Reactivity of $[NBu_4]_2[Mo_2Br_6]$ with Several Uni- and Poly-dentate Phosphines. *X*-Ray Structure of $[NBu_4][MoBr_4(Ph_2PCH_2CH_2PPh_2)]$ †

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The reactions of $[NBu_4]_2[Mo_2Br_6]$ with the unidentate phosphines $PEtPh_2$, PEt_2Ph, and PEt_3 and the polydentate phosphines $Ph_2PCH_2CH_2PPh_2$ and $PPh(CH_2CH_2PPh_2)_2$ have been studied. Substitution of one or two bromide ligands may take place depending upon the reaction conditions. Ionic and neutral, mono- and bi-nuclear molybdenum compounds were obtained and characterized by analytical and *X*-ray diffraction methods, and by visible, i.r., and ^{31}P n.m.r. spectroscopy. A general reaction scheme is proposed.

The reactions of $[NBu_4][Mo_2Br_6]$ (molybdenum formal oxidation state of +2.5 with a possible metal–metal bond order of 2.5 derived from the paramagnetism [1]) with uni- and bi-dentate phosphines afford molybdenum(II) complexes $[Mo_2Br_4L_4]$ and $[Mo_2Br_4(L\text{–}L)_2]$ respectively, where L = alkylphosphine or alkylphenylphosphine, L–L = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Ph_2AsCH_2CH_2PPh_2$.[2,3]

Recently, the synthesis and oxidation–reduction behaviour of the diamagnetic compound $[NBu_4]_2[Mo_2Br_6]$ were reported.[4] In this work we study the reactions of $[NBu_4]_2[Mo_2Br_6]$ with the unidentate phosphines $PEtPh_2$, PEt_2Ph, and PEt_3, and the polydentate phosphines dppe and $PPh(CH_2CH_2PPh_2)_2$ (bdpp). The products were characterized by analytical, spectroscopic (visible, i.r., and ^{31}P n.m.r.), and *X*-ray diffraction methods. A general reaction scheme is proposed.

Results and Discussion

Reaction of $[Mo_2Br_6]^{2-}$ *with Unidentate Phosphines.*—The reaction of $[NBu_4]_2[Mo_2Br_6]$ with the phosphines (L) $PEtPh_2$, PEt_2Ph, and PEt_3 affords different products depending upon the time of reaction and stoicheiometry, according to equations (1)—(3). Reactions (1) and (3) show the stepwise substitution of Br by L with subsequent formation of NBu_4Br. However, if reaction (3) is stopped after 15–30 h (depending upon the type of phosphine, see Experimental section) we obtain single complexes as in reaction (2), which shows that these substitution reactions may take place in several steps, *e.g.* phosphine addition followed by NBu_4Br elimination. The single complex obtained in reaction (2) also shows that the elimination is slow for reactions with unidentate phosphines.

$$[NBu_4]_2[Mo_2Br_6] + 2L \xrightarrow[24\text{—}48\ h]{\text{reflux, }Me_2CO} [NBu_4][Mo_2Br_5L_2] + NBu_4Br \quad (1)$$

$$[NBu_4]_2[Mo_2Br_6] + 4L \xrightarrow[15\text{—}30\ h]{\text{reflux, }Me_2CO} [NBu_4][Mo_2Br_5L_4] + NBu_4Br \quad (2)$$

$$[NBu_4]_2[Mo_2Br_6] + 4L \xrightarrow[24\text{—}48\ h]{\text{reflux, }Me_2CO} [Mo_2Br_4L_4] + 2NBu_4Br \quad (3)$$

