

PREPARATION OF DIMOLYBDENUM CATIONS WITH TRIPLY BRIDGED CORES $[Mo_2(\mu-F)_2(\mu-X)(CO)_4(PPh_3)_4]^+$ (X = F, Cl, Br, OH), $[Mo_2(\mu-Br)_n(\mu-OH)_{3-n}(CO)_4(PPh_3)_4]^+$ (n = 1, 2) AND DITUNGSTEN CATIONS $[W(\mu-F)_n(\mu-Br)_{3-n}(CO)_4(PPh_3)_4]^+$ CRYSTAL STRUCTURE OF $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]F$

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Abstract—The reaction of $Mo_2Br_2(CO)_2(PPh_3)_2$ with aqueous $NaBF_4$ in CH_2Cl_2 leads to $[Mo_2(\mu-X)(\mu-F)_2(CO)_4(PPh_3)_4]^+$ (X = Br, F, Cl, OH). The initially formed bromide can be isolated under appropriate conditions and crystallographically characterized as the unusual fluoride salt $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]F$ (x hexane). The molecular unit is a triply bridged dimer with very long Mo—Br distances [2.694(3) and 2.693(3) Å], which are accounted for by the trans-influence of two nearly co-linear CO ligands (Br—Mo—CO *ca* 165°). The bromide is fluxional, Mo—Br cleavage processes are evident from the variable temperature ³¹P NMR spectra. Under the reaction conditions the bromide is expelled leading to the formation of $[Mo_2(\mu-X)(\mu-F)_2(CO)_4(PPh_3)_4]^+$ (X = F, Cl, OH). Under identical conditions WBr₂(CO)₂(PPh₃)₂ reacts to form $[W(\mu-F)_n(\mu-Br)_{3-n}(CO)_4(PPh_3)_4]^+$ (n = 1, 2) while reaction of $Mo_2Br_2(CO)_2(PPh_3)_2$ with aqueous KPF₆ leads to the hydroxo bridged dimers $[Mo_2(\mu-Br)_n(\mu-OH)_{3-n}(CO)_4(PPh_3)_4]^+$ (n = 1, 2).

In the wake of the burgeoning interest in fluorinecontaining organometallic systems,¹ there have been reports of crystallographically confirmed trifluoro-bridged dimolybdenum² and ditungsten³ carbonyl and related complexes. These papers, which appeared during the course of our own studies, prompt us to report here some mechanistic aspects of how these compounds are formed and the chemistry of some related hydroxo complexes.

An old observation that $MoBr_2(CO)_2(PEt_3)_2$ reacts with NaBPh₄ in MeOH (presumably containing moisture) to give yellow solutions from which unidentified tetraphenylborate salts precipitate⁴ led us to investigate the reaction of $MoBr_2(CO)_2(PPh_3)_2$ 1 with various salts (NaBF₄, NaF, KPF₆, NaClO₄, and NaBPh₄) in the presence of water.

We find that the reaction of $MoBr_2(CO)_2(PPh_3)_2$ 1 with aqueous $NaBF_4$ in two-phase $CH_2Cl_2/water$ mixtures results in the formation of a number of triply-bridged Mo₂ products, including [Mo₂(μ - F)₃(CO)₄(PPh₃)₄]⁺, recently reported by Beck and co-workers.² However, the conditions we employ allow the formation of a number of new complexes the most interesting of these being crystallographically characterized $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4$ (PPh₃)₄]⁺ **2**. We also find that the reaction of **1**, and its tungsten analogue, with other aqueous salts leads to structurally diverse products and these together with the formation, fluxional behaviour, and reactions of **2** are discussed below.

RESULTS AND DISCUSSION

Reaction of MoBr₂(CO)₂(PPh₃)₂1 with NaBF₄

Reaction of blue MoBr₂(CO)₂(PPh₃)₂ 1 with excess NaBF₄ in H₂O/CH₂Cl₂ at ambient temperature rapidly produces a green colour in the organic phase, and this changes to orange after about 15 min. Investigation of the reaction mixture by ³¹P NMR spectroscopy reveals the presence of 1, PPh₃, POPh₃, [HPOPh₃]BF₄ and three other species: [Mo₂(μ -Br)(μ -F)₂(CO)₄(PPh₃)₄]⁺ 2 (δ_P 64.0 t, $J_{PF} = 43.3$ Hz, major species), and two lesser

