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**SYNTHESIS AND STRUCTURE OF BIS(1,2-BISDIPHENYL-
PHOSPHINOETHANE)HEXAHALODIMOLYBDENUM(III),
Mo₂X₆(dppe)₂ (X = Cl, Br, I) (*) (**)**

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Summary - The title compounds have been obtained by dimerization of MoX₂(dppe)(THF) following THF loss in non-coordinating solvents. The chloride compound has been crystallographically characterized as Mo₂Cl₆(dppe)₂·4CH₂Cl₂: monoclinic, space group *P2₁/n*, *a* = 13.846(1), *b* = 18.204(2), *c* = 15.479(1) Å, *β* = 108.589(7)°, *V* = 3698(1) Å³, *Z* = 2, *D_c* = 1.38 g cm⁻³, *μ*(Cu-Kα) = 86.21 cm⁻¹, *R* = 0.073, *R_w* = 0.104 for 365 parameters and 4804 unique data, of which 2823 were observed [*F_o*² > 3σ(*F_o*²)]. The compound has an edge-sharing bioctahedral configuration and the two metals are separated at a distance of 2.767(2) Å.

(*) Work supported by the Petroleum Research Fund, administered by the American Chemical Society. Additional support from the Camille and Henry Dreyfus foundation through a Distinguished New faculty Award to R.P. (1987-92) is also gratefully acknowledged.

(**) Observed and calculated structure factors for Mo₂Cl₆(dppe) have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW, U.K.

(°) To whom correspondence should be addressed. Camille and Henry Dreyfus Distinguished New Faculty, 1987-92; Presidential Young Investigator, 1990-95.

We have recently reported the large-scale preparation of $\text{MoBr}_3(\text{THF})_3$ ¹ and $\text{MoI}_3(\text{THF})_3$ ² (THF = tetrahydrofuran) by a new synthetic approach, via oxidative decarbonylation of lower-valent carbonyl derivatives. We have also reported the ligand exchange reactivity of the $\text{MoX}_3(\text{THF})_3$ (X = Cl, Br, I) series of compounds with the ligand 1,2-bis(diphenylphosphino)ethane, henceforth abbreviated dppe. The mixed-ligand compounds $\text{MoX}_3(\text{dppe})\text{L}$ (L = THF, MeCN, PMe₃) were obtained and isolated.¹ We have observed that when the $\text{MoX}_3(\text{dppe})(\text{THF})$ derivatives are placed in a non-coordinating solvent, the THF molecule is lost and new compounds corresponding to the formulation $\text{MoX}_3(\text{dppe})$ are obtained. The results obtained on the bromide system have been previously communicated.³ In this paper we report a full account of this reactivity and the crystal structure of the chloride compound, $\text{Mo}_2\text{Cl}_6(\text{dppe})_2 \cdot 4\text{CH}_2\text{Cl}_2$.

EXPERIMENTAL

All operations were carried out under an atmosphere of predried dinitrogen. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. FTIR spectra were recorded on a Nicolet SDXC spectrophotometer. EPR experiments were carried out on a Bruker ER200 spectrometer. Magnetic susceptibility studies were performed at room temperature by a modified Gouy method with a magnetic balance developed by Professor D.F. Evans at the Imperial College of Science and Technology, London, and commercially available from Johnson Matthey.

Elemental analyses were by Galbraith Laboratories, Knoxville, TN, and by Midwest Microlab, Indianapolis, IN. The $\text{MoX}_3(\text{dppe})(\text{THF})$ (X = Cl, Br, I) compounds were prepared in situ as described previously.¹

