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SYNTHESIS, STRUCTURE AND PROPERTIES OF THE FACE-SHARING BIOCTAHEDRAL $\text{Mo}_2\text{X}_6(\text{PMe}_2\text{Ph})_3$ ($\text{X} = \text{Br}, \text{I}$) COMPOUNDS

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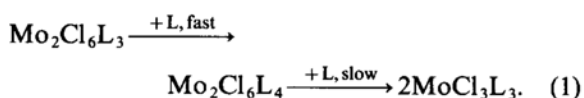
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Abstract—The title compounds were obtained by reacting the corresponding $\text{MoX}_3(\text{THF})_3$ complexes with PMe_2Ph in a 2:3 ratio in refluxing toluene. The compounds assume a face-sharing, bioctahedral structure with three bridging halide ligands, the coordination geometries being completed by one terminal halide and two phosphines for one metal centre, and by two terminal halides and one phosphine for the other one. A comparison with the known chloride analogue shows that the metal–metal separation increases in the order $\text{Cl} < \text{Br} < \text{I}$ and, correspondingly, the paramagnetism of the molecule also increases as shown by solid-state magnetic susceptibility measurements and by the paramagnetic shifts in the solution ^1H NMR spectrum. The NMR spectrum indicates an equilibrium in solution between *anti* and *gauche* isomers. NMR monitoring of the reaction between $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$ and PMe_2Ph shows evidence for the formation of the edge-sharing bioctahedral $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_4$ as a short-lived intermediate, the mononuclear $\text{MoBr}_3(\text{PMe}_2\text{Ph})_3$ being the final product.

We have recently detailed the factors that govern the interconversion between molybdenum(III) complexes of mononuclear, octahedral (MO), MoCl_3L_3 , edge-sharing, bioctahedral (ESBO), $\text{Mo}_2\text{Cl}_6\text{L}_4$, and face-sharing, bioctahedral (FSBO), $\text{Mo}_2\text{Cl}_6\text{L}_3$ structures, where $\text{L} = \text{THF}^1$ or tri-substituted phosphine.² In particular, we found that the THF-substituted compounds have the order of relative stability $\text{MO} < \text{ESBO} < \text{FSBO}$, whereas the phosphine-substituted analogues have an exactly opposite trend. The ESBO compounds are unstable towards disproportionation to a mixture of MO and FSBO systems. However, the ESBO compounds could be prepared by taking advantage of the faster kinetics of the FSBO to ESBO step

during the phosphine addition reaction, eq. (1):²



Since the ESBO chloride complexes show unexpected behaviour in terms of metal–metal bond formation [e.g. the PMe_2Ph complex has a relatively strong metal–metal bond² with a Mo–Mo separation of 2.8036(8) Å, whereas the PEt_3 complex³ has a non-bonded Mo–Mo distance of 3.730(1) Å], we naturally wondered how the metal–metal bonding capability would change on going to the corresponding bromide- and iodide-bridged systems.

We report here the synthesis and structure of the bromide- and iodide-bridged FSBO complexes with

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PMe_2Ph as the neutral ligand and attempt to convert them into the corresponding ESBO systems by the strategy illustrated in eq. (1).

EXPERIMENTAL

All operations were carried out under an atmosphere of dinitrogen using standard glove-box and Schlenk-line techniques. Solvents were dehydrated by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: NMR, Bruker AF200 and WP200; UV-vis, Shimadzu UV-240; magnetic susceptibility, Johnson-Matthey magnetic balance. The elemental analyses were by Midwest Microlab, Indianapolis, Indiana. $\text{MoBr}_3(\text{THF})_3$,⁴ $\text{MoI}_3(\text{THF})_3$ ⁵ and $\text{Mo}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_3$ ² were prepared by literature methods, and PMe_2Ph was purchased from Strem Chemicals and used as received.