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species, $[Mo_2(\mu-F)_3(CO)_4(PPh_3)_4]^+$ 3 (δ_P 66.6 q, $J_{\rm PF} = 33.4$ Hz) and $[Mo_2(\mu-F)_2(\mu-OH)(CO)_4]$ $(PPh_3)_4]^+$ 4 (δ_P 66.7 t, $J_{PF} = 39.5$ Hz) (Scheme 1). The isolated material despite being highly crystalline can be shown by ³¹P NMR spectroscopy to be a mixture of 2, 3, 4 and the chloride 5 $[Mo_2(\mu-Cl)(\mu-F)_2(CO)_4(PPh_3)_4]^+ 2(\delta_P 65.6 t,$ $J_{\rm PF} = 41.3$ Hz). The latter only being present in reaction mixtures that have been stirred for long periods (>1 h). Typical ³¹P NMR spectra of the isolated mixtures are shown in Fig. 1. Given the similar nature of the cations 2-5 their co-crystallization while unwelcome is not altogether unexpected. Multinuclear NMR studies (¹⁹F and ¹¹B) and IR spectroscopy indicate that the major counter ion present is BF₄⁻ ($\delta_{\rm F}$ -155.2 relative to CCl₃F; $\delta_{\rm B}$ 0.63 relative to external NaBF₄ in D₂O), but traces of fluoride are also detectable by ¹⁹F NMR $(\delta_{\rm F}$ –144.0) and electrochemically with fluoride selective electrodes. Compound 3 is usually the predominant (sometimes exclusive) species in the material isolated after stirring for a long time. It is possible to prepare mixtures enriched with 2 by stirring for shorter periods followed by prompt workup, however, labile 2 shows a marked tendency to expel bromide in solution leading to secondary products. This behaviour makes the isolation of analytically pure samples of 2 impossible. Identical mixtures of compounds 2–5 are obtained from the reaction of 1 with NaF directly but in this case only very low yields are isolable. Samples enriched in 2 can be prepared by the reaction of $MoBr_2(CO)_2(PPh_3)_2 1$ with two equivalents of NaF in the presence of excess KPF₆ in saturated NaBr solution/CH₂Cl₂ although of course under these conditions the counter anion is $[PF_6]^-$.

Attempts to further characterise 2–5 by ⁹⁵Mo NMR spectroscopy were unsuccessful due to multiple heteronuclear coupling problems. Evidence of some very broad signals, almost lost in the baseline, were detected in the region δ_{Mo} – 3000 to – 4000 but the experiments were otherwise uninformative.

The purple-coloured WBr₂(CO)₂(PPh₃)₂ **6** reacts with excess NaBF₄ in H₂O/CH₂Cl₂ to give two products : W₂(μ -F)₂(μ -Br)(CO)₄(PPh₃)₄7 and W₂(μ -F)(μ -Br)₂(CO)₄(PPh₃)₂**8** (Scheme 1). The greater strength of the W—Br bond versus the Mo—Br bond means that the Br atoms are less labile and not as prone to replacement by fluoride or other species.

Crystal structure of $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4P-Ph_3)_4]F.(x hexane) [2F.(x hexane)]$

Despite the propensity for the cations 2-5 to cocrystallize repeated attempts at the crystallization of samples enriched with $2BF_4$ finally allowed the



Fig. 1. Phosphorus-31 NMR spectra of the products from the reaction of 1 with NaBF₄. (a) After total conversion of 1. (b) Sample A after prolonged stirring in CH₂Cl₂-water. Compound 2 (+), $3(\triangle), 4(\Box)$ and $5(\bigcirc)$.





isolation of a small sample of 2 but as its fluoride salt rather than $2BF_4$. The selective crystallization of 2F.(x hexane) (x = variable amounts) as opposed to the $2BF_4$ which comprises most of the bulk material is a genuine, albeit highly unusual, phenomenon. Several crystals with identical cell parameters are isolated and the presence of small amounts of fluoride in the outer coordination sphere of the bulk material may be detected with fluoride selective electrodes. The total fluoride analysis of the mixture (typically *ca* 2.9%) is consistent with a mixture of $2BF_4$, with some $3BF_4$, and $4BF_4$; calculated fluorine analyses (F⁻ only) 2.4, 3.8 and 2.5%, respectively.

An ORTEP drawing of the dimolybdenum core of 2F.x hexane is shown in Fig. 2 while selected bond lengths and angles are given in Table 1. The crystal structure and refinement data are summarized in Table 2.