Reaction of $[Mo_2Br_6]^{2-}$ *with Polydentate Phosphines.*—The reaction of $[NBu_4]_2[Mo_2Br_6]$ with the phosphines (L–L) dppe and bdpp affords analogues of the complexes formed in reactions (1) and (3), depending upon the reaction time and stoicheiometry, according to equations (4) and (5). The corresponding analogue to the complex formed in reaction (2) can be obtained when $[NBu_4][Mo_2Br_5(L\text{–}L)_2]$ is isolated from a sample of the mixture obtained after 2 h of reaction (5). The components of this sample were isolated and their analyses (see Table 1) revealed the products $[NBu_4][Mo_2Br_5(L\text{–}L)]$, $[NBu_4][Mo_2Br_5(L\text{–}L)_2]$, and $[Mo_2Br_4(L\text{–}L)_2]$. Thus, in addition to reactions (4) and (5), which show the same stepwise substitutions of Br by L–L as those shown for unidentate phosphines, we found, an analogous mechanism of phosphine addition followed by NBu_4Br elimination. The mixture of complexes obtained from the sample after 2 h of reaction shows that the elimination is faster for reactions with polydentate phosphines.

$$[NBu_4]_2[Mo_2Br_6] + L\text{–}L \xrightarrow[5\ h]{\text{reflux, }Me_2CO} [NBu_4][Mo_2Br_5(L\text{–}L)] + NBu_4Br \quad (4)$$

$$[NBu_4]_2[Mo_2Br_6] + 2(L\text{–}L) \xrightarrow[5\ h]{\text{reflux, }Me_2CO} [Mo_2Br_4(L\text{–}L)_2] + 2NBu_4Br \quad (5)$$

Spectroscopic Study.—Table 1 gives electronic and i.r. data. The electronic spectra of these compounds exhibit bands, in the visible region, which cannot be assigned to triple or quadruple metal–metal bonds.[1,3,5] In contrast with the diamagnetism, at room temperature, of $[NBu_4]_2[Mo_2Br_6]$,[4] all compounds in Table 1 are paramagnetic at 20 °C ($\mu_{eff.}$ = 4.3—4.6), indicating the probable absence of a metal–metal bond. The possibility of these compounds being mononuclear may be eliminated on the basis of the analytical results and the instability of co-ordination numbers lower than 5 in mononuclear compounds of Mo^{II}.

The i.r. spectra for the ionic compounds show the presence of the N–C stretching bands of $NBu_4{}^+$, between 1 200 and 1 000 cm^{-1}. The presence of characteristic skeletal (Ph) and out-of-

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† Tetrabutylammonium [1,2-bis(diphenylphosphino)ethane-*PP′*]tetrabromomolybdate(III).

Supplementary data available (No. SUP 56288, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical results, colour, i.r. and electronic spectra data for the compounds formed in the reactions of $[NBu_4]_2[Mo_2Br_6]$ with PEt_3, PEt_2Ph, $PEtPh_2$, dppe, and bdpp