Synthesis of $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$

(a) From $\text{MoCl}_3(\text{dppe})(\text{THF})$ in CH_2Cl_2 - $\text{MoCl}_3(\text{THF})_3$ (1.891 g, 4.517 mmol) was suspended in a solution of dppe (1.800 g, 4.52 mmol) in 50 ml of THF. Stirring at room temperature for 24 h produced a solution of $\text{MoCl}_3(\text{dppe})(\text{THF})$ as described previously.¹ After filtration, the solvent was completely removed by evaporation under reduced pressure and the residue redissolved in CH_2Cl_2 (50 ml). The solution immediately turned reddish-purple. A small crop of purple crystalline material (63 mg) was obtained upon cooling to -20 °C. Partial removal of the solvent and further cooling to -20 °C produced another 532 mg of the same material (total 595 mg, 17.1% yield). A single crystal of this crop was used for the X-ray crystallographic study. IR (Nujol mull/cm⁻¹): 1585 w, 1575 m, 1485 s, 1435 vs, 1415 w, 1410 w, 1365 m, 1335 w, 1310 w, 1305 w, 1275 vw, 1260 m, 1190 m, 1160 m, 1095 s, 1070 m, 1030 m, 1000 s, 970 vw, 965 vw, 865 s, 835 m, 810 w, 705 sh, 700 vs, 690 vs, 655

m, 615 m, 525 vw, 515 vs, 495 m, 490 m, 480 m, 440 w, 420 w, 415 m. UV/VIS [CH_2Cl_2 ; λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 306 (41,800) 385 sh (430), 508 (1920). This crystalline solid did not redissolve in CD_2Cl_2 to an extent sufficient for an NMR investigation to be carried out. In a separate synthetic run, the purple solution obtained after dissolution in CH_2Cl_2 was concentrated to a small volume and a portion was added to 1 g of CD_2Cl_2 . The resulting solution was investigated by NMR. ^1H -NMR, δ : 8.3-7.0 m (Ph); 2.88 ppm (CH_2 , broad). Peaks due to free THF at δ 3.71 and 1.84 ppm (THF/dppe = 1:1) were also observed. ^{31}P [^1H]-NMR, δ : 42.96 ppm. The solid compound shows a marked tendency to loose solvent of crystallization upon evacuation. An analyzed sample showed the approximate composition $\text{Mo}_2\text{Cl}_6(\text{dppe})_2\text{-CH}_2\text{Cl}_2$: calcd. for $\text{C}_{53}\text{H}_{50}\text{Cl}_8\text{Mo}_2\text{P}_4$: C, 49.9; H, 3.9%. Found: C, 50.1; H, 3.8.

When the mother solution of the purple crystals was exposed to air, the crystallization of an orange material was observed. This material has similar solid-state IR and identical UV/VIS spectroscopic properties as those of the purple material and its properties and colour seem identical to those of the compound reported by Cotton *et al.*⁴ Yield 2.040 g, 58.6%.

(b) From $\text{MoCl}_3(\text{dppe})(\text{THF})$ in toluene - $\text{MoCl}_3(\text{dppe})(\text{THF})$ (1.043 g, 1.550 mmol) was placed in toluene (50 ml), affording a purple solution and generating a purple flocculent precipitate. After stirring at room temperature for 24 h, the solid was filtered, washed with toluene, and dried in vacuo; yield 0.468 g (50.3%). *Elem. anal.*, found % (calcd. for $\text{C}_{26}\text{H}_{24}\text{Cl}_3\text{MoP}_2$): C, 52.5 (52.0); H, 4.2 (4.0); Cl, 16.8 (17.7). The IR spectrum closely parallels that of the compound obtained from dichloromethane. When either the purple or the orange material was placed in THF at room temperature for long periods of time (several days), the formation of a less soluble pink precipitate was observed. This material was also obtained from THF solutions of $\text{MoCl}_3(\text{dppe})(\text{THF})$ at room temperature or, more rapidly, at reflux. The IR properties of this compound are similar to those of the purple and the orange crystals. *Elem. anal.*, found %: C, 51.49; H, 4.12; Cl, 17.15.

This pink material was also obtained, in admixture with the previously reported¹ $\text{MoCl}_3(\text{dppe})(\text{MeCN})$, when the orange crystals were placed in MeCN, as shown by IR spectroscopy.

