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TETRADENTATE LIGANDS FOR THE Mo—Mo QUADRUPLE BOND FROM *CIS*-COORDINATED PHOSPHONITES

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Abstract—Deprotonated *cis*-$[M(CO)_4(PhPO_2)_2H_3]^-$ (M = Cr, Mo, W) are tetradentate ligands capable of displacing two carboxylate bridges each in $Mo_2(acetate)_4$ to give mixed-valent tetrametallic complexes of the type $Mo_2[M(CO)_4(PhPO_2)_2]_2^{4-}$ (M = Cr, Mo, W). The molecular structure of $(n\text{-}Bu_4N)_2H_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$ has been determined by X-ray crystallography. It crystallizes in the orthorhombic system, space group *Pbca*, with cell parameters $a = 20.858(1)$, $b = 17.131(1)$, $c = 21.072(1)$ Å, $V = 7529.14$ Å^3 and $Z = 4$. A total of 3262 reflections were considered significant and used in the refinement, yielding final $R_f = 0.056$ and $R_w = 0.063$. The tetraanion has a centre of symmetry and features a Mo^{II}—Mo^{II} bond of 2.186(2) Å spanned by two *cis*-$Mo(CO)_4(PhPO_2)_2$ metallo-ligands. Chemically, only weak interactions are found between this tetraanion and potential axial ligands like tertiary amines, pyridine, phosphine and isonitrile. Its iodination occurred at the molybdenum(0) tetracarbonyl sites with CO loss to give $Mo_2[Mo(CO)_3I_2(PhPO_2)_2]_2^{4-}$.

Metal complexes containing *cis*-coordinated phosphonites can potentially present a square or rectangular array of oxygen nucleophiles upon deprotonation (Fig. 1). Recently we have used *cis*-$[M(CO)_4(PhPO_2)_2]^{4-}$ (M = Cr, Mo, W; complexes **1**, **2**, **3**) in preparing adamantane-like cage complexes of the type $[M(CO)_4[PhPO]_4M(CO)_4]$, where the metals are linked by POP bridges.[1] Since P—O ligands with their soft/hard donor combination are known for their ability to bridge heterometallic and mixed-valent centres,[2] we have investigated the use of **1**–**3** as metallo-ligands. We report here their employment as doubly-bridging groups for the quadruply-bonded Mo_2^{4+} dimer.

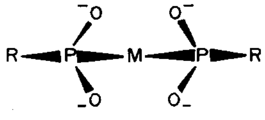

Fig. 1.

RESULTS

Synthesis and spectra

Deprotonation of the tetrabutylammonium salts of *cis*-$[M(CO)_4(PhPO_2)_2H_3]^-$ (M = Cr, Mo, W; complexes **4**, **5**, **6**, respectively)[1] with sodium hydride in THF afforded the corresponding tetraanions: **1**, **2** and **3**. Substitution of two of these for the bridging acetates in $Mo_2(OAc)_4$ proceeded readily at room temperature:

$$2\,cis\text{-}[M(CO)_4(PhPO_2)_2]^{4-} + Mo_2(OAc)_4 \longrightarrow Mo_2[M(CO)_4(PhPO_2)_2]_2^{4-} + 4OAc^-$$

(**7**–**9**)
(M = Cr, Mo, W).

These tetrametallic products were isolated as disodium di(*n*-butylammonium) salts in moderate yields and are air-stable orange–red solids (**7**, **8**, **9** for M = Cr, Mo, W, respectively). They are soluble in polar organic solvents such as THF, DMSO,

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Table 1. IR and ^{31}P NMR data