	Analysis[a]/%						
Compound	C	H	N	Mo	Colour	Electronic[b] bands (nm)	I.r. bands[c] (cm^{-1})
$[NBu_4][Mo_2Br_5(PEt_3)_2]$	31.6 (31.4)	6.3 (6.2)	1.4 (1.3)	17.5 (17.9)	Yellow-orange	470m, 420m, 375s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 1 380 (CH_3)
$[NBu_4][Mo_2Br_5(PEt_3)_4]$	38.5 (37.0)	7.4 (7.35)	1.2 (1.1)	14.5 (14.7)	Yellow	470m-w, 420m, 375s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 1 380 (CH_3)
$[Mo_2Br_4(PEt_3)_4]$	29.4 (29.3)	6.1 (6.1)	—	19.3 (19.5)	Yellow-orange	435m, 365s	1 380 (CH_3)
$[NBu_4][Mo_2Br_5(PEt_2Ph)_4]$	45.0 (44.9)	6.6 (6.4)	1.0 (0.9)	12.2 (12.8)	Yellow-orange	460m, 420m, 375s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 770—680 (o.o.p. Ph–H), 490 (ske. Ph)
$[Mo_2Br_4(PEt_2Ph)_4]$	41.3 (40.8)	5.3 (5.1)	—	15.7 (16.3)	Orange	430m, 370s	770—680 (o.o.p. Ph–H), 490 (ske. Ph)
$[Mo_2Br_4(PEtPh_2)_4]$	48.7 (49.1)	4.5 (4.4)	—	13.7 (14.0)	Orange	470w, 420m, 380s	740—690 (o.o.p. Ph–H), 500 (ske. Ph)
$[NBu_4][Mo_2Br_5(dppe)]$	41.9 (41.0)	5.0 (4.9)	1.0 (1.1)	14.9 (15.6)	Brown	460m, 420m, 375s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 740, 680 (o.o.p. Ph–H), 515 (ske. Ph)
$[NBu_4][Mo_2Br_5(dppe)_2]$	50.7 (50.1)	5.3 (5.15)	0.9 (0.85)	11.5 (11.8)	Yellow-orange	460m-w, 420m, 375s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 750—680 (o.o.p. Ph–H), 530—470 (ske. Ph)
$[Mo_2Br_4(dppe)_2]$	48.2 (47.7)	3.7 (3.65)	—	14.2 (14.6)	Orange	420m, 375s	750—680 (o.o.p. Ph–H), 530—470 (ske. Ph)
$[NBu_4][Mo_2Br_5(bdpp)]$	65.3 (65.0)	6.7 (6.5)	1.1 (1.0)	13.8 (14.0)	Yellow-orange	475m, 450, 370s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 740—690 (o.o.p. Ph–H), 530—480 (ske. Ph)
$[NBu_4][Mo_2Br_5(bdpp)_2]$	53.7 (53.0)	5.5 (5.3)	0.7 (0.7)	10.4 (10.1)	Yellow-orange	475w, 450m, 370s	3 000—2 800 (C–H), 1 200—1 000 (N–C), 730—690 (o.o.p. Ph–H), 530—480 (ske. Ph)
$[Mo_2Br_4(bdpp)_2]$	52.3 (51.7)	4.5 (4.2)	—	11.8 (12.1)	Orange	450m, 370s	730, 690 (o.o.p. Ph–H), 540, 510 (ske. Ph)

[a] Calculated values in parentheses. [b] Spectra of degassed dichloromethane solutions. [c] Spectra of KBr discs. o.o.p. = Out of plane; ske. = skeletal.

Table 2. Atomic positional parameters

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo	4 458(2)	3 868(3)	7 388(1)	C(123)	5 742(22)	1 215(20)	5 346(10)
Br(1)	3 435(3)	4 219(6)	8 240(2)	C(124)	4 871(22)	1 189(20)	5 017(10)
Br(2)	3 215(3)	4 283(5)	6 474(2)	C(125)	4 216(22)	1 796(20)	5 179(10)
Br(3)	8 996(3)	2 849(5)	7 341(2)	C(126)	4 432(22)	2 429(20)	5 669(10)
Br(4)	5 170(4)	5 486(6)	7 446(2)	C(211)	6 244(31)	4 456(25)	8 804(14)
P(1)	5 576(7)	3 378(8)	6 672(4)	C(212)	5 627(31)	4 870(25)	9 148(14)
P(2)	5 779(8)	3 418(7)	8 203(5)	C(213)	5 929(31)	5 456(25)	9 651(14)
C(11)	6 448(29)	2 623(23)	7 204(13)	C(214)	6 848(31)	5 629(25)	9 810(14)
C(21)	6 785(29)	3 224(19)	7 769(16)	C(215)	7 465(31)	5 215(25)	9 466(14)
C(111)	6 147(22)	4 182(12)	6 187(9)	C(216)	7 163(31)	4 629(25)	8 963(14)
C(112)	7 077(22)	4 203(12)	6 184(9)	C(221)	5 711(23)	2 389(11)	8 664(17)
C(113)	7 460(22)	4 906(12)	5 861(9)	C(222)	4 954(23)	2 256(11)	8 965(17)
C(114)	6 914(22)	5 587(12)	5 542(9)	C(223)	4 781(23)	1 384(11)	9 206(17)
C(115)	5 985(22)	5 566(12)	5 545(9)	C(224)	5 365(23)	646(11)	9 145(17)
C(116)	5 601(22)	4 863(12)	5 868(9)	C(225)	6 122(23)	780(11)	8 844(17)
C(121)	5 303(22)	2 455(20)	5 998(10)	C(226)	6 295(23)	1 651(11)	8 604(17)
C(122)	5 958(22)	1 848(20)	5 836(10)				

plane (Ph–H) deformation bands for the metal-bonded phenylphosphines[6] was found between 550 and 470 and 800 and 680 cm^{-1} respectively. The identification either of the chelating or bridging behaviour of the metal-bonded dppe was achieved from the skeletal (Ph) deformation bands. Figure 1 shows this region for our compounds compared with others from the literature,[3] revealing the clear and more intense band below 500 cm^{-1} when chelating dppe is present.