Synthesis of $\text{Mo}_2\text{Br}_6(\text{dppe})_2$. Green isomer

(a) From $\text{MoBr}_3(\text{dppe})(\text{THF})$ in toluene - $\text{MoBr}_3(\text{dppe})(\text{THF})$ was generated from $\text{MoBr}_3(\text{THF})_3$ (537 mg, 0.973 mmol) and dppe (392 mg, 0.984 mmol) in THF (20 ml) as described previously.¹ The solvent was completely removed by evaporation under reduced pressure and the residue was treated with toluene (10 ml). The resulting dark yellow-brown solution, containing a small amount of a flocculent precipitate, was stirred at room temperature overnight, resulting in the precipitation of more solid. This was filtered, washed with toluene and dried under vacuum: 0.424 g

(59.4%) of a pale green-brown solid was obtained. *Elem. anal.*, found % (calcd for $C_{26}H_{24}Br_3MoP_2$): C, 42.5 (42.5); H, 3.5 (3.3); Br, 30.7 (32.6). $\chi_g = 2.90 \times 10^{-6}$ cgsu; $\mu = 3.43 \mu_B$ ($2.42 \mu_B$ per Mo) (diamagnetic correction = 334.4×10^{-6} cgsu from Pascal's constants). IR (Nujol mull/cm⁻¹): 3060 w, 1590 m, 1575 m, 1485 s, 1435 vs, 1415 1112, 1370 s, 1340 vw, 1315 vw, 1275 vw, 1190 m, 1160 m, 1100 s, 1075 w, 1030 m, 1000 m, 870 m, 850 w, 825 w, 750 sh, 730 s, 705 sh, 695 vs, 650 vw, 620 w, 525 sh, 515 vs, 495 m, 465 w. Any attempt to dissolve this material (THF, CH₂Cl₂, hot toluene) resulted in at least partial conversion to the purple isomer, *vide infra*.

(b) From $MoBr_3(THF)_3$ and dppe in toluene - $MoBr_3(THF)_3$ (0.130 g, 0.236 mmol) and dppe (0.094 g, 0.24 mmol) were placed in toluene (4 ml) and stirred at room temperature. The solid changed colour to green over ca. 7 days. The solid was filtered, washed with toluene, and dried *in vacuo*; yield 81 mg (47%). Analytical and IR properties of this material compared with those of the compound obtained from $MoBr_3(dppe)(THF)$ (see above).

Synthesis of $Mo_2Br_6(dppe)_2$. Purple isomer

$MoBr_3(dppe)(THF)$ was generated from $MoBr_3(THF)_3$ (2.257 g, 4.089 mmol) and dppe (1.630 g, 4.091 mmol) as described above. After removal of the THF solvent, the residue was dissolved in 30 ml of CH₂Cl₂ and the resulting solution stirred at room temperature. A purple crystalline solid slowly precipitated. It was filtered, washed with CH₂Cl₂, and dried under vacuum. Yield 1.558 g (52%). $\chi_g = (0.00 \pm 0.03) \times 10^{-6}$ cgsu. IR (Nujol mull/cm⁻¹): 3050 w, 1590 m, 1580 m, 1490 s, 1440 vs, 1415 m, 1365 s, 1300 w, 1275 vw, 1195 m, 1160 m, 1100 s, 1075 w, 1030 m, 1005 m, 870 m, 830 w, 815 w, 735 s, 730 s, 705 s, 695 vs, 650 vw, 620 w, 525 s, 520 s, 500 m, 475 w. UV/VIS [CH₂Cl₂, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)]: 345 (25,800), 555 (2,040). This compound gave analyses consistent with the incorporation of variable amounts of crystallization solvent. A sample obtained from $MoBr_3(dppe)(THF)$ in refluxing toluene analyzed correctly. Found: C, 42.8; H, 3.2; Br, 32.2. A single crystal was obtained by recrystallization from hot CHCl₃ and was found to consist of the dinuclear $Mo_2Br_6(dppe)_2$ unit with four CHCl₃ molecules of solvation.³

Treatment of $MoI_3(dppe)(THF)$ in toluene. Formation of $[MoI_3(dppe)]_x$.