Both the fluoride counter anion and the hexane solvates show extensive positional disorder and are therefore not discussed; no such problems are present in the $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]^+$ core. The most striking features of the structure are the highly acute Mo(1)—Br—Mo(2) angle of 76.84(9)° and associated long Mo-Br distances 2.694(3) and 2.693(3) Å. Of the ten crystal structures in the Cambridge Crystallographic Data Base containing a $Mo_2(\mu$ -Br) fragment only two have longer Mo-Br distances.⁵ The origin of this phenomenon in 2 is the *trans* influence⁶ of the two nearly co-linear carbonyl ligands [Br-Mo-CO = 165.3(4), $165.6(3)^{\circ}$]. As expected for the complex the two d^4 molybdenum centres are well separated and show no indications of a bonding interaction, Mo1-Mo2 = 3.348 Å. The Mo—CO_{ave} (1.951 Å) and Mo— P_{ave} (2.507 Å) distances are in the range expected for these compounds and in particular are similar to those



Fig. 2. An ORTEP view of the tri-bridged core of $Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]F.(x hexane)$ [2F.x hexane (x \approx 1)]. The fluoride counter anion, co-crystallised hexane, and all except the ipso carbons of the phenyl rings have been omitted for clarity.

Table 1. Selecte	d bond length and	d angle data	for crystal	structure of	f [Mo ₂ (μ-Br)(μ-
	F)2(CO)4(PPh3)4]J	F.(x hexane)	[2F.x hexa	ane (x \approx 1)]	

(a) Dis	stances (Å	.)						
Mol	Br	2.694(3)	Mo2	B	r	2.693(3)	
Mol	F1	2.15(1)	Mo2	F	1	2.13(1)	
Mol	F2	2.156(8)	Mo2	F	2	2.148(9)	
Mol	P 1	2.500(5)	Mo2	Р	3	2.512(5)	
Mol	P2	2.509(5)	Mo2	Р	4	2.501	5)	
Mol	C1	1.97(2)	Mo2	С	3	1.92(2)	
Mol	C2	1.97(2)	Mo2	С	4	1.94(2)	
(b) An	gles (°)					,	,	
Mol	Br	Mo2	76.84(9)	Br	Mo1	C2	165.6(4)
Mo1	F1	Mo2	103.0(4)	Br	Mo2	C3	165.3(4)
Mol	F2	Mo2	102.1(4)	C 1	Mo1	C2	105.3(6)
Br	Mo1	F1	72.6(3)	Br	Mo2	F1	73.0(3)
F1	Mol	F2	69.8(4)	F1	Mol	F2	70.5(4)
Br	Mo1	F2	73.3(3)	Br	Mo2	F2	73.4(3)

Table 2. Crystal structure and refinement data for $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]F.(x hexane)$ [2F.x hexane $(x \approx 1)]$

a	18.221(5)Å	Crystal dimensions	0.3 mm ^a
b	18.761(4)Å	Abs. Corrections (max/ave/min)	1.21/0.97/0.73
с	15.402(7)Å	Scan mode	$\theta/2\theta$
α	95.1(4)°	Scan width	$0.7 + 0.4 \tan\theta$
β	112.4(4)°	Unique data measured	12274
γ	118.4(4)°	Unique data used	$6129 (> 3\sigma)$
V	4047(9) Å ³	No. of variables	917
Space group	Triclinic P1 (No. 2)	$R\left(\Sigma \ F_{o} - F_{c} / \Sigma F_{o} \right)$	8.0%
Z	2	$R_{\rm w} \left(\left[(\Sigma_{\rm w} (F_{\rm o} - F_{\rm c})^2 / \Sigma_{\rm w} F o^2) \right]^{0.5} \right)$	10.1%
D _{calc}	1.301 g cm^{-3}	Shift/error	0.49
μ	9.19 cm^{-1}	$\Delta ho_{ m max}$ eÅ $^{-3}$	1.10

^aIrregular fragment.

observed in the structure of $[Mo_2(\mu-F)_3]$ (CO)₄(PPh₃)₄]⁺,² and the cation of the complex $[Mo_2(\mu-Cl)_3(CO)_4{P(OMe)_3}_3][Mo(=O)Cl_4{P(=O)}{OMe}_2]$,⁷ $[Mo-CO_{ave} 1.92 \text{ Å}; Mo-P_{ave} 2.42 \text{ Å}]$.