Table 3. Selected interatomic distances (Å) and angles (°) in $[MoBr_4(dppe)]^-$

Br(1)–Mo	2.593(4)	Br(2)–Mo–Br(1)	93.1(1)	C(111)–P(1)–Mo	124.5(7)	C(21)–C(11)–P(1)	105.7(12)
Br(2)–Mo	2.580(4)	Br(4)–Mo–Br(1)	94.1(2)	C(111)–P(1)–C(11)	110.8(13)	C(11)–C(21)–P(2)	105.0(23)
Br(3)–Mo	2.568(4)	Br(4)–Mo–Br(2)	94.5(2)	C(121)–P(1)–Mo	123.2(8)	C(112)–C(111)–P(1)	124.0(8)
Br(4)–Mo	2.561(6)	P(1)–Mo–Br(1)	171.9(2)	C(121)–P(1)–C(11)	96.2(10)	C(116)–C(111)–P(1)	115.6(8)
P(1)–Mo	2.528(8)	P(1)–Mo–Br(2)	94.2(2)	C(121)–P(1)–C(111)	94.4(9)	C(122)–C(121)–P(1)	121.7(8)
P(2)–Mo	2.536(8)	P(1)–Mo–Br(4)	88.7(2)	C(21)–P(2)–Mo	107.3(7)	C(126)–C(121)–P(1)	118.3(8)
C(11)–P(1)	1.944(25)	P(2)–Mo–Br(1)	92.6(2)	C(211)–P(2)–Mo	114.5(10)	C(212)–C(211)–P(2)	117.1(11)
C(111)–P(1)	1.844(18)	P(2)–Mo–Br(4)	85.4(2)	C(211)–P(2)–C(21)	101.1(13)	C(216)–C(211)–P(2)	121.7(11)
C(121)–P(1)	1.954(15)	P(2)–Mo–P(1)	80.0(2)	C(221)–P(2)–Mo	119.5(9)	C(222)–C(221)–P(2)	118.8(8)
C(21)–P(2)	1.901(37)	P(2)–Mo–Br(2)	174.2(2)	C(221)–P(2)–C(21)	105.0(11)	C(226)–C(221)–P(2)	119.6(8)
C(211)–P(2)	2.032(18)	C(11)–P(1)–Mo	104.3(8)	C(221)–P(2)–C(221)	107.5(12)		
C(221)–P(2)	1.793(18)						
C(21)–C(11)	1.517(27)						

Table 4. Selected dihedral angles (°) in $[MoBr_4(dppe)]^-$

Br(1)–Mo–P(1)–C(11)	−5.6(3)	P(2)–Mo–P(1)–C(121)	126.6(3)
Br(1)–Mo–P(1)–C(111)	−133.9(3)	Br(1)–Mo–P(2)–C(21)	−173.5(3)
Br(1)–Mo–P(1)–C(121)	101.9(3)	Br(1)–Mo–P(2)–C(221)	67.4(3)
Br(2)–Mo–P(1)–C(11)	−160.9(3)	Br(2)–Mo–P(2)–C(21)	8.9(3)
Br(2)–Mo–P(1)–C(111)	70.7(3)	Br(2)–Mo–P(2)–C(221)	−110.2(3)
Br(2)–Mo–P(1)–C(121)	−53.5(3)	Br(3)–Mo–P(2)–C(21)	94.7(3)
Br(3)–Mo–P(1)–C(11)	−69.6(3)	Br(3)–Mo–P(2)–C(221)	−24.4(3)
Br(3)–Mo–P(1)–C(111)	162.1(3)	Br(4)–Mo–P(2)–C(21)	−79.6(3)
Br(3)–Mo–P(1)–C(121)	37.9(3)	Br(4)–Mo–P(2)–C(221)	161.3(3)
Br(4)–Mo–P(1)–C(11)	104.7(3)	P(1)–Mo–P(2)–C(21)	9.9(3)
Br(4)–Mo–P(1)–C(111)	−23.7(3)	P(1)–Mo–P(2)–C(221)	−109.3(3)
Br(4)–Mo–P(1)–C(121)	−147.8(3)	Mo–P(1)–C(11)–C(21)	−54.9(1)
P(2)–Mo–P(1)–C(11)	19.1(3)	Mo–P(2)–C(21)–C(11)	−16.9(1)
P(2)–Mo–P(1)–C(111)	−109.2(3)		