Complex	IR (KBr, cm^{-1})		$^{31}P\{^1H\}$ NMR (ppm)[a]
	ν_{CO}	ν_{PO}	
$Mo_2[M(CO)_4(PhPO_2)_2]_2^{4-}$	1998m, 1886s, 1842s	835m,b	237.6[b]
[M = Cr (**7**), Mo (**8**), W (**9**)]	1999m, 1880s, 1849s	839m,b	217.3[c]
	1998m, 1875s, 1840s	839m,b	196.5[c] ($^1J_{PW}$ = 134 Hz)
$Mo_2[Mo(CO)_4(PhPO_2)_2]_2 \cdot 2DMAP^{4-}$ (**10**)	1997m, 1884s, 1870s, 1831s	848m	219.7[b]
$Mo_2[Mo(CO)_3I_2(PhPO_2)_2]_2^{4-}$ (**11**)	2002m, 1941s, 1881s,	881m	208 (broad)[b]

[a] Referenced to 85% H_3PO_4.
[b] d_6-acetone.
[c] d_6-DMSO.

acetonitrile and acetone, moderately soluble in methylene chloride, and insoluble in ether.

Typical *cis*-$M(CO)_4L_2$ carbonyl bands (C_{2v}) are observed for the tetraanionic complexes **7**–**9** with A_1 stretches below 2000 cm^{-1} (Table 1). Their $^{31}P\{^1H\}$ NMR spectra (Table 1) exhibited singlets which are all shifted downfield by about 70 ppm from the corresponding precursor (complexes **4**–**6**) values of δ 170.0, 145.5 and 120.5 ppm, respectively.[1] Electronic spectra of **7**–**9** featured absorptions at 338 nm ($\varepsilon = 4.4 \times 10^3$ M^{-1} cm^{-1}) for **7**, 351 nm ($\varepsilon = 9.6 \times 10^3$) for **8**, and 341 nm ($\varepsilon = 5.4 \times 10^3$) for **9**.

Structure of complex 8

Recrystallization of **8** from methylene chloride–hexane yielded orange crystals of the tetraanion as the $(n\text{-}Bu_4N)_2H_2$ salt. Elemental analyses and ^1H NMR of the crystals confirmed the exchange of two sodium cations for two protons. Electronic and ^{31}P NMR spectra further corroborated retention of the basic Mo_2^{4+} unit. The molecular structure of the complex is shown in Fig. 2. Important bond distances and angles are listed in Table 2. The tetrametallic anion possesses an inversion centre which relates the pair of molybdenum(II) centres, Mo(1) and Mo(1a), as well as the two $Mo(CO)_4$ moieties, around Mo(2) and Mo(2a). Each *cis*-$Mo(CO)_4(PhPO_2)_2$ metallo-ligand doubly bridges the Mo_2^{4+} unit using all four oxygen donor sites. Around each molybdenum(II), the Mo—Mo quadruple bond is 2.186(2) Å, while the Mo—O distances range from 1.988(7) to 1.998(7) Å. At the zero-valent molybdenum centres, average axial Mo—CO distances are marginally longer at 2.02(2) Å compared to the equatorial average of 1.96(2) Å. Metal–phosphorus bonds average 2.518(4) Å. The tetrabutylammonium cations fill the packing vacancies and exhibit no unusual contacts with the anion.

Reactions of complex 8

Lewis bases form only weak adducts with **8** in solution presumably by coordination at the vacant axial sites of the Mo_2^{4+} dimeric unit. For example, a $^{31}P\{^1H\}$ NMR spectrum indicated formation of a complex with pyridine (δ 214 ppm). However, no adduct could be isolated as the Lewis base was lost upon solvent evaporation. Only the better donating 4-dimethylaminopyridine (DMAP) formed an isolable 2 : 1 adduct, complex **10**. π-Acceptor ligands like triphenylphosphine and *t*-butylisocyanide failed to react with **8** even under forcing conditions.

Reaction of 2 equivalents of iodine with **8** resulted in CO evolution and formation of a tetramolybdenum(II) product, complex **11** ($^{31}P\{^1H\}$ NMR in THF: δ 195, broad singlet; IR (KBr): ν_{CO} 2002, 1941, 1881 cm^{-1}; ν_{PO} 881 cm^{-1}; CHN analyses consistent with $(n\text{-}Bu_4N)_2Na_2Mo_2[MoI_2(CO)_3(PhPO_2)_2]_2 \cdot 2THF$). This orange, crystalline solid rapidly decomposed with loss of CO upon standing.