Formation and fluxionality of $[Mo_2(\mu-F)_2(\mu-X)$ (CO)₄PPh₃)₄]⁺ (X = Br, F, OH, Cl) 2–5

The formation of 2 is best accounted for by abstraction of F^- from BF_4^- by 1 or more probably by $[MoBr(H_2O)(CO)_2(PPh_3)_2]^+$ to form transient $[MoBrF(H_2O)(CO)_2(PPh_3)_2]^+$; examples of such abstractions are well documented.⁸ While such a mechanism is speculative there is some indirect evidence to suggest the presence of aquo complexes. If reactions of 1 with NaBF₄ (aq) are stopped just after the reaction turns yellow and worked up in

the normal way the first material that crystallizes from the yellow mother liquors is recovered blue 1 rather than any dimer suggesting an equilibrium between 1 and $MoBr_2(H_2O)(CO)_2(PPh_3)_2$. Formation of $[MoBrF(H_2O)(CO)_2(PPh_3)_2]^+$ followed by dimerisation fashions 2. The bromide bridge in 2 is labilized by the double *trans* effect⁶ of the two carbonyl ligands, and it can easily be replaced by F⁻, H₂O or Cl⁻ to form 3, 4 and 5, respectively. The source of Cl⁻ may be traced to adventitious HCl present in the CH₂Cl₂ used. Deliberate addition of HCl to solutions of 2 or 3 causes some conversion to 5.

Further evidence for a large *trans* effect in 2 comes from variable temperature ³¹P NMR studies. On cooling a sample of 2 and 3 from room temperature the signals due to 2 first broaden then split, while those of 3 are not effected (Fig. 3). At -100° C



Fig. 3. Variable temperature ³¹P NMR spectra of 2(+) and $3(\triangle)$.



Scheme 2.

the $\delta_{\rm P}$ 64.0 triplet of 2 becomes two broad signals at $\delta_{\rm P}$ 67.6 and 60.6 in a 1 : 1 ratio which are assigned to 2a, which has two equivalent sets of phosphine ligands (Scheme 2). The system is close to coalescence at -80° C, using standard formulae⁹ an activation barrier of *ca* 34 kJmol⁻¹ can be obtained for cleavage of one Mo—Br bond. An alternative mechanism involving simultaneous rotation of the bridge atoms may be discounted as this would give rise to two signals in a 2 : 1 ratio for the three rotomers 2, 2b, and 2c (Scheme 2).

The ¹³C NMR spectrum in the carbonyl region of the same sample, recorded at room temperature, provides additional information on the fluxionality of **2** and **3**. Both complexes show a single CO resonance indicating a fluxional process that equivalences all the carbonyls. While the resonance for **3** shows the expected splitting pattern for coupling to two phosphines and three fluorines the signal due to **2** shows a line broadening of about 11 Hz as the smaller coupling is not resolved. Application of standard formulae yield an activation barrier of *ca* $64 \text{ kJ mol}^{-1,9}$ approximately twice that required for the cleavage of one Mo—Br in **2**. The simplest explanation in accord with these facts is the process outlined in Scheme 3. Addition of Br⁻ to either of the faces of $[Mo(\mu-F)_2(CO)_4(PPh_3)_4]^{2+}$ equivalences the carbonyls in **2**.

The situation is not so clear cut for 3 as only time averaged NMR spectra (either ³¹P or ¹³C) can be observed, even at -100° C. Both bridge-atom rotation or fluoride ionization could in theory be responsible for equilibration of the ³¹P and ¹³C NMR signals. The structure of $[W(\mu-F)_3(CO)_4]$



Scheme 3.

 $(PMePh_2)_4$ ⁺ lacks any elongated W—F bonds [W-F = 2.126(4), 2.124(3), and 2.124(3) Å].³ That of $[Mo(\mu-F_3)(CO)_4(PPh_3)_4]^+$ 3 shows only one [Mo-F = 2.151(4), 2.095(6), and 2.206(5) Å], present in an asymmetric Mo-F-Mo bridge, and due to а single trans influencing carbonyl $[F-Mo-CO = 171.1^{\circ}]^2$ The structure of related $[Mo_2(\mu-F)_3H_4(PMePh_2)_4]BF_4$, in which the fluorides are substitutionally inert, shows Mo-F distances ranging 2.118(9)—2.216(9) Å.³ Given these results it is difficult to differentiate between the two possible exchange mechanisms for 3. We slightly favour a bridge-atom rotation process for 3 but further experiments are needed to support this hypothesis. Whichever operates the dimer remains intact as no cross-over product is detected when equimolar solutions of 3 and $[Mo_2(\mu-F)_3(CO)_4(PEt_3)_4]^+$ are mixed and monitored by ¹⁹F NMR spectroscopy. No $[Mo_2(\mu-F)_3(CO)_4(PEt_3)_2(PPh_3)_2]^+$ is formed.¹⁰