Preparation of $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$

To a suspension of $\text{MoBr}_3(\text{THF})_3$ (1.46 g, 2.64 mmol) in 30 cm³ of toluene was added PMe_2Ph (0.56 cm³, 3.9 mmol). The mixture was refluxed for *ca* 7 h, resulting in the formation of a dark, crystalline precipitate and a golden yellow solution. The solid was separated by filtration, washed twice with 5 cm³ of toluene and dried *in vacuo*. Yield: 523 mg (36.4%). The compound is only sparingly soluble in chloroform and hot toluene. It is somewhat more soluble in dichloromethane to yield intensely coloured forest green solutions. Found: C, 26.5; H, 2.9; P, 8.6. Calc. for $\text{C}_{24}\text{H}_{33}\text{Br}_6\text{Mo}_2\text{P}_3$: C, 26.5; H, 3.1; P, 8.6%. μ_{eff} (293 \pm 2 K) = 0.94 μ_{B} per molybdenum atom (diamagnetic correction = 403.4×10^{-6} c.g.s.u. per dinuclear unit). UV-vis [CH_2Cl_2 , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 244 (34,500), 340 (14,200), 418 sh (3000), 612 (2000). A single crystal for the X-ray analysis was obtained by diffusion of n-heptane into a dichloromethane solution.

Preparation of $\text{Mo}_2\text{I}_6(\text{PMe}_2\text{Ph})_3$

This compound was prepared from $\text{MoI}_3(\text{THF})_3$ (1.26 g, 1.82 mmol) and PMe_2Ph (0.39 cm³, 2.7 mmol) in toluene (20 cm³), following the general

procedure described above for the corresponding bromide compound. The mixture was refluxed overnight. Yield: 1.04 g (83%). When the mixture was refluxed only for a short time (*ca* 1/2 h), a comparable amount of dark, crystalline solid was present, but ¹H NMR analysis indicated the presence of impurities. The compound is even less soluble than the bromide analogue, and its dichloromethane solutions are golden yellow. A single crystal for the X-ray analysis was obtained from $\text{CH}_2\text{Cl}_2/\text{n-heptane}$. Found: C, 20.9; H, 2.3. Calc. for $\text{C}_{24}\text{H}_{33}\text{I}_6\text{Mo}_2\text{P}_3$: C, 21.1; H, 2.4%. μ_{eff} (293 \pm 2 K) = 1.68 μ_{B} per molybdenum atom (diamagnetic correction = 498.8×10^{-6} c.g.s.u. per dinuclear unit). UV-vis [CH_2Cl_2 , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 231 (57,000), 318 (20,200), 406 (12,400), 450 sh (10,100), 661 (449).

Magnetism of $\text{Mo}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_3$

μ_{eff} (293 \pm 2 K) = 0.23 μ_{B} per molybdenum atom (diamagnetic correction = 347.6×10^{-6} c.g.s.u. per dinuclear unit).

X-ray crystallography for $\text{Mo}_2\text{X}_6(\text{PMe}_2\text{Ph})_3$ (X = Br, I)

The experimental details are given in Table 1. The cell constants and orientation matrix for data collection for both $\text{Mo}_2\text{X}_6(\text{PMe}_2\text{Ph})_3$ (X = Br, I) compounds were based on 24 carefully centred reflections in the range $20 < 2\theta < 30^\circ$. Acceptable ω scans were obtained. The structures were solved by a combination of direct methods and heavy atom Fourier techniques. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were placed in calculated ($d_{\text{C-H}} = 0.95 \text{ \AA}$) positions. All calculations for the solution and refinement of the structures were performed using the Nicolet SHELXTL PLUS crystallographic package. Selected bond distances and angles for both compounds are listed in Table 2.†

$\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$

A black, needle-shaped crystal of approximate dimensions 0.25 \times 0.20 \times 0.40 mm was mounted on the tip of a glass fibre with epoxy resin. θ - 2θ scans over the 2θ range 3.5–55.0° produced 7857 unique reflections, of which 3274 [$I > 3\sigma(I)$] were used for structure refinement. The data indicated the centrosymmetric $P\bar{1}$ space group, which was confirmed by the successful solution of the structure. Refinement converged at $R = 0.0485$ and $R_w = 0.0528$.

† Full tables of crystal data, bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atom coordinates and F_o/F_c data for the compounds $\text{Mo}_2\text{X}_6(\text{PMe}_2\text{Ph})_3$ (X = Br, I) have been deposited with the Editor as supplementary material. The atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre.