DISCUSSION

Syntheses and spectra of complexes 7, 8 *and* 9

The feasibility of using the metallo-ligands *cis*$[M(CO)_4(PhPO_2)_2]^{4-}$ (M = Cr, Mo, W) as tetradentate donors has been confirmed. Replacement of two carboxylates in $Mo_2(OAc)_4$ by each ligand proceeded at ambient temperature in THF. Previously, reactions of phosphinates with Mo_2^{4+} produced only polymeric species that are weakly paramagnetic and devoid of multiple bonds.[3] The chromium reaction was complete within 1 h, while

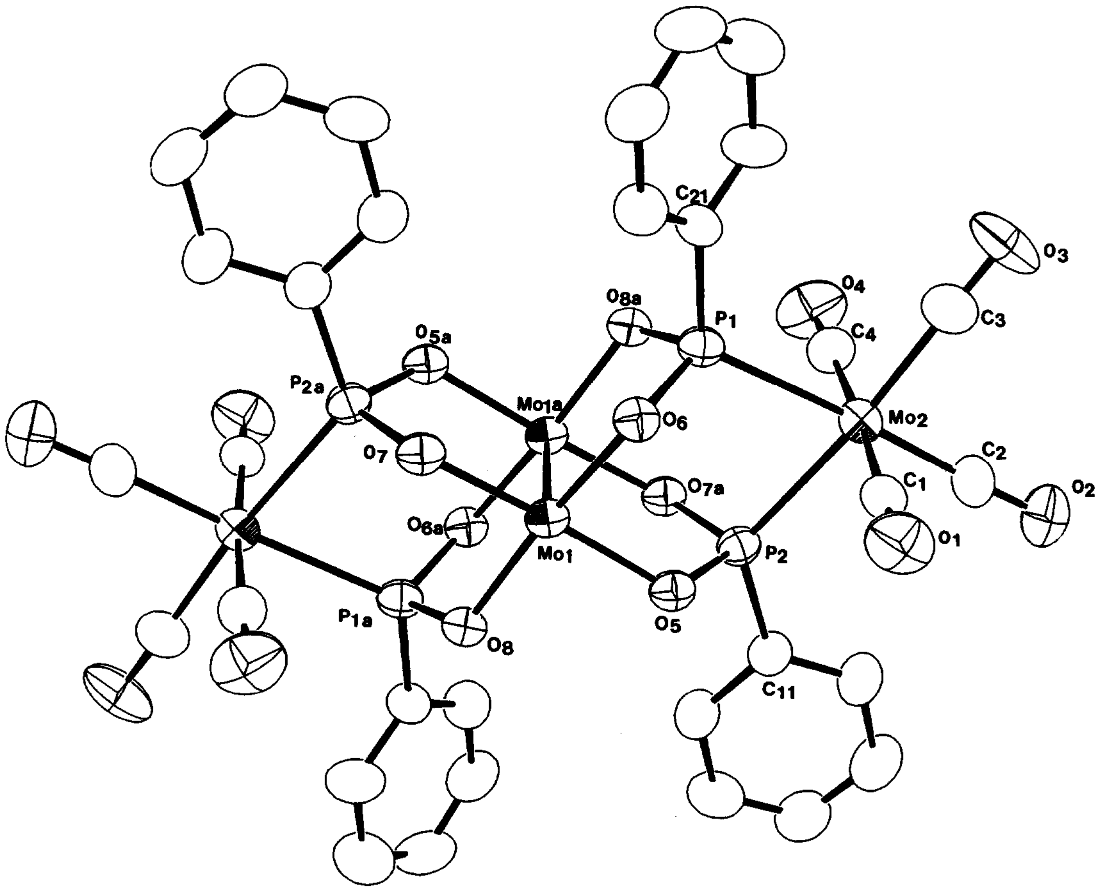

Fig. 2. Molecular structure of $Mo_2[Mo(CO)_4(PhPO_2)_2]_2^{4-}$ (**8**) with atoms at 50% probability ellipsoids.