The chelating or bridging behaviour of the molybdenum-bonded dppe may also be investigated by ^{31}P n.m.r. spectroscopy, since it shows a peak at *ca.* 54 p.p.m. {52 p.p.m. for $[Mo_2Br_4(dppe)_2]$, this work} when behaving as a chelating ligand and a peak shifted upfield {38 p.p.m. for $[NBu_4][Mo_2Br_5(dppe)]$, this work} when behaving as a bridging ligand.[7]

Formation of Mononuclear Molybdenum Compounds.—The reaction of $[NBu_4]_2[Mo_2Br_6]$ with dppe in Me_2CO gives as a major product $[Mo_2Br_4(dppe)_2]$ (see above), however, the minor products $[NBu_4]_2[MoBr_3(dppe)(Me_2CO)]$ and $[NBu_4][MoBr_4(dppe)]$ were obtained from the filtrate and characterized by analyses. The latter was crystallized from the filtrate and its structure (Figure 2) determined by single-crystal *X*-ray diffraction. The atomic positional parameters are listed in Table 2, bond lengths and angles in Table 3, and dihedral angles in Table 4. The structure consists of discrete ions linked by ionic and van der Waals forces. The Mo atom displays a distorted octahedral co-ordination with narrow P(1)–Mo–P(2), P(1)–Mo–Br(4), and P(2)–Mo–Br(4) bond angles, which produces an enlargement of the remaining bond angles at Mo.

To conclude, the general reaction Scheme may be proposed, for the above reaction conditions.

Experimental

Materials.—All products were reagent grade. Solvents were degassed and dried. Compounds were prepared by standard Schlenk techniques, and using a vacuum–nitrogen manifold.

Apparatus.—Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. The molybdenum determination was performed according to a literature procedure.[8] Electronic and vibrational spectra were recorded with Beckman 5260 and 4260 spectrophotometers using KBr discs for the latter. Phosphorus-31 n.m.r. spectra, relative to external H_3PO_4, were recorded with a Varian XL 200 spectrometer, using *ca.* 0.5 mol dm^{-3} solutions in degassed CD_2Cl_2.

$$\begin{tikzcd}
{[NBu_4]_2[Mo_2Br_6] + 2L\ (\mathrm{or}\ L\text{–}L)} \arrow[r, "-NBu_4Br"] & {[NBu_4][Mo_2Br_5L_2]\ \{\mathrm{or}\ [NBu_4][Mo_2Br_5(L\text{–}L)]\}} \arrow[d, "+2L\ (\mathrm{or}\ L\text{–}L)"] \\
{[Mo_2Br_4L_4]\ \{\mathrm{or}\ [Mo_2Br_4(L\text{–}L)_2]\}} & {[NBu_4][Mo_2Br_5L_4]\ \{\mathrm{or}\ [NBu_4][Mo_2Br_5(L\text{–}L)_2]\}} \arrow[l, "-NBu_4Br"']
\end{tikzcd}$$

$$[NBu_4][Mo_2Br_5(dppe)_2] + 2NBu_4Br \xrightarrow{+Me_2CO} [NBu_4][MoBr_4(dppe)] + [NBu_4]_2[MoBr_3(dppe)(Me_2CO)]$$

