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Detailed description of the X-ray analysis for $[PPh_4]_3[Mo_3I_{12}]\cdot 3/2CH_2Cl_2\cdot 1/2Et_2O$

Abstract:

$[Mo_3I_{12}][P(C_6H_5)_4]_3[CH_2Cl_2]_{1.5}[C_2H_5OC_2H_5]_{0.5}$ Mr=2993.18, triclinic, P-1, a=11.385(2) Å, b=12.697(3) Å, c=16.849(2) Å, α=76.65(2)°, β=71.967(12)°, γ=84.56(2)°, V=2252.5(7) $Å^3$, Z=1, D_c=2.207 g cm^{-3}, λ(Mo Kα)=0.71069 Å, μ(Mo Kα)=4.704 mm^{-1}, F(000)=1375, T=153 K, R(F)=9.25, R(wF2)=13.23% for all 5871 reflections (±hk±l). There are two unique Mo atoms, Mo(1), being positioned on an inversion center (0,1/2,0) and Mo(2), both possessing octahedral geometries with Mo(1)-I(11)= 2.7644(12), Mo(1)-I(12)=2.7797(12), Mo(1)-I(13)= 2.7616(14), and Mo(2)-I(1)=2.749(2), Mo(2)-I(2)=2.751(2), Mo(2)-I(3)=2.757(2), Mo(2)-I(11)=2.816(2), Mo(2)-I(12)=2.810(2), and Mo(2)-I(13)=2.824(2). There exists one full occupancy PPh_4 cation with tetrahedral geometry and a second half occupancy PPh_4 cation sharing its site with three partial occupancy (0.5:0.125:0.125) CH_2Cl_2 molecules and an additional partial occupancy (0.25) $C_2H_5OC_2H_5$ molecule.

Experimental:

A dark purple, nearly black, crystal with dimensions 0.20 x 0.20 x 0.50 mm with a parallelepiped habit was placed on the Enraf-Nonius CAD4 diffractometer. The crystal final cell parameters and crystal orientation matrix were determined from 25 reflections in the range $15.0 < \theta < 17.0°$; these constants were confirmed with axial photographs. Data were collected [MoKα] with Omega scans over the θ range 3.5 - 22.5° using a variable scan speed of 1.5 - 8.24° $min.^{-1}$ with each scan recorded in 96 steps with the outermost 16 steps on each end of the scan being used for background determination. The diffractometer was controlled with a Digital Equipment Corporation MicroVAX II (MVII) computer and the automated Enraf-Nonius program Express (version 5.1). Three nearly orthogonal standard reflections were monitored at 1 hour intervals of X-ray exposure. Minor, 1 - 3 %, variations in intensity were observed; data were not corrected. Seven ψ-scan reflections were collected over the θ range 3.8 - 16.2° with an observed 39% variation in intensity. An absorption correction was applied with transmission factors ranging from 0.6777 - 1.000; average 0.8728. One form of unique data were collected in the hemisphere ±hk±l; resulting in the measurement of 5871 unique reflections.

Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a 486 DX2/66 processor and 16Mb of extended memory. Data were transferred from the MVII to the PC. Data were corrected for Lorentz and polarization factors, absorption and reduced to observed structure-factor amplitudes using the program package NRCVAX. Intensity statistics clearly favored the centrosymmetric case. Data were now exported as F_o^2 and $\sigma(F_o^2)$ to the crystallographic program package SHELX. The structure was determined with the successful location of all eight unique 'heavy atoms' (two molybdenums and six iodines). Subsequent difference-Fourier maps revealed the location of one full occupancy PPh_4^+ ion and another PPh_4^+ at half occupancy. This second cation proved troublesome and rigid group refinement of the phenyl rings was found necessary not only to form planar rings but also to enable refinement of atoms found to lie nearly on top of one another. Apparently, two of the phenyl rings (C5x and C8x) and the central phosphorus atom lie in a plane that, due to crystallographic symmetry, has substantial overlap of one PPh_4^+ with its neighboring PPh_4^+. This gives these two phenyl rings the appearance of having full occupancy in the lattice while the remaining two phenyl rings (C6x and C7x) clearly have half occupancy. It became readily apparent early on that it was these latter phenyl rings shared their location with other yet undefined molecules. SHELXL rigidly refined all four of these phenyl rings and then the C6x series was first removed and then relocated along with several misfits. These were identified to be a half occupancy CH_2Cl_2 molecule that proved to have some disorder that was resolved by allowing one of the chlorine atoms to have two positions. The occupancies of these two atoms were refined with equal thermal parameters and then fixed at 0.355:0.145. The C6x ring was again allowed rigid group refinement with the presence of this partial occupancy moiety. Next, the C7x ring was removed and a similar procedure followed only this proved to be tedious and eventually led to the successful location of two 12.5% occupancy CH_2Cl_2 molecules and an additional 0.25% occupancy diethyl ether molecule. This last molecule is perhaps the most questionable in regard to bond distances and angles and may in fact be an additional two 12.5% partial occupancy methylene chloride molecules although the structural refinement at this stage became transparent to change. The fragment of interest, Mo_3I_{12}, was also found to possess a series of satellite peaks, actually these were the highest twenty peaks in the final difference map, that did not form a cohesive set and were therefore not included in the final refinement. Hydrogen atoms were placed in calculated positions, these being dependent on both the type of bonding at the carbon and the temperature (153K in this case) and U_H was set equal to 1.2.U(parent). The structure was refined to convergence [$\Delta/\sigma \leq 0.003$] with R(F)=9.61%, $wR(F^2)$=14.70% and GOF=1.074 for all 5871 unique reflections [R(F)=6.11%, $wR(F^2)$=13.75% for those 3957 data with $F_o > 4\sigma(F_o)$. A final difference-Fourier map possessed many peaks in the vicinity, i.e., within 1.2 Å, of their respective iodine atoms with height ≤ 1.37 e·Å^{-3} as described above.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(F_o^2-F_c^2)$ where $w=1/[\sigma^2(F_o^2) + (0.0609 * P)^2 + 30.51 * P]$ and $P=(\max(F_o^2 ,0) + 2 * F_c^2)/3$. An empirical correction for extinction was also applied to the data in the form $(F_c^2,\text{corr}) = k[1 + 0.001 * x * F_c^2 * \lambda^3/\sin(2\theta)]^{-1/4}$ where k is the overall scale factor. The value determined for x was 0.00048(13).

Refinement in the noncentrosymmetric space group P1

The completed structure in space group P-1 was now refined in space group P1 by the addition of the required symmetrical equivalents in the $[Mo_3I_{12}]$ moiety and the addition of the symmetrically equivalent full occupancy $[P(C_6H_5)_4]$. This portion of the structure was refined and then a difference Fourier was performed, resulting in the location of two half-occupancy phosphorus atoms that are symmetrically related in P-1, thus confirming our original hypothesis that the true space group is indeed P-1.

Table 1S. Crystal data and structure refinement for $[PPh_4]_3[Mo_3I_{12}]\cdot 3/2CH_2Cl_2\cdot 1/2Et_2O$

Empirical formula	$C_{75.5}H_{68}Cl_3I_{12}Mo_3O_{0.5}P_3$
Formula weight	2993.18
Temperature	153(2) K
Wavelength	.71069 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 11.385(2) Å alpha = 76.65(2) deg.
	b = 12.697(3) Å beta = 71.967(12) deg.
	c = 16.849(2) Å gamma = 84.56(2) deg.
Volume	2252.5(7) $Å^3$
Z	1
Density (calculated)	2.207 Mg/m^3
Absorption coefficient	4.704 mm^{-1}
F(000)	1375
Crystal size	0.50 x 0.20 x 0.20 mm
Theta range for data collection	3.54 to 22.50 deg.
Index ranges	-12<=h<=12, 0<=k<=13, -17<=l<=18
Reflections collected	6177
Independent reflections	5871 [R(int) = 0.0650]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5871 / 0 / 383
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1375 [3957 data]
R indices (all data)	R1 = 0.0961, wR2 = 0.1470
Extinction coefficient	.00048(14)
Largest diff. peak and hole	1.367 and -1.016 $e\cdot Å^{-3}$