Although the hydroxo complex 4 and chloro species 5 have not been isolated as pure solids due to their labile nature several facts support these formulations. Samples containing mostly 2 smoothly convert to mostly 4 as the organic layer is repeatedly washed with water. This process may be monitored by ³¹P or ¹⁹F NMR spectroscopy which indicates that a little extra 3 is formed as well. The dry recrystallized materials isolated from these stepwise washing reactions show the smooth growth of a IR stretch at 3540 cm⁻¹ attributed to v(OH). The hydroxo complex 4 shows a double quintet in its ¹⁹F NMR spectrum. A 1H-19F coupling of 8 Hz is detected for this signal. The magnitude of this coupling constant is larger than is expected and we currently cannot completely exclude the possibility of a hydride structure $[Mo_2(\mu-H)(\mu-F)_2(CO)_4(PPh_3)_4]^+$, although we can find no evidence to support this formulation. The balance of evidence presently indicates a hydroxide bridge. Support for the formulation of 5 as a chloro complex comes from the treatment of solutions containing 4 with gaseous HCl which results in the instantaneous formation of new resonances exactly coincident with those of 5 in the ³¹P and ¹⁹F NMR spectra strongly supporting the assignment of both these complexes.

Reaction of $MoBr_2(CO)_2(PPh_3)_2$ 1 with the salts KPF_6 , $NaClO_4$, and $NaBPh_4$

The reaction of $MoBr_2(CO)_2(PPh_3)_2 1$ with excess KPF₆ in H₂O/CH₂Cl₂ is slightly different to that with NaBF₄. The ³¹P NMR of the isolated product reveals that, in addition to triphenylphosphine derived by-products, there are three new molybdenum species formed : $[Mo_2(\mu-Br)(\mu-OH)_2(CO)_4]$

 $(PPh_3)_4]PF_6$ 9, $[Mo_2(\mu-Br)_2(\mu-OH)(CO)_4(PPh_3)_4]$ PF_6 10 and a third tentatively assigned as $[Mo_2(\mu OH_3(CO)_4(PPh_3)_4]PF_6$ 11 (Scheme 1). The presence of a $[PF_6]^-$ counter anion is confirmed by ¹⁹F NMR spectroscopy. Species 9 forms first and short reaction times favour higher yields of this compound. Additionally, shorter reaction times engender a considerably cleaner reaction. Reactions that are stirred for longer times result in higher yields of 10. Species 11 is never formed in great amounts—sometimes not at all—and the fact that it never appears in mass spectra of the mixture suggests that the $(\mu$ -OH)₃ core may not be not very stable. The presence of μ -OH ligands in all of these complexes is confirmed by the presence of OH stretching bands in the IR spectra (v_{OH} 3560 cm⁻¹, KBr disc). This band is shifted to lower frequency when the reaction is carried out in D₂O instead of H₂O $(v_{OD} 2460 \text{ cm}^{-1}, \text{KBr disc})$. There is a much lower tendency for fluoride abstraction from $[PF_6]^-$ than from $[BF_4]^-$, presumably because 1 or $[MoBr(H_2O)]$ $(CO)_2(PPh_3)_2$, is an inferior Lewis acid to PF₅, and hence μ -F products are not formed, except occasionally at trace levels. Because of the low tendency to abstract fluoride, only OH⁻ and Br⁻ bridges can form.

Addition of various stoichiometric equivalents of the halides NaF, NaCl, or NaBr, to Mo_2Br_2 $(CO)_2(PPh_3)_2$ 1 in the presence of excess KPF₆ results in halo-bridged products. If two or three equivalents of fluoride are added, 3 is the major product. However, when two equivalents of fluoride are used along with saturated NaBr solution then 2 is the major product (Scheme 4). Addition of three equivalents of either NaCl or NaBr results in complex mixtures of products for which assignment of all the species present in the ³¹P and ¹⁹F NMR spectra is not possible.