A THF solution of $MoI_3(dppe)(THF)$ was generated as reported earlier¹ from $MoI_3(THF)_3$ (1.420 g, 2.049 mmol) and dppe (0.817 g, 2.050 mmol). After filtration, the solvent was completely removed by evaporation under reduced pressure, and the residue was taken up in toluene (40 ml). The resulting suspension was stirred at room temperature for 10 h. The red-brown precipitate was filtered, washed with toluene, and dried under vacuum. Yield 1.04 g (72%). *Elem. anal.*, found % (calcd. for $C_{26}H_{24}I_3MoP_2$): C, 35.5 (35.7); H, 2.6 (2.8); I, 42.6 (43.5). $\chi_g = 1.52 \times 10^{-6}$ cgsu; $\mu = 2.87 \mu_B$ ($2.01 \mu_B$

per Mo) (diamagnetic correction = 757.1×10^{-6} cgsu from Pascal's constants). IR (Nujol mull/cm⁻¹): 1590 m, 1575 m, 1495 m, 1485 s, 1435 vs, 1365 s, 1335 w, 1310 w, 1275 w, 1199 m, 1160 w, 1090 m, 1070 vw, 1025 m, 1000 m, 970 vw, 940 vw, 915 vw, 860 m, 830 w, 815 vw, 720 m, 690 s, 615 w, 520 s, 510 s, 485 w, 470 w, 460 vw.

A compound with similar colour and IR properties was obtained by repeating the same procedure in CH₂Cl₂. The analysis of this material indicated the presence of dichloromethane of solvation.

X-ray data collection and structure analysis of Mo₂Cl₆(dppe)₂·4CH₂Cl₂

A single crystal was selected and mounted in a capillary under a solution of dichloromethane in mineral oil. The capillary was closed at both ends with epoxy resin and mounted on the goniometer head of the diffractometer. Crystal data are reported in table 1. No decay of intensity was observed during data collection. The data were corrected for Lorentz and polarization effects and for absorption.^{5a}

TABLE 1 - CRYSTAL DATA FOR Mo₂Cl₆(dppe)₂·4CH₂Cl₂

Formula	C ₅₆ H ₅₆ Cl ₁₄ Mo ₂ P ₄
FW	1541.18
Space group	<i>P</i> 2 ₁ / <i>n</i>
Systematic absences	<i>0k0</i> : <i>k</i> ≠ 2 <i>n</i> ; <i>h0l</i> : <i>h</i> + <i>l</i> ≠ 2 <i>n</i>
<i>a</i> , Å	13.846(1)
<i>b</i> , Å	18.204(2)
<i>c</i> , Å	15.479(1)
<i>α</i> , deg	90
<i>β</i> , deg	108.589(7)
<i>γ</i> , deg	90
<i>V</i> , Å ³	3698(1)
<i>Z</i>	2
<i>d</i> _{calc} , g/cm ³	1.38
Cryst. size, mm	0.5 x 0.4 x 0.3
μ(Cu Kα), cm ⁻¹	86.21
Data collection instrument	Enraf-Nonius CAD-4
Radiation (monochromated in incident beam)	Cu Kα (λ = 1.54178 Å)
Orientation reflcns: No.; range (2θ), deg	25; 30-50
<i>T</i> , °C	20
Scan method	ω-2θ
Data collecn range (2θ), deg	4-110
No. of unique data, total obsd	4804, 2823
No. of parameters refined	365
Transmission factors: max, min.	1.000, 0.828
<i>R</i> ^a	0.073

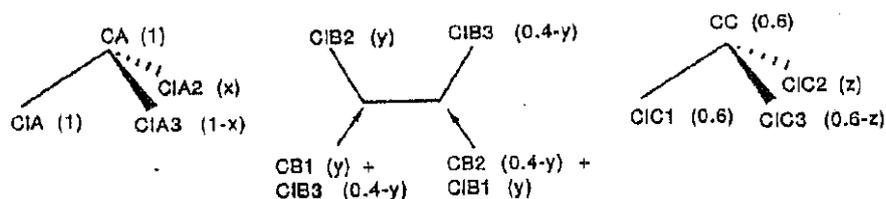
R_w^b	0.104
Quality of fit indicator ^c	3.26
Largest shift/esd, final cycle	0.62 ^d
Largest peak, e/Å ³	1.26 ^e

(^a) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. (^b) $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. (^c) Quality of fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{\text{observns}}-N_{\text{parameters}})]^{1/2}$. (^d) Largest shift/esd for the Mo₂Cl₂(dppe)₂ molecule: 0.107. (^e) Largest peak not associated with the interstitial solvent molecule: 0.53 e/Å³.