Table 2S. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[PPh_4]_3[Mo_3I_{12}]\cdot 1.5CH_2Cl_2\cdot 0.5Et_2O$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	0	5000	0	54(1)
Mo(2)	-1988(1)	3969(1)	1815(1)	32(1)
I(1)	-3098(1)	5043(1)	3109(1)	48(1)
I(2)	-1469(1)	2202(1)	2961(1)	37(1)
I(3)	-4225(1)	3126(1)	1999(1)	43(1)
I(11)	331(1)	4797(1)	1587(1)	42(1)
I(12)	2407(1)	4227(1)	-601(1)	40(1)
I(13)	827(1)	7094(1)	-462(1)	33(1)
P(1)	4439(4)	8875(3)	1961(2)	29(1)
C(11)	3463(14)	10052(12)	1771(9)	32(4)
C(12)	3890(15)	11082(12)	1526(11)	42(4)
C(13)	3149(16)	11961(14)	1406(12)	52(5)
C(14)	1900(17)	11810(15)	1541(11)	50(5)
C(15)	1441(14)	10773(14)	1799(11)	44(5)
C(16)	2216(14)	9887(13)	1901(9)	37(4)
C(21)	4142(13)	8372(11)	3087(8)	25(3)
C(22)	4968(15)	7628(13)	3378(10)	40(4)
C(23)	4691(17)	7159(13)	4232(10)	49(5)
C(24)	3675(17)	7505(15)	4797(12)	52(5)
C(25)	2899(16)	8258(16)	4529(10)	56(5)
C(26)	3101(14)	8655(13)	3678(10)	41(4)
C(31)	4119(12)	7890(12)	1451(9)	29(4)
C(32)	4248(14)	6795(14)	1787(11)	42(4)
C(33)	4034(15)	6049(15)	1374(12)	49(5)
C(34)	3727(16)	6379(16)	607(11)	48(5)
C(35)	3640(15)	7454(15)	290(11)	47(5)
C(36)	3849(14)	8211(13)	698(9)	36(4)
C(41)	6011(12)	9236(11)	1548(9)	24(3)
C(42)	6466(14)	9906(13)	1933(9)	38(4)
C(43)	7680(14)	10230(13)	1601(9)	37(4)
C(44)	8430(14)	9904(12)	867(11)	43(5)
C(45)	8018(14)	9253(13)	469(11)	42(4)
C(46)	6810(14)	8928(12)	803(10)	36(4)
P(2)	1667(8)	1721(8)	5220(5)	43(2)
C(51)	614(24)	705(20)	5064(17)	20(8)
C(52)	-39(25)	-17(21)	5787(17)	30(10)
C(53)	-708(26)	-827(20)	5707(19)	38(12)
C(54)	-724(28)	-915(21)	4903(21)	38(11)
C(55)	-71(28)	-192(24)	4180(18)	51(14)
C(56)	598(26)	617(22)	4260(17)	32(10)
C(61)	1029(22)	2002(22)	6260(14)	57(11)
C(62)	-206(21)	2318(22)	6541(15)	58(10)
C(63)	-673(18)	2618(20)	7325(15)	49(9)
C(64)	95(25)	2603(24)	7828(14)	64(12)
C(65)	1331(24)	2287(27)	7547(18)	189(50)
C(66)	1798(17)	1986(22)	6763(19)	20(8)

Table 3S. (continued)

	x	y	z	U(eq)
C(71)	1680(22)	2996(17)	4499(15)	40(8)
C(72)	2626(21)	3705(23)	4336(19)	56(10)
C(73)	2565(29)	4755(22)	3869(23)	159(28)
C(74)	1558(34)	5095(18)	3564(22)	113(19)
C(75)	612(26)	4386(24)	3727(19)	92(15)
C(76)	673(20)	3337(22)	4194(18)	66(11)
C(81)	3191(10)	1047(9)	5064(6)	46(9)
C(82)	4130(11)	1327(11)	4301(6)	53(10)
C(83)	5268(12)	782(13)	4189(8)	91(16)
C(84)	5467(13)	-44(13)	4841(9)	49(10)
C(85)	4528(13)	-324(11)	5604(8)	47(9)
C(86)	3390(12)	221(9)	5715(7)	56(10)

Table 3S. Bond lengths [Å] and angles [°] for $[PPh_4]_3[Mo_3I_{12}]\cdot 3/2CH_2Cl_2\cdot 1/2Et_2O$.