In view of the early observation of Moss and Shaw that $MoBr_2(CO)_2(PEt_3)_2$ reacts with NaBPh₄ in MeOH to give "uncharacterised yellow cations", we briefly investigated the reaction of 1 with NaBPh₄ suspecting that similar dimolybdenum halo-bridged compounds would be isolated. The material we isolate from this reaction has IR stretches characteristic of the $Mo_2(\mu-X)_3(CO)_4(PPh_3)_4$ core [v_{CO} (KBr disc) 1950, 1865 cm⁻¹]. The FAB mass spectrum has a cluster with Mo₂ isotope pattern centred at m/z 1442 (probably not a molecular ion). Other than this, no data has been collected because the yield of the reaction is very low. The crude compound is rather uncrystalline, and attempts to recrystallize it result in decomposition to Mo = O species containing coordinated OPPh₃ ligands, suggested by the infrared spectrum, (KBr disc) 970 (Mo = O) cm⁻¹, and by a partial X-ray





crystal structure which although very disordered confirms the presence of a $MoBr_2(=O)_n(OPPh_3)_2$ core.¹¹ Given the uncooperative nature of this reaction it is not surprising that Moss and Shaw encountered difficulties in isolating tractable materials. We also encountered similar problems in isolating tractable materials from the reaction of $Mo_2Br_2(CO)_2PPh_3)_2$ 1 with aqueous NaClO₄, although in this case this is probably due to the oxidising nature of this particular counter anion.

EXPERIMENTAL

Reactions were carried out in air unless otherwise stated. Proton NMR were recored on a Jeol-270 (270 MHz) spectrometer, ¹³C NMR were recorded on Jeol-270 (67.8 MHz) or Bruker-AM250 (62.9 MHz) spectrometers, ³¹P NMR were recorded on Jeol-270 (109.3 MHz) or Bruker-AM250 (101.3 MHz) spectrometers, ¹⁹F NMR were recorded on a Jeol-270 (254.1 MHz) spectrometer and ¹¹B NMR were recorded on a Jeol-270 (86.6 MHz) spectrometer. Infrared spectra were recorded using a Perkin-Elmer 983G instrument. The Fluoride selective electrode was a Radiometer F1052F electrode. FAB mass spectra were obtained on a VG-ZAB (FAB) machine. Elemental analyses were performed by the University of Sheffield Microanalytical Service. The complexes MoBr₂(CO)₂ $(PPh_3)_2^{12}$ and $WBr_2(CO)_3(PPh_3)_2^{13}$ were prepared by literature methods or slight variations on literature methods.

Decarbonylation of WBr₂(CO)₃(PPh₃)₂

This was achieved by refluxing the orange tricarbonyl in 1,2-dichloroethane with a nitrogen purge. Cooling the resulting purple solution yielded $WBr_2(CO)_2(PPh_3)_2 6$ as purple microcrystals.

Representative preparation of $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]^+$ 2, $[Mo_2(\mu-F)_3(CO)_4(PPh_3)_4^+]$ 3, $[Mo_2(\mu-F)_2(\mu-OH)(CO)_4(PPh_3)_4]^+$ 4 and $[Mo_2(\mu-F)_2(\mu-Cl)(CO)_4(PPh_3)_4^+]$ 5

The compound $MoBr_2(CO)_2(PPh_3)_2 1$ (0.20 g, 0.24 mmol) and NaBF₄ (0.26 g, 2.4 mmol [10-fold excess]) were placed in $CH_2Cl_2/H_2O(30 \text{ cm}^3/10 \text{ cm}^3)$ and stirred at room temperature until a yellow or pale olive green solution was obtained (approx. 45 min). The organic layer was separated and dried over Na₂SO₄. Evaporation followed by recrystallization from CH₂Cl₂-hexane yielded mainly 3, with some 2, 4 and 5 also present, as mixed BF_4^{-}/F^{-} salts (Yield 0.09 g). The conductance of a mixture of 2–5 is $ca 260 \mu$ -S cm⁻¹ (MeCN, 4mg cm⁻³). Infrared, ³¹P NMR, and ¹⁹F NMR spectroscopic data for 2-5 are given in Table 3. Additional data for 2-**5**: ¹H NMR (270 MHz, CDCl₃): $\delta_{\rm H}$ 6.25–7.75 (m, Ph of 2–5). Other than this the ¹H NMR spectra of these compounds are rather uninformative. ¹³C NMR (67.8 MHz, CD_2Cl_2) δ_C 14.2, 22.9, 31.9 (cocrystallized hexane), 129.0-134.6 (Ph of 2-5), 244.9 (t, broad, $J_{CP} \approx 34$ Hz, CO of 2), 246.5 (tq, $J_{CP} = 34$ Hz, $J_{CF} = 11.5$ Hz, CO of 3). Mass spectrum (FAB) 3 1409 [M⁺·]. Elemental analysis for

 $3BF_4$: Found C, 60.3; H, 4.1; Calc. for $C_{76}H_{60}BF_7Mo_2O_4P_4$ C, 61.0; H, 4.0%.