Mo₂X₆(PMe₂Ph)₃ compounds

Table 1. Summary of crystallographic data for Mo₂X₆(PMe₂Ph)₃ (X = Br, I)

Compound	Mo ₂ Br ₆ (PMe ₂ Ph) ₃	Mo ₂ I ₆ (PMe ₂ Ph) ₃
Formula	C ₂₄ H ₃₃ Br ₆ Mo ₂ P ₃	C ₂₄ H ₃₃ I ₆ Mo ₂ P ₃
Formula weight	1085.75	1367.75
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.567(4)	11.749(2)
<i>b</i> (Å)	11.711(4)	12.036(2)
<i>c</i> (Å)	13.495(6)	13.741(3)
α (°)	90.27(3)	89.79(2)
β (°)	108.06(3)	72.13(2)
γ (°)	101.33(3)	81.63(2)
<i>V</i> (Å ³)	1699(1)	1828.0(6)
<i>Z</i>	2	2
<i>d</i> _{calc} (g cm ⁻³)	2.12	2.48
μ (Mo-K α) (cm ⁻¹)	83.44	59.42
Radiation (monochromated in incident beam)	Mo-K α (λ = 0.71073 Å)	Mo-K α (λ = 0.71073 Å)
Temperature (°C)	23	23
Transmission factors: max., min.	0.718, 0.657	0.956, 0.799
<i>R</i> ^a	0.0485	0.0371
<i>R</i> _w ^b	0.0528	0.0413

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|) + 0.002(|F_o|)^2.$$

The maximum shift/ESD in the last cycle of refinement was less than 0.02 and the maximum intensity in the final difference Fourier map was < 0.5 e Å⁻³. An absorption correction based on ψ scans was attempted, without any improvement in the agreement figures.

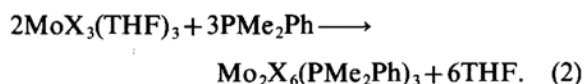
Mo₂I₆(PMe₂Ph)₃

A black, parallelepiped-shaped crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was mounted on the tip of a fibre with epoxy resin. θ -2 θ scans over the 2 θ range 4.5–50.0° produced 6488 unique reflections, of which 4823 [*I* > 3 σ (*I*)] were used for structure refinement. The space group *P* $\bar{1}$ was chosen and the structure solved and refined to *R* = 0.0371 and *R*_w = 0.0413. The overall geometry of the molecule is very similar to the one observed for Mo₂Br₆(PMe₂Ph)₃. The maximum shift/ESD in the last cycle of refinement was less than 0.01. The maximum intensity in the final difference Fourier map was < 0.8 e Å⁻³. An absorption correction based on ψ scans was applied.

RESULTS AND DISCUSSION

The synthesis of the FSBO Mo₂X₆(PMe₂Ph)₃ (X = Br, I) compounds is analogous to that described before² for the corresponding chloride

compound, eq. (2):



Compounds of the Mo₂X₆L₃ class (X = halogen, L = neutral donor) are well-known for X = Cl, for instance with L = PEtPh₂,⁶ PEt₃, PMe₂Ph,^{2,7} SMe₂,⁸ tetrahydrothiophene,⁹ THF,^{1,10} or MeCN.¹¹ Anionic derivatives are known also for the other halides, for instance Mo₂X₉³⁻ (X = Br, I)¹² and Mo₂X₇L₂⁻ (X = I, L = PMe₃).¹³ The two compounds reported in the present paper are the first, uncharged molybdenum(III) systems of the class of FSBO complexes that contain bridging bromide or iodide ligands and, together with the Mo₂Cl₆(PMe₂Ph)₃ compound recently described by us, allow a comparison of the properties for the entire series of Mo₂X₆(PMe₂Ph)₃ compounds with X = Cl, Br and I to be made.

This comparison is analogous to but presents additional advantages with respect to others done before. It is known that, upon replacement of the chloride bridging ligands with the larger bromide and iodide ions, the metal centres are forced farther from each other and the magnetism in molybdenum(III) FSBO complexes increases. This is the case for Cs₃Mo₂X₉ (X = Cl, Br, I)^{12a,c} and [Mo₂X₇(PMe₃)₂]⁻ (X = Cl,¹⁴ I¹³). However, it has recently become apparent that the energy of these systems must have a fairly shallow minimum as a

Table 2. Selected bond distances (Å) and angles (°) for $\text{Mo}_2\text{X}_6(\text{PMe}_2\text{Ph})_3$ (X = Br, I)^a