The structure was solved by direct methods and refined by alternate full-matrix least-squares cycles and difference Fourier maps with the TEXSAN package.^{5b} At the end of the refinement for the isotropic Mo₂Cl₆(dppe)₂ molecule ($R = 0.155$) several sets of peaks, which could be attributed to disordered dichloromethane molecules, were seen in the difference Fourier map. This situation is analogous to that described previously for the other crystalline phase of the same compound.⁴ A first molecule showed up as represented in A (numbers in parentheses are occupancies as used in the refinement). Free refinement on all the parameters did not result in good convergence because of high correlation. To eliminate this problem it was decided to constrain the occupancy of CIA2 and CIA3 such that their sum be one, and to restrain the C-Cl distances to 1.57(2) Å and the CIA1-CIA2 and CIA1-CIA3 distances to 2.65(5) Å. Two additional molecules were identified (molecules B and C). C presents the same type of disorder as A, whereas B has a new type of disorder as shown. The same restraints applied to cluster A (C-Cl and Cl-Cl distances) were also applied to clusters B and C.

Neither B nor C refined with acceptable thermal parameters at full occupancy. Therefore, they were treated as giving a total full occupancy among the two of them. The best refinement was achieved with a 40% occupancy for cluster B and 60% occupancy for cluster C.

The four highest peaks in the last difference Fourier map ($>1 \text{ e } \text{Å}^{-3}$) were at $<1.0 \text{ Å}$ from atoms of the B cluster. We cannot exclude that other, low occupancy, solvent regions are present, although we could not clearly identify any.



Refinement on these was carried out with the SHELX-76 package.^{5c} Hydrogen atoms were not included in the refinement. At the end of the full isotropic refinement, all the atoms of the Mo₂Cl₆(dppe)₂ molecule and all of the chlorine atoms of the disordered CH₂Cl₂ interstitial molecules except ClA3 and those of cluster B were allowed to refine with anisotropic thermal parameters. The agreement factor converged at $R = 0.073$. The high final agreement factor is probably the result of some residual disorder which could not be properly modelled. This is indicated by several peaks in the final difference Fourier map with a density between 1 and 1.26 e Å⁻³, all of which were found at <1 Å from chlorine atoms of the dichloromethane molecules.

Positional parameters are in table 2, and selected bond distances and angles are listed in table 3.

TABLE 2 - ATOMIC POSITIONAL PARAMETERS FOR Mo₂Cl₆(dppe)₂·4CH₂Cl₂^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.4902(1)	0.4251(1)	0.4850(1)
Cl(1)	0.5577(3)	0.5095(3)	0.3993(3)
Cl(2)	0.3235(3)	0.4254(3)	0.3744(3)
Cl(3)	0.6504(3)	0.3892(3)	0.5922(3)
P(1)	0.5324(4)	0.3292(3)	0.3814(3)
P(2)	0.4220(4)	0.3095(3)	0.5417(3)
C(1)	0.512(1)	0.240(1)	0.427(1)
C(2)	0.418(2)	0.241(1)	0.458(1)
C(10)	0.662(2)	0.320(1)	0.375(1)
C(11)	0.737(2)	0.375(1)	0.421(2)
C(12)	0.836(2)	0.364(2)	0.412(2)
C(13)	0.861(2)	0.304(2)	0.361(2)
C(14)	0.783(2)	0.254(2)	0.318(2)
C(15)	0.679(2)	0.259(2)	0.326(2)
C(20)	0.457(2)	0.325(1)	0.263(1)
C(21)	0.484(2)	0.368(2)	0.206(2)
C(22)	0.431(2)	0.379(2)	0.106(2)
C(23)	0.353(2)	0.322(2)	0.075(2)
C(24)	0.327(2)	0.273(2)	0.134(2)
C(25)	0.383(2)	0.276(1)	0.227(2)
C(30)	0.500(1)	0.270(1)	0.651(2)
C(31)	0.511(2)	0.308(2)	0.726(1)
C(32)	0.571(2)	0.276(2)	0.813(2)
C(33)	0.614(2)	0.210(2)	0.816(2)
C(34)	0.602(2)	0.177(2)	0.742(3)
C(35)	0.544(2)	0.202(2)	0.653(2)
C(40)	0.295(1)	0.306(1)	0.556(1)
C(41)	0.256(2)	0.235(1)	0.566(2)
C(42)	0.156(2)	0.227(2)	0.577(2)
C(43)	0.102(2)	0.289(2)	0.576(2)