Scheme. L = $PEtPh_2$, PEt_2Ph, or PEt_3; L–L = dppe or bdpp

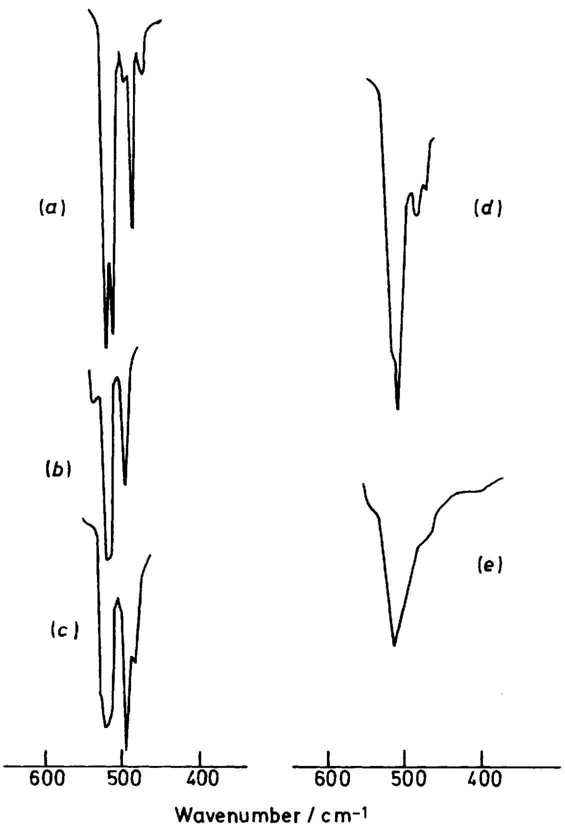

Figure 1. Comparative i.r. bands (σ skeletal Ph) of chelating [(*a*)–(*c*)] and bridging [(*d*), (*e*)] dppe ligand in molybdenum compounds: (*a*) α-$[Mo_2Cl_4(dppe)_2]$,[3] (*b*) $[NBu_4][MoBr_4(dppe)]$ (this work), (*c*) $[Mo_2Br_4(dppe)_2]$ (this work), (*d*) β-$[Mo_2Cl_4(dppe)_2]$,[3] and (*e*) $[NBu_4][Mo_2Br_5(dppe)]$ (this work)

Preparation of Dimolybdenum(II) *Bromo-complexes*.—(*a*) Addition of unidentate phosphine (0.44 mmol; L = $PEtPh_2$, PEt_2Ph, or PEt_3) or bidentate phosphine (0.22 mmol; L–L = dppe or bdpp) to a solution of $[NBu_4]_2[Mo_2Br_6]$ (0.25 g, 0.22 mmol) in Me_2CO (20 cm^3) afforded $[NBu_4][Mo_2Br_5L_2]$ after reflux for 24 h, or $[NBu_4][Mo_2Br_5(L\text{–}L)]$ after reflux for 5 h. The precipitates obtained after addition of Et_2O were filtered off, washed with MeOH and Et_2O, and dried *in vacuo*. Yields: 20, 29, 44, 34, and 34% for the $PEtPh_2$, PEt_2Ph, PEt_3, dppe, and bdpp derivatives, respectively.

(*b*) To a solution of $[NBu_4]_2[Mo_2Br_6]$ (0.25 g, 0.22 mmol) in Me_2CO (20 cm^3) was added unidentate phosphine (0.88 mmol; L = PEt_2Ph or PEt_3) or bidentate phosphine (0.44 mmol; L–L = dppe or bdpp). The solutions were refluxed for 20, 15, or 2 h, respectively. The products obtained, $[NBu_4][Mo_2Br_5L_4]$ or $[NBu_4][Mo_2Br_5(L\text{–}L)_2]$, were filtered off, washed with MeOH and Et_2O, and dried *in vacuo*. Yields: 44, 53, 26, and 22% respectively.

(*c*) Addition of unidentate phosphine (1.15 mmol; L = $PEtPh_2$, PEt_2Ph, or PEt_3) or bidentate phosphine (0.57 mmol; L–L = dppe or bdpp) to a solution of $[NBu_4][Mo_2Br_6]$ (0.33 g, 0.29 mmol) in Me_2CO (25 cm^3) afforded $[Mo_2Br_4L_4]$ after refluxing for 48, 40, and 24 h, respectively, or $[Mo_2Br_4(L\text{–}L)_2]$ after 5 h. The precipitates obtained after addition of Et_2O were filtered off, washed with MeOH and Et_2O, and dried *in vacuo*. Yields: 20, 30, 46, 30, and 30% respectively.