	X = Br		X = I	
	(a) Bond distances			
Mo—(μ -X)	Mo(1)—Mo(2)	2.749(2)	Mo(1)—Mo(2)	2.909(1)
	Mo(1)—Br(1)	2.610(2)	Mo(1)—I(1)	2.781(1)
	Mo(1)—Br(2)	2.602(2)	Mo(1)—I(3)	2.788(1)
	Mo(1)—Br(3)	2.558(2)	Mo(1)—I(2)	2.739(1)
	Mo(2)—Br(1)	2.599(3)	Mo(2)—I(1)	2.773(1)
	Mo(2)—Br(2)	2.598(2)	Mo(2)—I(3)	2.782(1)
Mo—X	Mo(2)—Br(3)	2.632(2)	Mo(2)—I(2)	2.800(1)
	Mo(1)—Br(5)	2.547(2)	Mo(1)—I(6)	2.772(1)
	Mo(2)—Br(4)	2.521(2)	Mo(2)—I(4)	2.744(1)
Mo—P	Mo(2)—Br(6)	2.527(3)	Mo(2)—I(5)	2.753(1)
	Mo(1)—P(2)	2.548(4)	Mo(1)—P(2)	2.570(2)
	Mo(1)—P(3)	2.574(4)	Mo(1)—P(1)	2.599(3)
	Mo(2)—P(1)	2.537(4)	Mo(1)—P(3)	2.574(3)
	(b) Bond angles			
Mo—(μ -X)—Mo	Mo(1)—Br(1)—Mo(2)	63.7(1)	Mo(1)—I(1)—Mo(2)	63.2(1)
	Mo(1)—Br(2)—Mo(2)	63.8(1)	Mo(1)—I(3)—Mo(2)	63.0(1)
	Mo(1)—Br(3)—Mo(2)	64.0(1)	Mo(1)—I(2)—Mo(2)	63.3(1)
(μ -X)—Mo—(μ -X)	Br(1)—Mo(1)—Br(2)	88.6(1)	I(1)—Mo(1)—I(3)	88.2(1)
	Br(1)—Mo(1)—Br(3)	95.4(1)	I(2)—Mo(1)—I(3)	96.9(1)
	Br(2)—Mo(1)—Br(3)	100.9(1)	I(1)—Mo(1)—I(2)	100.8(1)
	Br(1)—Mo(2)—Br(2)	89.0(1)	I(1)—Mo(2)—I(3)	88.5(1)
	Br(1)—Mo(2)—Br(3)	93.9(1)	I(2)—Mo(2)—I(3)	95.7(1)
	Br(2)—Mo(2)—Br(3)	99.1(1)	I(1)—Mo(2)—I(2)	99.5(1)
(μ -X)—Mo—L _t	Br(1)—Mo(1)—Br(5)	92.2(1)	I(1)—Mo(1)—I(6)	90.9(1)
	Br(1)—Mo(1)—P(2)	172.0(1)	I(1)—Mo(1)—P(1)	170.7(1)
	Br(1)—Mo(1)—P(3)	86.1(1)	I(1)—Mo(1)—P(2)	82.7(1)
	Br(2)—Mo(1)—Br(5)	89.8(1)	I(3)—Mo(1)—I(6)	91.5(1)
	Br(2)—Mo(1)—P(2)	83.4(1)	I(3)—Mo(1)—P(1)	86.2(1)
	Br(2)—Mo(1)—P(3)	170.0(1)	I(3)—Mo(1)—P(2)	170.7(1)
	Br(3)—Mo(1)—Br(5)	167.0(1)	I(2)—Mo(1)—I(6)	165.7(1)
	Br(3)—Mo(1)—P(2)	85.4(1)	I(2)—Mo(1)—P(1)	87.3(1)
	Br(3)—Mo(1)—P(3)	88.1(1)	I(2)—Mo(1)—P(2)	86.6(1)
	Br(1)—Mo(2)—Br(4)	87.7(1)	I(1)—Mo(2)—I(4)	88.9(1)
	Br(1)—Mo(2)—Br(6)	175.4(1)	I(1)—Mo(2)—I(5)	171.8(1)
	Br(1)—Mo(2)—P(1)	90.9(1)	I(1)—Mo(2)—P(3)	87.6(1)
	Br(2)—Mo(2)—Br(4)	172.7(1)	I(3)—Mo(2)—I(4)	175.9(1)
	Br(2)—Mo(2)—Br(6)	88.1(1)	I(3)—Mo(2)—I(5)	87.5(1)
	Br(2)—Mo(2)—P(1)	86.8(1)	I(3)—Mo(2)—P(3)	92.2(1)
	Br(3)—Mo(2)—Br(4)	87.6(1)	I(2)—Mo(2)—I(4)	87.9(1)
	Br(3)—Mo(2)—Br(6)	90.0(1)	I(2)—Mo(2)—I(5)	88.0(1)
	Br(3)—Mo(2)—P(1)	172.4(1)	I(2)—Mo(2)—P(3)	169.5(1)
L _t —Mo—L _t	Br(5)—Mo(1)—P(2)	88.5(1)	I(6)—Mo(1)—P(2)	86.8(1)
	Br(5)—Mo(1)—P(3)	82.0(1)	I(6)—Mo(1)—P(1)	81.8(1)
	P(2)—Mo(1)—P(3)	101.8(1)	P(1)—Mo(1)—P(2)	102.6(1)
	Br(4)—Mo(2)—Br(6)	94.8(1)	I(4)—Mo(2)—I(5)	94.7(1)
	Br(4)—Mo(2)—P(1)	86.7(1)	I(4)—Mo(1)—P(3)	84.5(1)
	Br(6)—Mo(2)—P(1)	85.4(1)	I(5)—Mo(2)—P(3)	85.5(1)