the molybdenum and tungsten substitutions required 1 day. Monitoring of the reaction of $[Mo(CO)_4(PhPO_2)_2]^{4-}$ (**2**) with $Mo_2(OAc)_4$ by ^{31}P NMR spectroscopy revealed an intermediate resonance at δ 197 ppm in addition to singlets at 142 (**2**) and 217 (**8**). It is reasonable to assign the transient resonance to a partially-substituted intermediate:

$$Mo_2(OAc)_4 + [Mo(CO)_4(PhPO_2)_2]^{4+} \longrightarrow 2OAc^- + Mo_2(OAc)_2[Mo(CO)_4(PhPO_2)_2]^{2-}.$$

The substantial and uniform 67–76 ppm downfield coordination shift observed in the ^{31}P NMR spectra of complexes **7**–**9** can be attributed to the diamagnetic anisotropic deshielding of the Mo—Mo quadruple bond.[4] These chemical shifts are also solvent dependent; for example, in acetone, complex **8** has δ at 222, in THF it is at δ 217 and in pyridine at δ 214. Adduct formation at the vacant Mo_2^{4+} axial sites can be expected to reduce diamagnetic anisotropy.

Complexes **7**–**9** each has an absorption maximum in the region 338–351 nm with extinction coefficients of the order of 10^3 M^{-1} cm^{-1}. Burlitch and co-workers have reported an absorption at 334 nm ($\varepsilon = 6.4 \times 10^3$) for $Mo_2(S_2PEt_2)_4$.[3] As previously discussed by Trogler and Gray, assignment of these bands is problematic in the absence of polarized spectra.[5]

Structure of complex 8

The value of 2.186(2) Å for the Mo—Mo bond in **8** is slightly longer than any other Mo—Mo quadruple bond spanned by four bridging ligands.[6] For example, $Mo_2(SO_4)_4^{4-}$ at 2.140(1) Å, $Mo_2(OAc)_4$ at 2.093(2) Å, $Mo_2(S_2PEt_2)_4 \cdot THF$ at 2.137(1) Å, $Mo_2(OSPEt_2)_4 \cdot THF$ at 2.128(2) Å and $Mo_2[O_2P(OPh)_2]_4 \cdot 2THF$ at 2.141(2) Å.[3,6,7] For comparison, $Mo_2[SO_4]_4^{3-}$ with a Mo—Mo bond order of 3.5 has a similar separation of 2.17 Å.[8] Significantly, the average Mo—O bond length in **8** at 1.99(1) Å is shorter than those in $Mo_2(OAc)_4$ (2.11(1) Å), $[Mo_2(SO_4)_4]^{4-}$ (2.14(1) Å), $Mo_2(OSPEt_2)_4 \cdot THF$ (2.15(3) Å), $Mo_2[O_2P(PEt)_2]_4$ (2.15 Å), and is at least as short as the 2.01(1) Å found in the triply-bonded dimolybdenum(III)