Preparation of Mononuclear Molybdenum Bromo-complexes.—If the filtrate from procedure (*c*) for the dppe derivative is left to stand for 24 h, red crystals of the mononuclear compound $[NBu_4][MoBr_4(dppe)]$ can be separated from the yellow product $[NBu_4]_2[MoBr_3(dppe)(Me_2CO)]$. Analyses (calc. values in parentheses): C, 47.4 (47.7); H, 5.6 (5.6); Mo, 7.0 (7.1); N, 1.3 (1.3); and C, 58.1 (57.4); H, 8.3 (8.0); Mo, 7.3 (7.5); N, 2.1 (2.2)%, respectively.

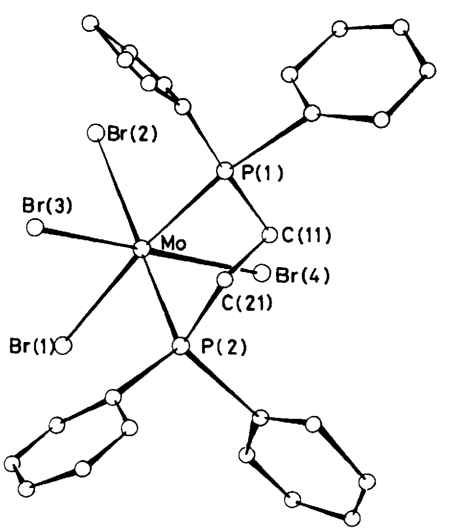

Figure 2. View of the crystal structure of $[MoBr_4(dppe)]^-$ with the atom numbering

Crystallography for $[NBu_4][MoBr_4(dppe)]$.—*Crystal data*. $C_{38}H_{34}Br_4MoNP_2$, $M = 982.22$, monoclinic, $a = 14.992(5)$, $b = 14.441(5)$, $c = 21.438(7)$ Å, $\beta = 98.02(3)^\circ$, $U = 4\,586(5)$ Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.42$ g cm^{-3}, $F(000) = 1\,924$, $\lambda(\text{Cu-}K_\alpha) = 1.540\,56$ Å, $\mu(\text{Cu-}K_\alpha) = 78.34$ cm^{-1}.

A small crystal (0.1 × 0.1 × 0.08 mm) was mounted on a Picker *P*2, four-circle diffractometer. Cell parameters were measured from 15 independent reflections. Intensities were collected with graphite-monochromatized Cu-K_α radiation using the ω-scan technique with a scan width of 1.2°. 4 567 Independent reflections were collected for $\theta \leqslant 56.5^\circ$, 2 000 of which were considered 'observed' [$I \geqslant 2.5\sigma(I)$]. Three control reflections were measured every 2 h, but significant differences were not observed. Lorentz, polarization, and absorption corrections were made.

The structure was solved by direct methods using the MULTAN system of computer programs.[9] An *E* map computed from the set with the highest combined figure of merit revealed peaks for 34 atoms. The structure was refined by full-matrix least squares using the SHELX 76 computer program.[10] The function minimized was $w||F_o| - |F_c||^2$, where $w = 1/\sigma(F_o)$ and the phenyl rings were refined with lengths and bond angles constrained to 1.395 Å and 120°, respectively. Isotropic refinements converged at $R = 0.21$. A difference synthesis at this stage showed sensitive peaks assigned to C atoms of the tetrabutylammonium group. Anisotropic refinements for non-hydrogen atoms of the anion isotropic for the cation led to $R = 0.12$. Difference syntheses at different stages of this refinement did not locate the disorder of the tetrabutylammonium ion. Absorption corrections and an ulterior least-squares refinement led to a final *R* of 0.089 for all observed reflections. A final Fourier difference synthesis did not yield the hydrogen-atom co-ordinates, owing to the disorder of the tetrabutylammonium ion, and showed several peaks of 0.3 e Å^{-3} around the cation.

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