Alternative preparation of 2-5

Solid MoBr₂(CO)₂(PPh₃)₂ 1 (0.10 g, 0.12 mmol) and NaF (50 mg, 1.2 mmol) were placed in CH₂Cl₂/H₂O (15 cm³/5 cm³) and stirred for 30 min at room temperature until a pale olive green solution had formed. The organic layer was separated, dried and evaporated, then recrystallized from CH₂Cl₂-hexane. The product was obtained as an orange powder, shown by ³¹P NMR to be an impure mixture of 2–5 in low yield.

Preparation of 2 enriched mixture

The complex $MoBr_2(CO)_2(PPh_3)_2 \mathbf{1}$ (0.10 g, 0.12 mmol) and NaF(10 mg, 0.24 mmol) and KPF₆ (excess) were placed in CH₂Cl₂/saturated NaBr solution (15 cm³/5 cm³) and stirred for 3 h, after which time the blue suspension had turned dark green. Similar work up to that described above yielded mainly 2, with some 3–5 also present, as orange microcrystals (yield 60 mg).

Preparation of $[W_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]^+$ 7 and $[W_2(\mu-Br)_2(\mu-F)(CO)_4(PPh_3)_4]^+$ 8

Solid WBr₂(CO)₂(PPh₃)₂ 6 (50 mg, 0.054 mmol) and NaBF₄ (59 mg, 0.54 mmol) were placed in CHCl₂/H₂O (15 cm³/5 cm³) and stirred at room temperature. After 2 min the purple suspension had changed to a grey colour. After 5 min the colour was olive green, and after 10 min the organic layer was yellow–green. The organic layer was separated and dried (Na₂SO₄), evaporated and recrystallized from CH_2Cl_2 -hexane (yield 25 mg). Infrared, ³¹P NMR, and ¹⁹F NMR spectroscopic data for 7 and 8 are given in Table 3.

Representative preparation of $[Mo_2(\mu-Br)_2(\mu-OH)(CO)_4(PPh_3)_4]^+$ 9, $[Mo_2(\mu-OH)_2(\mu-Br)(CO)_4(PPh_3)_4]^+$ 10 and $[Mo_2(\mu-OH)_3(CO)_4(PPh_3)_4]^+$ 11

The dicarbonyl $MoBr_2(CO)_2(PPh_3)_2 1$ (0.10 g, 0.12 mmol) and KPF_6 (0.22 g, 1.2 mmol) were placed in CHCl₂/H₂O (15 cm³/5 cm³) and stirred for 20 min, by which time the blue suspension in the organic layer had changed to an pale orange–green colour. After separation and drying (Na₂SO₄), the organic layer was evaporated to a dark orange oil and recrystallized from CH₂Cl₂-Et₂O as orange microcrystals (yield 55 mg). The relative quantities of **9** and **10** formed depends on the reaction time, shorter reactions favouring higher yields of **9**. Infrared, ³¹P NMR, and ¹⁹F NMR spectroscopic data for **9–11** are given in Table 3. Mass spectra (FAB) 1531 [M⁺ ·] **9**, 1466 [M⁺ ·] **10**.

Reaction of MoBr₂(CO)₂(PPh₃)₂ 1 with NaBPh₄

The compound MoBr₂(CO)₂(PPh₃)₂ 1 (99 mg, 1.18 mmol) and NaBPh₄ (0.41 g, 1.23 mmol) were stirred in CHCl₂/H₂O (15 cm³/5 cm³). The organic phase immediately turned orange. After about 10 min, the organic layer was separated and dried. Evaporation followed by crystallization from CH₂Cl₂-hexane afforded 7 mg of product. IR (KBr disc) 1950, 1865 cm⁻¹, mass spectrum (FAB) m/z1442. Subsequent attempts to carry out the reaction failed to reproduce the same product, decompo-

Table 3. Infrared, ³¹P NMR and ¹⁹F NMR spectroscopic data for the complexes (coupling constants in Hz where applicable)