Table 2. Selected bond distances (Å) and angles (°) for complex **8**

Mo(1)—Mo(1a)	2.186(2)	P(1)—O(6)	1.603(8)
Mo(1)—O(5)	1.988(7)	P(1)—O(8a)	1.595(8)
Mo(1)—O(6)	1.988(8)	P(1)—C(21)	1.815(12)
Mo(1)—O(7)	1.998(7)	P(2)—O(5)	1.593(8)
Mo(1)—O(8)	1.990(8)	P(2)—O(7a)	1.602(8)
Mo(2)—P(1)	2.517(3)	P(2)—C(11)	1.828(12)
Mo(2)—P(2)	2.519(4)	C(1)—O(1)	1.13(2)
Mo(2)—C(1)	2.027(15)	C(2)—O(2)	1.15(2)
Mo(2)—C(2)	1.988(15)	C(3)—O(3)	1.20(2)
Mo(2)—C(3)	1.918(16)	C(4)—O(4)	1.17(2)
Mo(2)—C(4)	2.001(16)		
Mo(1a)—Mo(1)—O(5)	94.7(2)	C(1)—Mo(2)—C(2)	91.7(5)
Mo(1a)—Mo(1)—O(6)	94.5(2)	C(1)—Mo(2)—C(3)	91.6(6)
Mo(1a)—Mo(1)—O(7)	94.3(2)	C(1)—Mo(2)—C(4)	176.2(6)
Mo(1a)—Mo(1)—O(8)	94.5(2)	C(2)—Mo(2)—C(3)	88.2(6)
O(5)—Mo(1)—O(6)	86.3(3)	C(2)—Mo(2)—C(4)	89.5(6)
O(5)—Mo(1)—O(7)	170.9(3)	C(3)—Mo(2)—C(4)	92.0(6)
O(5)—Mo(1)—O(8)	91.9(3)	Mo(2)—P(1)—O(6)	112.3(3)
O(6)—Mo(1)—O(7)	91.9(3)	Mo(2)—P(1)—O(8a)	110.0(3)
O(6)—Mo(1)—O(8)	170.9(3)	Mo(2)—P(1)—O(21)	125.1(4)
O(7)—Mo(1)—O(8)	88.5(3)	O(6)—P(1)—O(8a)	102.8(4)
P(1)—Mo(2)—P(2)	79.46(10)	O(6)—P(1)—C(21)	100.7(5)
P(1)—Mo(2)—C(1)	90.2(3)	O(8a)—P(1)—C(21)	103.5(5)
P(1)—Mo(2)—C(2)	174.5(5)	Mo(2)—P(2)—O(5)	114.1(3)
P(1)—Mo(2)—C(3)	96.9(4)	Mo(2)—P(2)—O(7a)	110.8(3)
P(1)—Mo(2)—C(4)	88.3(4)	Mo(2)—P(2)—C(11)	121.5(5)
P(2)—Mo(2)—C(1)	89.6(4)	O(5)—P(2)—O(7a)	103.0(4)
P(2)—Mo(2)—C(2)	95.3(5)	O(5)—P(2)—C(11)	101.6(5)
P(2)—Mo(2)—C(3)	176.2(4)	O(7a)—P(2)—C(11)	103.8(5)
P(2)—Mo(2)—C(4)	86.7(4)	Mo(2)—C(1)—O(1)	179(1)
Mo(1)—O(5)—P(2)	118.1(4)	Mo(2)—C(2)—O(2)	178(1)
Mo(1)—O(6)—P(1)	119.1(4)	Mo(2)—C(3)—O(3)	176(1)
Mo(1)—O(7)—P(2a)	117.4(4)	Mo(2)—C(4)—O(4)	178(1)
Mo(1)—O(8)—P(1a)	118.8(8)		

anion $[Mo_2(HPO_4)_4]^{2-}$.[3,6,9] The formally dianionic $PhPO_2$-bridging ligand should be significantly more electron-rich than the monanionic $(PhO)_2PO_2$ and acetate, for example. Qualitatively, mixing of oxygen lone-pairs with the Mo_2^{4+} dimer should strengthen the Mo—O bonds at the expense of Mo—Mo bonding. This is consistent with the observed structural data and the low tendency of **8** to adduct axial ligands.

Comparing the molybdenum(0) coordination geometry with that found in the $[Mo(CO)_4[PhPO]_4Mo(CO)_4]$ cage complex,[1] we note the slightly lengthened Mo—P distance at 2.518(4) Å vs 2.435(2) Å. Otherwise, metal–carbonyl geometrical data are quite similar. Using Kepert's definition of ligand bite angle ($b = 2\sin(\theta/2)$, where θ is the P—Mo—P angle), each molybdenum(0) centre in **8** is chelated by a diphosphine ligand with a b value of 1.27.[10]

Reactions of complex **8**

Like its precursor, $Mo_2(OAc)_4$, **8** appears to have little tendency to form stable axial adducts with hard donors.[8] Only the strong σ-donor 4-dimethylaminopyridine afforded an isolable 2:1 adduct, complex **10**. In contrast to $Mo_2(OAc)_4$,[8] complex **8** is also inert to π-acid ligands. Neither triphenylphosphine nor butylisonitrile gave any indication of adduct formation.