C(44)	0.143(2)	0.360(2)	0.569(2)
C(45)	0.238(2)	0.368(1)	0.553(2)
C(A)	0.405(2)	0.041(2)	0.167(2)
Cl(A1)	0.4472(7)	-0.0080(5)	0.1023(7)
Cl(A2) ^b	0.480(2)	0.092(2)	0.241(3)
Cl(A3) ^c	0.442(7)	0.123(2)	0.179(6)
C(B1) ^d	0.343(3)	0.023(2)	0.381(3)
C(B2) ^e	0.249(2)	0.074(2)	0.360(2)
Cl(B1) ^d	0.249(2)	0.074(2)	0.360(2)
Cl(B2) ^d	0.371(4)	-0.033(3)	0.461(3)
Cl(B3) ^e	0.343(3)	0.023(2)	0.381(3)
Cl(B4) ^e	0.179(2)	0.054(2)	0.419(2)
C(C) ^f	0.809(3)	-0.011(3)	0.374(3)
Cl(C1) ^f	0.863(2)	0.049(1)	0.336(2)
Cl(C2) ^g	0.728(3)	-0.044(2)	0.290(3)
Cl(C3) ^h	0.691(3)	-0.004(5)	0.345(5)

(^a) Standard deviations in the least significant digit are given in parentheses. (^b) s.o.f. = 0.645. (^c) s.o.f. = 0.355. (^d) s.o.f. = 0.117. (^e) s.o.f. = 0.283. (^f) s.o.f. = 0.600. (^g) s.o.f. = 0.392. (^h) s.o.f. = 0.208.

TABLE 3 - SELECTED DISTANCES (Å) AND ANGLES (deg) FOR Mo₂Cl₆(dppe)₂·4CH₂Cl₂

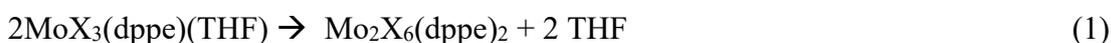
a) Bond distances			
Mo-Cl(1)	2.405(4)	Mo-Cl(1')	2.414(4)
Mo-Cl(2)	2.396(3)	Mo-Cl(3)	2.398(3)
Mo-P(1)	2.561(4)	Mo-P(2)	2.571(4)
Mo-Mo'	2.767(2)		
b) Bond angles			
Cl(1)-Mo-Cl(1')	109.9(1)	Cl(1)-Mo-Cl(2)	93.4(1)
Cl(1)-Mo-Cl(3)	96.9(1)	Cl(1)-Mo-P(1)	83.3(1)
Cl(1)-Mo-P(2)	163.8(1)	Cl(2)-Mo-Cl(1')	95.7(1)
Cl(2)-Mo-Cl(3)	164.3(2)	Cl(2)-Mo-P(1)	85.1(1)
Cl(2)-Mo-P(2)	82.6(1)	Cl(3)-Mo-Cl(1')	91.9(1)
Cl(3)-Mo-P(1)	84.4(1)	Cl(3)-Mo-P(2)	84.3(1)
P(1)-Mo-Cl(1')	166.6(1)	P(1)-Mo-P(2)	80.7(1)
P(2)-Mo-Cl(1')	86.2(1)	Mo-Cl(1)-Mo'	70.1(1)

RESULTS AND DISCUSSION

The previously described¹ MoX₃(dppe)(THF) compounds lose tetrahydrofuran and dimerize when dissolved in non-coordinating solvents. For X = Cl and Br, the product has been identified as the dinuclear Mo₂X₆(dppe)₂ with an edge-sharing bioctahedral coordination geometry (equation 1; see crystal structure below). The chloride compound has also been obtained by an alternative route by Cotton and coworkers,⁴ *i.e.* the oxidation of Mo₂Cl₄(dppe)₂ with Cl₂. We have isolated the chloride compound in three different crystalline phases, purple, orange, and pink. The orange phase appears

