N$  at room temperature for 14 h. No reaction was observed and compound **8** was quantitatively recovered.

Similarly, tetrahydrofuran solutions of **8** (0.42 mmol) failed to react with excess of either  $CH_3CN$  or t-BuNC in the same conditions as those employed above for triethylamine.

#### 4.9 Reaction of 5 with NaBH<sub>4</sub>

A solution of complex **5** (400 mg, 0.53 mmol) in acetonitrile (50 ml) was stirred in the presence of 3 equiv. of NaBH<sub>4</sub>. (60 mg, 1.59 mmol) for 4 h at room temperature . The colour of the solution turned from red to maroon. The solvent was then removed under vacuum and the organometallic products were extracted with diethylether ( $2 \times 40$  ml). Evaporation of the volatiles gave a solid, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and chromatographed on silica gel. Elution with a mixture CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) removed a green band. Evaporation of the volatiles afforded **12a** as a green powder (24 mg, 10% yield). Further elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (2.3:1) removed an orange band, which gave, after evaporation of solvent, compound **13** as an orange powder (76 mg, 30% yield). Further work-up did not lead to isolation or identification of additional products.

**13.** Anal. Calcd. for C<sub>14</sub>H<sub>24</sub>BMo<sub>2</sub>NS<sub>2</sub>:C,35.5; H, 5.1; N, 2.9. Found C, 34.3; H, 5.1; N, 2.3%. <sup>1</sup>H{<sup>11</sup>B}NMR δ/ppm (Told8;298 K):7.59 (q, $^{3}J_{H-H} = 4.7$  Hz, H,N=CHCH<sub>3</sub>), 5.13 (s,5H,C<sub>5</sub>H<sub>5</sub>), 4.93 (s,5H,C<sub>5</sub>H<sub>5</sub>), 2.07 (s,3H,SMe), 1.61 (d,  $^{3}J_{H-H} = 4.7$  Hz, 3H, N=CHCH<sub>3</sub>), 1.60 (br,2H,BH<sub>1</sub>), 1.02 (s,3H,SMe), -15.57 (br, 1H, BH<sub>b</sub>), -15.97 (br, 1H, BH<sub>b</sub>). <sup>11</sup>B NMR δ/ppm (CDCl<sub>3</sub>; 298 K):-27.5 (br).

#### 4.10 X-ray crystallographic studies of 1/2, 4, 10, 12a and 13

All crystallographic measurements (Table 4) were made on a Nonius Kappa CCD diffractometer with Mo–K $\alpha$  radiation,  $\lambda = 0.70173$  Å, typically at 100 K. Absorption corrections were applied. Final least-squares refinements used all unique  $F^2$  with weights chosen to give a goodness-of-fit near unity.<sup>43</sup> Data : parameter ratios range from 18 for **12a** to 54 for **13**. H atoms bonded to boron were freely refined for **12a** and **13**. Otherwise H atoms rode on their parent C atoms. The quality of the analysis of **1**/**2** is poor because of the low quality of the available crystals and the final difference map is noisy in the vicinity of the metal atoms. Crystals of **12a** usually shatter on

# Table 4Crystal data for complexes 1/2, 4, 10, 12a and 13

	1/2	4	10	12a	13
Formula	C37H45Cl2M04PS5	$C_{25}H_{29}Mo_2Mo_2PS_3$	$C_{26}H_{30}Mo_2NPS_2$	$C_{12}H_{22}B_2Mo_2S_2$	C14H24BM02NS2
М	1135.6	648.51	643.48	443.92	473.15
Crystal size/mm <sup>3</sup>	$0.40 \times 0.14 \times 0.02$	$0.55\times0.19\times0.17$	$0.31\times0.31\times0.02$	$0.23\times0.14\times0.08$	$0.4 \times 0.3 \times 0.05$
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$P2_1/c$	C2/c	C2/m	Pbca
a/Å	15.3646(4)	9.2543(1)	16.3590(7)	11.0564(3)	9.9585(1)
b/Å	15.4438(4)	15.2706(2)	10.5114(6)	11.3265(4)	15.6735(1)
c/Å	17.1043(5)	17.6299(3)	16.3765(7)	13.7056(4)	22.1327(2)
$\beta/^{\circ}$	98.892(1)	98.215(1)	116.269(2)	109.919(2)	
$\mu/Å^3$	4009.9(2)	2465.87(6)	2525.2(2)	1613.68(9)	3454.57(5)
Z	4	4	4	4	8
$D_{\rm c}/{ m mg}~{ m mm}^{-3}$	1.881	1.747	1.693	1.827	1.819
T/K	100	100	120	293	100
$\mu/\mathrm{mm}^{-1}$	1.684	1.348	1.237	1.792	1.683
Range $\theta/^{\circ}$	2.1-27.5	3.5-30.1	2.4-30.1	3.2-27.5	3.4-45.0
$I(hk\bar{l})$ collected	34406	22647	8885	5835	39136
$R_{\rm int}$	0.079	0.028	0.055	0.037	0.0262
I(hkl) unique/parameters	8856/447	6891/283	3653/181	1922/102	10699/199
$R_1(unique)$	0.109	0.023	0.068	0.029	0.0495
$wR_2(unique)$	0.217	0.051	0.095	0.061	0.0804
$\Delta  ho_{ m max}, \Delta  ho_{ m min}/e { m \AA}^{-3}$	3.0, -1.5	0.45, -0.59	0.80, -0.81	0.53, -0.37	1.41, -1.07

cooling and the unit cell volume is doubled at 100 K; the analysis is therefore based on data measured at room temperature.

CCDC reference numbers 239311–239315.

See http://www.rsc.org/suppdata/dt/b4/b407564a/ for crystallographic data in CIF or other electronic format.

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