^aIn each line, geometrically equivalent parameters for the two structures are compared.

function of metal–metal distance. For instance, the metal–metal distance in two different crystalline forms of Mo₂Cl₆(PET₃)₃^{2,7} with identical molecular geometry varies by 0.06 Å and the distances in [Mo₂Cl₉]³⁻ and [Mo₂Br₉]³⁻ vary over a 0.25 and 0.54 Å range, respectively, by the mere change of the cation.^{13c} Solid-state magnetic measurements may therefore reflect packing and/or counterion effects. The Mo₂X₆(PMe₂Ph)₃ molecules reported herein are uncharged (no counterion effects) and the presence of the phosphine protons give the opportunity to at least qualitatively assess the change of magnetic properties *in solution* (no packing effects) through an examination of the paramagnetic shifts in the ¹H NMR. In addition, the two molecules reported here are crystallographically isostructural with each other and with the chloride compound described earlier,² thus the packing forces in the solid state should be similar and the correlation between solid-state magnetic susceptibility and solution paramagnetic NMR shifts should be meaningful.

The ¹H NMR spectra of the three complexes show paramagnetic shifts which increase in the order Cl < Br < I, in agreement with the solid-state magnetic data (see Experimental) and with the increase in metal–metal distance on going from the chloride to the iodide derivatives (see crystallographic data below). The methyl proton resonances are shifted upfield, whereas the phenyl proton resonances are shifted downfield with respect to the characteristic regions in diamagnetic complexes. For each molecule, the paramagnetic shifts *increase* upon increasing the temperature. The methyl resonances move from the δ +1 to 0 range at 212 K to the δ -0.8 to -1.5 range at 291 K for the bromide complex, and from the δ 0.5 to -2.5 range at 226 K to the δ -1.2 to -3.4 range at 281 K for the iodide complex. This is consistent with the known electronic structure of these molecules which consists of a diamagnetic ground state (σ²π⁴ metal–metal bond) and low-lying paramagnetic excited states generated by promotion of electrons into the metal–metal π* orbitals.^{12c,15} A reviewer pointed out that the nature of the halogen may in itself cause a change of the phosphine proton chemical shift and thus a strict correlation of paramagnetic shift with magnetic properties is not possible. We note, however, that the position of the PMe₃ proton resonance in the homologous series of *diamagnetic* Mo₂X₄(PMe₃)₄ complexes shifts only by 0.29 δ on going from X = Cl to X = I.¹⁶ This shift is very small in comparison with the corresponding shifts observed for the methyl proton resonances in Mo₂X₆(PMe₂Ph)₃.