Compound	δ_{p}/ppm	$\delta_{ m F}/ m ppm$	IR (KBr disc) $v_{\rm max}$ cm ⁻¹
2	64.0 (t, $J_{\rm PF} = 43.3$)	-228.2 (quintet, $J_{\rm FP} = 43.3$)	1945, 1862 (v _{CO})
3	66.6 (q, $J_{\rm PF} = 33.4$)	-184.7 (quintet, $J_{\rm FP} = 33.4$)	1945, 1862 (v_{CO})
4	66.7 (t, $J_{\rm PF} = 39.5$)	-189.1, (double quintet, $J_{FP} = 39.0, 40.0; J_{HF} = 8.0$)	1945, 1862 (v _{со}) 3540 (v _{он})
5	65.6 (t, $J_{\rm PF} = 41.3$)	-214.5 (quintet, $J_{\rm FP} = 41.3$)	1945, 1862 (v _{CO})
6	65.1 (s), -144 (septet [PF ₆] ⁻ , $J_{\rm PF} = 710.4$)	$-74.3 (d [PF_6]^-, J_{FP} = 710.4)$	1940, 1853 (v _{со}), 3560 (v _{он})
7 ^a	60.1 (s), -144 (septet [PF ₆] ⁻ , $J_{\text{PE}} = 710.4$)	$-74.3 \ (d \ [PF_6]^-, J_{FP} = 710.4)$	1940, 1853 (v _{со}), 3560 (v _{он})
8 ^{<i>a</i>}	$61.9 (s), -144 (septet PF_6)^-, J_{PF} = 710.4)$	$-74.3 (d [PF_6]^-, J_{FP} = 710.4)$	1940, 1853 (v _{со}), 3560 (v _{он})
10	41.3 (t. $J_{\rm PF} = 40.4$)	_	1930, 1835 (v _{co})
11	41.3 (d , $J_{\rm PF} = 47.8$)	—	1930, 1835 (v _{co})

^{a 183}W satellites not apparent at signal-to-noise ratio in spectra.

sition occurred during crystallization which yielded yellow plates that were shown by X-ray crystallography to be a $MoBr_2(=O)_n(OPPh_3)_2$ (n = 1,2) complex. The quality of the structure was extremely poor and therefore it was not pursued further. Space group: monoclinic C_c , a = 14.046, b = 13.097, c = 19.221 Å; $\beta = 95.98^\circ$.

Reaction of MoBr₂(CO)₂(PPh₃)₂ 1 with NaClO₄

Solid MoBr₂(CO)₂(PPh₃)₂ 1 (97 mg, 1.16 mmol) and NaClO₄ (0.33 g, 2.6 mmol) were stirred in CH₂Cl₂/H₂O (15 cm³/5 cm³) for about 30 min. The organic phase was separated and dried. Attempts to recrystallize the product caused it to come out as an oil. Cooling and scratching with Et₂O resulted in the isolation of *ca* 5 mg of poor quality product. IR (KBr disc) 1945, 1865 cm⁻¹.

Crystallography—full details for the solution and refinement of $[Mo_2(\mu-Br)(\mu-F)_2(CO)_4(PPh_3)_4]F.(x$ hexane 2) (x \approx 1)

Orange crystals of 2F.(x hexane) were deposited from a saturated CH_2Cl_2 -hexane solution of $2BF_4$ on standing at room temperature (16 h).

A crystalline fragment of the complex, together with some of its mother liquors was mounted in a Lindeman tube with epoxy resin. Cell dimensions and space group data were obtained by standard methods on a Rigaku AFC6S four-circle diffractometer with graphite-monochromated Mo- K_{α} radiation. The θ -2 θ technique was used as previously described,¹⁴ to record the intensities of all non-equivalent reflections for which $3^{\circ} < 2\theta < 50^{\circ}$ on the AFC6S. Scan widths were calculated as A + Btan θ , where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to K α_1 -K α_2 splitting. Scan speeds were varied depending on the prescan reflection intensity. Data were collected as previously described.²⁻¹⁴

Solution and refinement of the structures

Computations were carried out using the data with $F_0^2 > 3 \sigma(F_0^2)$ where $\sigma(F_0^2)$ was estimated from counting statistics.¹⁵ Corrections were applied for Lorentz and polarization effects and for absorption, based on psi-scans. The positions of the metal and the bromine atoms were determined using a Patterson map. Other atoms were located from Fourier difference syntheses. The final full-matrix last-squares refinement was carried out using the TEXRAY program set.¹⁶ Full-matrix least squares refinement was based on F. The function minimized was Σ w $(|F_o| - |F_c|)^2$ where : w = $4Fo^2/\sigma^2(Fo^2)$, $\sigma^2(Fo^2) = [S^2\{(C+R^2B) + 0.03Fo^2\}^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and Lp = Lorentz polarization factor. Atomic scattering factors for both non-hydrogen¹⁷ and hydrogen¹⁸ atoms were taken literature values. The effects of anomalous dispersion were included using literature values for $\Delta f''$ and $\Delta f''$.¹⁹

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