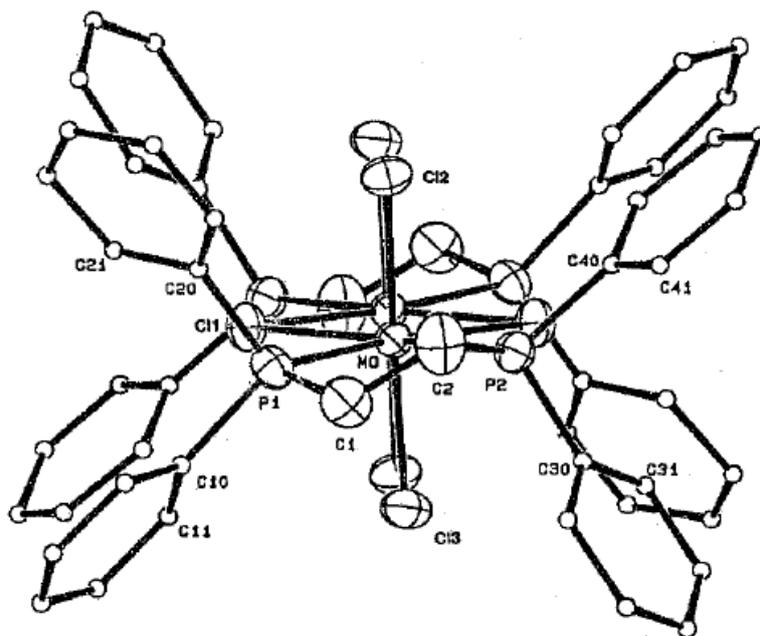
identical to that already reported by Cotton. The purple phase, whose structure is described below, is diamagnetic as shown by its ^1H NMR spectrum. The ^{31}P resonance of the coordinated ligand appears at δ 42.96 ppm, well in the range of coordinated dppe ligands in the chelating mode.⁶ The pink phase is the least soluble one and is slowly obtained from either the purple or the orange dimers or from $\text{MoCl}_3(\text{dppe})(\text{THF})$ upon standing in THF at room temperature for several days. We presume this phase to consist of some sort of higher oligomer or polymer.

The bromide compound has also been isolated in two different forms, green and purple, of which only the latter has been structurally characterized and shown to be isostructural with the chloride derivative.³ The purple phase is essentially diamagnetic, whereas the green phase shows a measurable paramagnetism. However, we cannot exclude that the compound is contaminated by small amounts of mononuclear precursor ($S = 3/2$) although the elemental analysis is satisfactory. Only one phase has been obtained for the iodide derivative, analyzing correctly for $[\text{MoI}_3(\text{dppe})]_x$. It is slightly paramagnetic, and its IR spectroscopic properties are similar to those of the bromide and chloride compounds.



The structure of the $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$ molecule is shown in the figure. The compound crystallizes in the monoclinic space group $P2_1/n$ with four disordered dichloromethane molecules, and the dinuclear unit sits on a crystallographic inversion centre. This crystalline phase has exactly the same composition as the other monoclinic phase examined by Cotton *et al.*,⁴ the difference being that the latter belongs to the monoclinic space group $C2/m$ and the molecule sits on a $2/m$ special position (C_{2h} point group symmetry). The phase reported by Cotton and coworkers was crystallized⁴ in air in the reaction solvent after being generated by oxidation of $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ with Cl_2 . We have obtained the purple crystalline phase reported here upon dissolution of $\text{MoCl}_3(\text{dppe})(\text{THF})$ in CH_2Cl_2 , and crystallization under a dinitrogen atmosphere.^a

^a The fact that two crystalline compounds with identical molecular structure have a different color does not appear to have a simple explanation. Both forms dissolve in CH_2Cl_2 to give solutions of identical color and UV/vis spectroscopic properties.

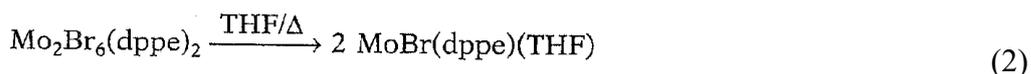


An ORTEP View of the $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$ molecule with the numbering scheme employed.