The pattern of ¹H NMR resonances in the methyl

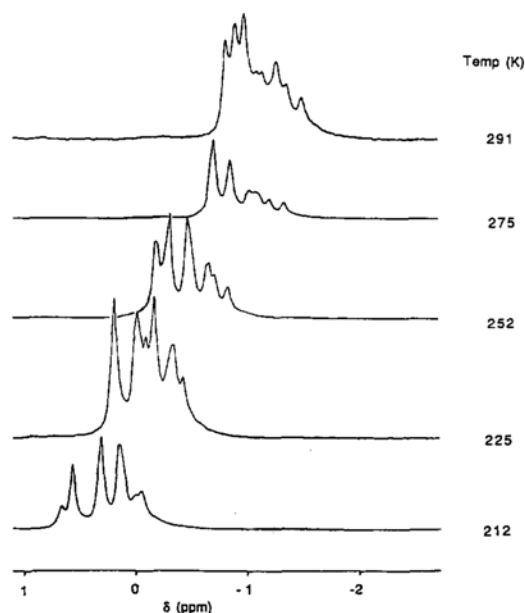


Fig. 1. Representative ¹H NMR spectra of the Mo₂Br₆(PMe₂Ph)₃ compound in the methyl region at various temperatures. Solvent = CD₂Cl₂.

region also shows, as already evidenced for the chloride complex,² the presence of an equilibrium mixture of *anti* and *gauche* isomers (see Fig. 1). Overlap of some of the peaks occurs in most conditions but examination of the pattern at all temperatures clearly reveals, both for the bromide and for the iodide complex, three absorptions of relative intensity 1 : 1 : 1 (*anti* isomer) and six absorptions of relative intensity 1 : 1 : 1 : 1 : 1 : 1 (*gauche* isomer). The crystalline material that we have obtained for the iodide system after a short (*ca* 1/2 h) reflux time shows more resonances in the methyl region of the ¹H NMR spectrum. These extra resonances have a temperature dependence similar to those of *anti* and *gauche* Mo₂I₆(PMe₂Ph) and are due to an, as yet, unidentified impurity which disappears when the material is refluxed for a longer period.

The optical properties of the three compounds (X = Cl, Br, I) are also consistent with the known electronic structure. Upon increasing the metal–metal distance and thereby reducing the metal–metal overlap, the HOMO–LUMO gap decreases and the absorption bands experience a red shift.

The Mo₂X₆(PMe₂Ph)₃ (X = Br, I) compounds, like their chloride analogue, crystallize in the triclinic space group *P* $\bar{1}$ with similar cell dimensions. The three molecules show the same face-sharing, bioctahedral geometry with the phosphine ligand system in a relative *anti* configuration. Figure 2 shows a view of the bromide molecule. The octahedral geometry around each metal is slightly distorted, at least in part because of the compression

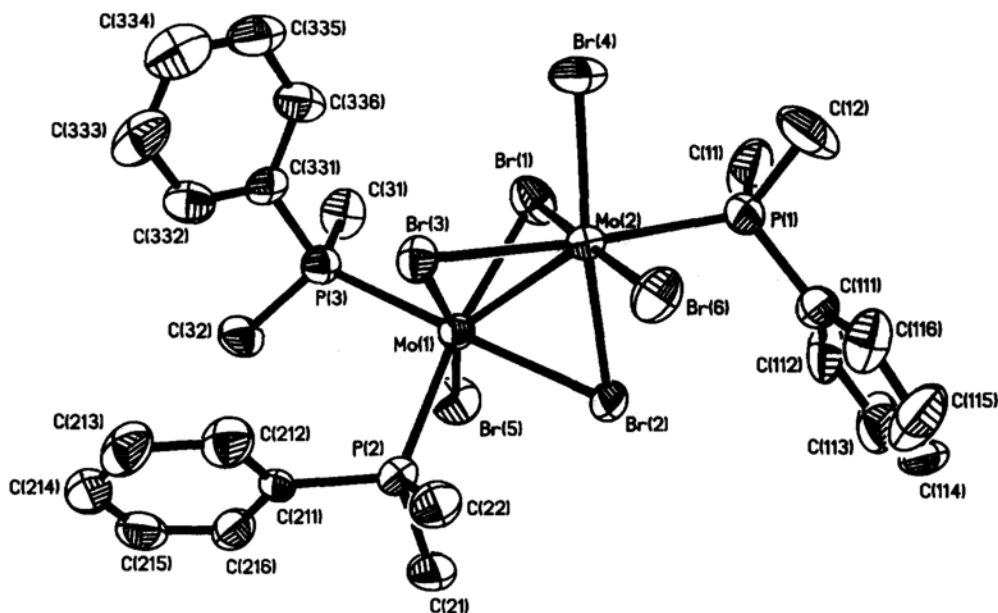


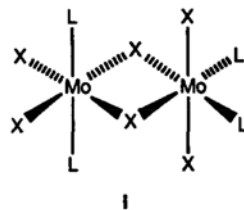
Fig. 2. ORTEP view of the $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$ molecule. The iodide analogue has an identical structure.