Halogenation oxidation of **8** could occur at either the molybdenum(0) or the molybdenum(II) dimeric unit. Iodination clearly resulted in oxidative elimination at the $Mo(CO)_4$ sites. Spectral and analytical data are consistent with the product being $Mo_2[Mo(CO)_3I_2(PhPO_2)_2]_2^{4-}$ (**11**). In contrast to **8**, this readily crystallizes with two molecules of THF, presumably in the axial positions. Variable-temperature $^{31}P\{^1H\}$ NMR of **10** in d_6-acetone

Table 3. Elemental analytical data

	Calculated			Found		
Complex	%C	%H	%N	%C	%H	%N
7	47.7	5.7	1.7	48.0	6.0	1.7
8	45.2	5.4	1.6	45.2	5.7	1.7
9	41.2	4.9	1.5	40.9	5.3	1.4
10	48.2	5.8	4.3	48.0	5.9	4.2
11	36.6	4.7	1.2	36.3	4.7	1.2

showed a limiting spectrum at -45°C of a singlet at δ 195.1 ppm, as well as a smaller set of AB doublets at δ 202.2 and 190.0 ppm ($J = 83$ Hz). While structural details are not yet available, the ligand bite angle of **8** ($b = 1.27$) would suggest capped trigonal prism or capped octahedron as most likely geometries at the seven-coordinate $Mo(CO)_3I_2P_2$ centres (Fig. 3).[10] Complex **11** is very unstable towards CO loss upon exposure to air, completely decomposing to a poorly-characterized dark grey residue after 24 h.

EXPERIMENTAL

All operations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under nitrogen. (n-$Bu_4N)M(CO)_4(PhPO_2)_2H_3$ (M = Cr, Mo, W) were prepared from *cis*-$M(CO)_4(PhPCl_2)_2$ as described previously.[1] $Mo_2(OAc)_4$ was synthesized according to the literature procedure.[8]

NMR spectra were recorded on a Bruker AM-360, JEOL-FX90Q, or a Varian 360A. IR spectra were run on a Perkin–Elmer 283B instrument. Electronic spectra were recorded using a Cary 219 spectrophotometer. Elemental analyses were performed at the University Instrumentation Center with a Perkin–Elmer 240B Elemental Analyser and the results are included in the supplementary material. All compounds below gave satisfactory (within 0.4%) carbon, hydrogen and nitrogen analyses.

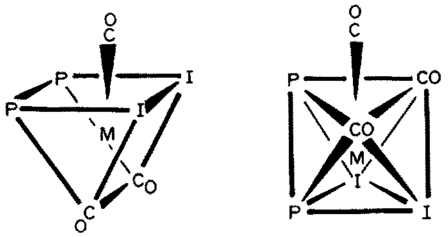

Fig. 3. Possible geometries at the $Mo(CO)_3I_2P_2$ portions of complex **11**.

Synthesis of (n-$Bu_4N)_2Na_2Mo_2[Cr(CO)_4(PhPO_2)_2]_2$ (7)

(n-$Bu_4N)Cr(CO)_4(PhPO_2)_2H_3$ (1.452 g, 2.1 mmol) was dissolved in THF (25 cm^3). Sodium hydride (*ca* 1 g of a 50% dispersion in oil) was added and the suspension stirred until effervescence ceased. The excess NaH was filtered off with a sintered-glass frit and $Mo_2(OAc)_4$ (0.226 g, 0.5 mmol) was added to the filtrate. The solution colour changed from yellow–brown to red. After 1 h of stirring, a white solid (NaOAc) was removed by filtration and 5 cm^3 of toluene was added to the filtrate. A brown solid was obtained. This was filtered off and recrystallized from THF–ether to give brown, rectangular crystals of **7** (0.39 g, 53% yield).