Mo(1)-I(13)	2.7613(12)
Mo(1)-I(11)	2.7652(12)
Mo(1)-I(12)	2.7798(12)
Mo(1)-Mo(2)	3.258(2)
Mo(2)-I(1)	2.749(2)
Mo(2)-I(2)	2.751(2)
Mo(2)-I(3)	2.757(2)
Mo(2)-I(12)	2.809(2)
Mo(2)-I(11)	2.817(2)
Mo(2)-I(13)	2.825(2)
P(1)-C(41)	1.770(14)
P(1)-C(21)	1.789(13)
P(1)-C(31)	1.79(2)
P(1)-C(11)	1.805(14)
C(11)-C(12)	1.36(2)
C(11)-C(16)	1.40(2)
C(12)-C(13)	1.35(2)
C(13)-C(14)	1.39(2)
C(14)-C(15)	1.39(2)
C(15)-C(16)	1.37(2)
C(21)-C(26)	1.37(2)
C(21)-C(22)	1.39(2)
C(22)-C(23)	1.37(2)
C(23)-C(24)	1.36(2)
C(24)-C(25)	1.34(2)
C(25)-C(26)	1.36(2)
C(31)-C(36)	1.36(2)
C(31)-C(32)	1.39(2)
C(32)-C(33)	1.38(2)
C(33)-C(34)	1.40(2)
C(34)-C(35)	1.35(2)
C(35)-C(36)	1.38(2)
C(41)-C(42)	1.40(2)
C(41)-C(46)	1.42(2)
C(42)-C(43)	1.38(2)
C(43)-C(44)	1.40(2)
C(44)-C(45)	1.37(2)
C(45)-C(46)	1.38(2)
P(2)-C(61)	1.78(2)
P(2)-C(71)	1.78(2)
P(2)-C(81)	1.831(14)
P(2)-C(51)	1.95(2)
P(2)-C(8)	2.218(14)
C(51)-C(52)	1.39
C(51)-C(56)	1.39
C(52)-C(53)	1.39
C(53)-C(54)	1.39
C(54)-C(55)	1.39
C(55)-C(56)	1.39
C(61)-C(62)	1.39
C(61)-C(66)	1.39

C(62)-C(63)	1.39
C(63)-C(64)	1.39
C(64)-C(65)	1.39
C(65)-C(66)	1.39
C(71)-C(72)	1.39
C(71)-C(76)	1.39
C(72)-C(73)	1.39
C(73)-C(74)	1.39
C(74)-C(75)	1.39
C(75)-C(76)	1.39
C(81)-C(82)	1.39
C(81)-C(86)	1.39
C(82)-C(83)	1.39
C(83)-C(84)	1.39
C(84)-C(85)	1.39
C(85)-C(86)	1.39
C(1)-Cl(2A)	1.72
C(1)-Cl(2B)	1.75
C(1)-Cl(1)	1.94
Cl(2A)-Cl(2B)	1.09
C(3)-C(6)	.87
C(3)-C(7)	1.24
C(3)-Cl(3A)	1.49
C(3)-Cl(3B)	1.68
C(3)-O(1)	1.72
C(3)-C(5)	1.87
C(3)-C(8)	2.02
Cl(3A)-C(8)	.83
Cl(3A)-C(7)	1.25
Cl(3A)-Cl(3B)	2.34
Cl(3B)-C(5)	1.38
Cl(3B)-C(6)	1.75
C(4)-Cl(4A)	1.61
C(4)-Cl(4B)	1.90
C(5)-C(6)	1.38
C(6)-O(1)	1.71
C(6)-C(7)	1.82
O(1)-C(7)	1.34
C(7)-C(8)	1.41