along the metal–metal axis which is caused by the metal–metal bond. For instance, the average angle between two $\text{Mo}-(\mu\text{-X})$ vectors is higher than 90° , whereas all the $\text{Mo}-(\mu\text{-X})-\text{Mo}$ angles are less than the value of 70.53° which is the calculated value for an undistorted FSBO structure.¹⁷ Another indication of $\text{Mo}-\text{Mo}$ bonding is the metal–metal separation, $2.749(2)$ Å for the bromide complex and $2.909(1)$ Å for the iodide complex, which compare with $2.6582(5)$ Å for the corresponding chloride complex.² The only other structurally characterized FSBO molybdenum(III) complexes with bridging bromides or iodides are $\text{Cs}_3\text{Mo}_2\text{Br}_9$ [$\text{Mo}-\text{Mo} = 2.816(9)$ Å],¹² and $[\text{Cat}]^+[\text{Mo}_2\text{I}_7(\text{PMe}_3)_2]^-$ [$\text{Mo}-\text{Mo} = 3.021(4)$ Å, Cat = PMe_3 ; $3.022(1)$ Å, Cat = AsPh_4].¹³

As one might have anticipated, the $\text{Mo}-\text{X}$ distances are, on average, shorter for terminal halides, and those involving bridging halide ligands reflect the higher *trans* influence of PMe_2Ph vs X. The $\text{Mo}-\text{P}$ distances for both compounds are in the range usually found for octahedrally coordinated molybdenum(III) compounds.^{4,13,18}

We now come to the original interest of our studies, that is the reaction of the FSBO bromide and iodide complexes with extra phosphine in an attempt to generate the corresponding ESBO complexes and whether the latter would or would not show a direct metal–metal interaction (see Introduction). The reaction of $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$ with three equivalents of PMe_2Ph was followed by ^1H

NMR at room temperature. Figure 3 shows the salient features of this experiment. Two peaks at $\delta -26.5$ and -39 in an approximate 1:1 ratio develop initially. These are assigned to the methyl groups of an ESBO $\text{Mo}_2\text{Br}_6(\text{PMe}_2\text{Ph})_4$ molecule containing two phosphine ligands in the axial positions on one molybdenum centre, and the other two in the equatorial positions on the other metal, as shown in structure I. This is the geometry that has been found both in the solid state and in solution for the corresponding chloride system.^{2,3}



The intensity of these resonances, however, never exceeds *ca* 1% of the total amount of the molybdenum complex and two new resonances at $\delta -26.5$ and -40 , in a 1:2 ratio, soon start to grow. These correspond to the mononuclear *mer*- $\text{MoBr}_3(\text{PMe}_2\text{Ph})_3$.² Two major conclusions can be drawn from this experiment. The reaction follows the same path as that of the corresponding chloride system,² see eq. (2), but the relative rates of the two steps are reversed, the first step (FSBO to ESBO) being slower than the second one (ESBO