Synthesis of (n-$Bu_4N)_2Na_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$ (**8**), *and* (n-$Bu_4N)_2Na_2Mo_2[W(CO)_4(PhPO_2)_2]_2$ (**9**)

Complexes **8** and **9** were prepared as above from the respective (n-$Bu_4N)M(CO)_4(PhPO_2)_2H_3$ salt, except that the reaction mixtures were allowed to stir at ambient temperature for 24 h. Yield of **8** is 65% of orange crystals. The yield of **9** is 40% of orange microcrystals.

Synthesis of (n-$Bu_4N)_2Na_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2 \cdot 2DMAP$ (**10**)

Complex **8** (0.209 g, 0.125 mmol) was dissolved in 10 cm^3 of THF. Dimethylaminopyridine (0.032 g, 0.258 mmol) was added and the solution stirred for 1 h. The orange precipitate was filtered off, washed with THF and dried to give **10** (0.165 g, 68% yield).

Synthesis of (n-$Bu_4N)_2Na_2Mo_2[Mo(CO)_3I_2(PhPO_2)_2]_2 \cdot 2THF$ (**11**)

Complex **8** (0.163 g, 0.09 mmol) was dissolved in 10 cm^3 of THF. With stirring, iodine (0.049 g, 0.19 mmol) was added and effervescence and darkening of the solution was observed. After 2 h, the suspension was filtered, the residue washed with THF and dried to give **11** (0.136 g, 70% yield). This orange, crystalline solid readily decomposed upon air-exposure to give a dark grey powder.

X-ray structural determination of (n-$Bu_4N)_2H_2Mo_2[Mo(CO)_4(PhPO_2)_2]_2$ (**8**)

Crystals of **8** were grown from methylene chloride–hexane by layering in a Schlenk tube. ^1H NMR of the resulting red–brown crystals in d$_6$-

Table 4. Crystallographic data for complex **8**

Formula	$C_{64}H_{94}Mo_4N_2O_{16}P_4$
Space group	*Pbca*
Crystal system	Orthorhombic
a (Å)	20.858(1)
b (Å)	17.131(1)
c (Å)	21.072(1)
Cell volume (Å^3)	7529.14
D_{calc} (g cm^{-3})	1.419
μ (mm^{-1})	0.78
Z	4
Radiation (Å)	Mo-K_α
Data collected	$0° < \theta < 50°$
Scan	θ–2θ
Unique reflections	6654
Observed reflections	3262
$F(000)$	2918.98
Dimensions (mm)	$0.25 \times 0.4 \times 0.4$
R_F	0.056
R_{WF}	0.063

acetone revealed the presence of two protons (δ 2.79 in d_6-acetone) which have been exchanged for the two sodium cations during the recrystallization. Elemental analyses (Table 3): Calc. for $C_{64}H_{94}Mo_4N_2O_{16}P_4$: C, 46.44; H, 5.68; N, 1.69. Found: C, 46.18; H, 5.76; N, 1.66%. An ethanol solution of the crystals has an absorption maximum at 350 nm in the visible region. Its ^{31}P NMR singlet signal was found at +222.5 ppm (d_6-acetone). Furthermore, ^{31}P NMR of a mixture of **8** before and after recrystallization gave a *single* resonance at +222.5 ppm in acetone. This is possible only if the Mo_2^{4+} unit has remained intact. A summary of crystal data, data refinement and structure refinement is presented in Table 4. The intensities of a $0.2 \times 0.40 \times 0.40$ mm crystal were collected with monochromatized Mo-K_α radiation using the θ–2θ scan technique and line profile analysis.[11] 6654 unique reflections were collected, of which 3262 were judged significant at the 3σ(Inet) level. Corrections were applied for Lorentz and polarization effects but absorption corrections were not made ($\mu = 0.78$ mm^{-1}).[12] Cell parameters were obtained from the setting angles of 56 reflections with $2\theta > 40°$. The structure was solved by MULTAN and hydrogen positions were calculated. The structure was refined by full-matrix least-squares to final residuals of $R_F = 0.056$ and $R_{WF} = 0.063$. The final atomic positional parameters of non-hydrogen atoms and equivalent isotropic thermal factors, as well as complete bond distance and angle tables are included in the supplementary materials.

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