The solvent molecules were found to be extensively disordered and we do not claim that this disorder was modelled in the best possible way. Four crystallization solvent molecules per dinuclear unit gave the best final agreement figures but we must allow for the possibility that our crystalline phase and that reported by Cotton⁴ contain slightly different amounts of solvent of crystallization. The minor differences observed in the metric parameters between the two phases are not chemically significant.

The $\text{Mo}_2\text{Br}_6(\text{dppe})_2$ compound was recrystallized from chloroform and was found to be isostructural with the chloride system reported by Cotton and coworkers.⁴ The molecule sits on a $2/m$ position. Unfortunately, the interstitial chloroform molecules are in this case even more disordered than the dichloromethane molecules of the chloride structure and a satisfactory refinement could not be achieved. At the end of the refinement on the $\text{Mo}_2\text{Br}_6(\text{dppe})_2$ molecule ($R = 0.13$), several agglomerates of electron density were noted in the difference Fourier map, but none of these could be interpreted in terms of a chemically reasonable crystallographic disorder of chloroform molecules. At this level of refinement the metal-metal distance is 2.799(7) Å. We use the result of this structural investigation only to assess the structural identity of the compound as an edge-sharing bioctahedral molecule, and as an indication that the metal-metal separation in this compound appears to be slightly longer than that of the corresponding chloride system.

We have chemical evidence suggesting that the metal-metal bond in the bromide dimer is weaker than that in the corresponding chloride dimer. The $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$ complex is stable in refluxing THF, except for the slow conversion to the pink isomeric form alluded to earlier. On the other hand, the corresponding $\text{Mo}_2\text{Br}_2(\text{dppe})_2$ compound slowly reacts to regenerate the parent THF adduct (equation 2).



This is, to the best of our knowledge, the first example of a metal-metal bonded edge-sharing bioctahedral complex being reversibly split into mononuclear systems by addition of a donor solvent. Example of analogous reversible monomer/dimer equilibria for systems without metal-metal bonds are common, for instance $\text{Ru}_2\text{Cl}_4(\text{CO})_6/\text{RuCl}_2(\text{CO})_3(\text{THF})^7$ or $\text{Re}_2\text{Br}_2(\text{CO})_8/\text{ReBr}(\text{CO})_4(\text{THF})^8$.

It is reasonable to assume that the metal-metal bond strength decreases on going from the chloride to the bromide to the iodide-bridged compound because the increased bulk of the bridging halogen atoms will force the two metals farther apart from each other, thereby decreasing the overlap of the metal orbitals. A similar situation has been observed in the related class of confacial bioctahedral molecules: typical distances for $[\text{Mo}_2\text{X}_9]^{3-}$ are 2.52-2.73 Å ($X = \text{Cl}$), 2.57-3.11 Å ($X = \text{Br}$), and 3.070 Å ($X = \text{I}$),⁹ and the metal-metal distances in the $[\text{Mo}_2\text{X}_7(\text{PMe}_3)_2]^-$ ions are 2.69-2.76 Å ($X = \text{Cl}$),^{10a} and 3.02 Å ($X = \text{I}$).^{10b} This kind of comparison for edge-sharing bioctahedral structures is not yet possible because, with the exception of the $\text{Mo}_2\text{Br}_6(\text{dppe})_2$ molecule mentioned here, crystal structural investigation of bis(bromide) and bis(iodide) bridged edge-sharing bioctahedral derivatives are not available to the best of our knowledge. We did not observe any reactivity of the brown insoluble iodide compound, $[\text{MoI}_3(\text{dppe})]_x$ with THF to regenerate the mononuclear $\text{MoI}_3(\text{dppe})(\text{THF})$. This result indicates that the insoluble iodide compound is likely not to possess an edge-sharing bioctahedral structure and it probably consists of higher oligonuclear units in analogy with the pink isomer within the chloride system. The preparation and Structural investigation of series of edge-sharing bioctahedral compounds where the bridging ligands vary from chloride to bromide to iodide is a continuing goal of our research.

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