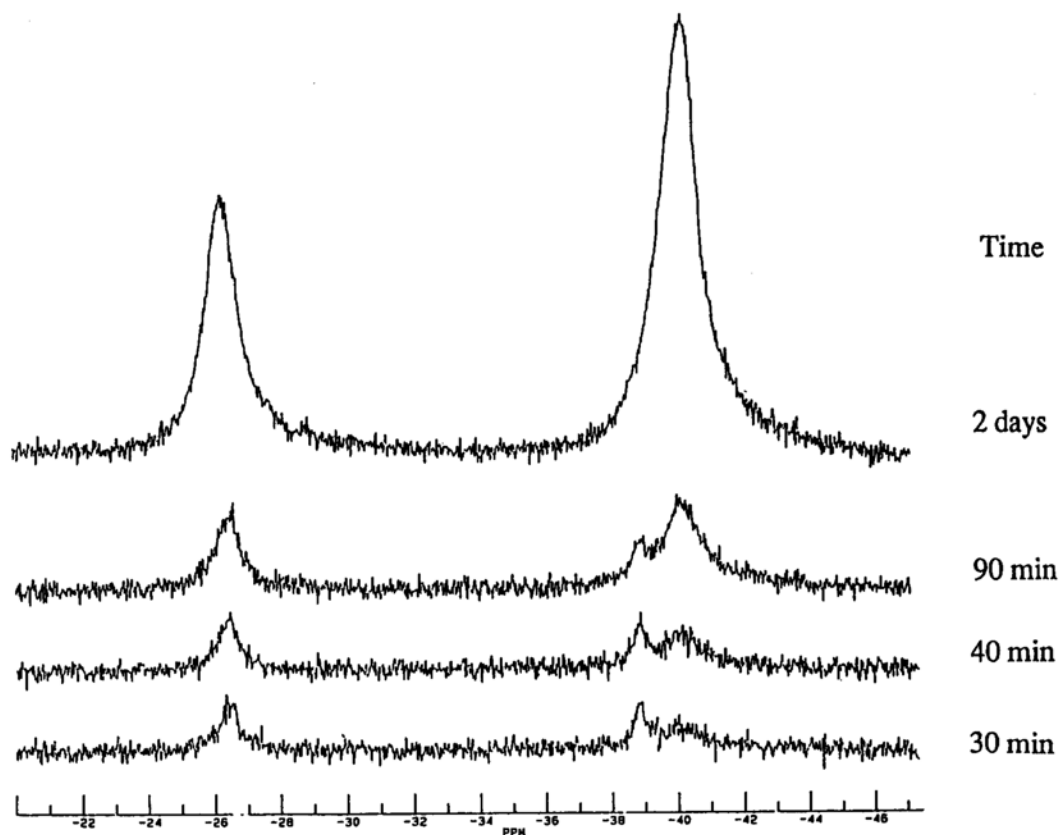
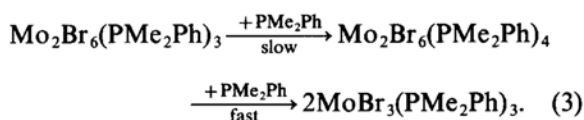


Fig. 3. ¹H NMR spectra in the phosphine methyl region during the reaction of Mo₂Br₆(PMe₂Ph)₃ with excess PMe₂Ph.

to MO), see eq. (3):



The second conclusion is that the ESBO Mo₂Br₆(PMe₂Ph)₄ molecule does not have a direct Mo—Mo bond and its magnetic properties (as indicated by the paramagnetic shifts in the ¹H NMR spectrum) are analogous to those of the mononuclear MoBr₃(PMe₂Ph)₃ molecule, i.e. there are three unpaired electrons per metal centre. Therefore, changing the nature of the bridging halide ligands from chloride to bromide is sufficient to change the metal–metal interaction from a situation of strong bonding² (σ²π²δ*²) to no bonding at all. This system differs from the corresponding Mo₂X₆(dppe)₂ system, in which a Mo—Mo bond exists for both X = Cl¹⁹ and X = Br.²⁰ The faster second step of eq. (3), as compared with the second step of eq. (1) (L = PMe₂Ph), may be attributed to the increased kinetic barrier in the latter case due to the change of spin state on going from the ESBO to the MO system.

Based on the relative intensities and positions of the peaks in Fig. 3, and comparing the geometrical features of the ESBO Mo₂Br₆(PMe₂Ph)₄ with the mononuclear *mer*-MoBr₃(PMe₂Ph)₃, it is possible to assign, for the methyl protons of the ESBO molecule, the upfield resonance (δ −39) to the ligands that are *trans* to each other and the downfield resonance (δ −26.5) to the ligands that are *trans* to bridging bromides.

Conclusions

The investigations reported here have shown that, although FSBO systems of the type Mo₂X₆(PMe₂Ph)₃ maintain a direct metal–metal bonding on going from X = Cl or X = I, this interaction is lost in the corresponding ESBO Mo₂X₆(PMe₂Ph)₄ systems on going from X = Cl to Br. Furthermore, the FSBO to ESBO transformation becomes slower relative to the ESBO to MO transformation on going from X = Cl to X = Br. As a result, although the thermodynamically unstable (toward ligand disproportionation) ESBO chloride system could be kinetically accumulated in solution and isolated by utilizing the strategy illustrated

in eq. (1),² the corresponding bromide system can only be generated as a short-lived intermediate. As a corollary, ESBO compounds with monodentate phosphine ligands and bridging *iodide* ligands are not likely to be stable species either.

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