I(13)-Mo(1)-I(13)#1	180.0
I(13)-Mo(1)-I(11)	89.73(3)
I(13)#1-Mo(1)-I(11)	90.27(3)
I(13)-Mo(1)-I(11)#1	90.27(3)
I(13)#1-Mo(1)-I(11)#1	89.73(3)
I(11)-Mo(1)-I(11)#1	180.0
I(13)-Mo(1)-I(12)#1	89.70(4)
I(13)#1-Mo(1)-I(12)#1	90.30(4)
I(11)-Mo(1)-I(12)#1	90.61(3)
I(11)#1-Mo(1)-I(12)#1	89.39(3)
I(13)-Mo(1)-I(12)	90.30(4)
I(13)#1-Mo(1)-I(12)	89.70(4)
I(11)-Mo(1)-I(12)	89.39(3)
I(11)#1-Mo(1)-I(12)	90.61(3)

I(12)#1-Mo(1)-I(12)	180.0
I(13)-Mo(1)-Mo(2)#1	55.24(4)
I(13)#1-Mo(1)-Mo(2)#1	124.76(4)
I(11)-Mo(1)-Mo(2)#1	124.97(4)
I(11)#1-Mo(1)-Mo(2)#1	55.03(4)
I(12)#1-Mo(1)-Mo(2)#1	125.22(3)
I(12)-Mo(1)-Mo(2)#1	54.78(3)
I(13)-Mo(1)-Mo(2)	124.76(4)
I(13)#1-Mo(1)-Mo(2)	55.24(4)
I(11)-Mo(1)-Mo(2)	55.03(4)
I(11)#1-Mo(1)-Mo(2)	124.97(4)
I(12)#1-Mo(1)-Mo(2)	54.78(3)
I(12)-Mo(1)-Mo(2)	125.22(3)
Mo(2)#1-Mo(1)-Mo(2)	180.0
I(1)-Mo(2)-I(2)	90.98(6)
I(1)-Mo(2)-I(3)	90.34(6)
I(2)-Mo(2)-I(3)	90.95(6)
I(1)-Mo(2)-I(12)#1	90.60(5)
I(2)-Mo(2)-I(12)#1	177.46(7)
I(3)-Mo(2)-I(12)#1	91.03(6)
I(1)-Mo(2)-I(11)	91.36(6)
I(2)-Mo(2)-I(11)	89.02(5)
I(3)-Mo(2)-I(11)	178.30(7)
I(12)#1-Mo(2)-I(11)	88.96(5)
I(1)-Mo(2)-I(13)#1	178.81(7)
I(2)-Mo(2)-I(13)#1	89.98(5)
I(3)-Mo(2)-I(13)#1	90.35(6)
I(12)#1-Mo(2)-I(13)#1	88.41(5)
I(11)-Mo(2)-I(13)#1	87.95(5)
I(1)-Mo(2)-Mo(1)	125.40(6)
I(2)-Mo(2)-Mo(1)	123.54(5)
I(3)-Mo(2)-Mo(1)	125.23(6)
I(12)#1-Mo(2)-Mo(1)	53.93(4)
I(11)-Mo(2)-Mo(1)	53.57(4)
I(13)#1-Mo(2)-Mo(1)	53.43(3)
Mo(1)-I(11)-Mo(2)	71.40(4)
Mo(1)-I(12)-Mo(2)#1	71.30(4)
Mo(1)-I(13)-Mo(2)#1	71.34(4)
C(41)-P(1)-C(21)	106.8(7)
C(41)-P(1)-C(31)	111.1(7)
C(21)-P(1)-C(31)	111.8(7)
C(41)-P(1)-C(11)	109.9(7)
C(21)-P(1)-C(11)	109.7(7)
C(31)-P(1)-C(11)	107.6(7)
C(12)-C(11)-C(16)	119.5(14)
C(12)-C(11)-P(1)	122.8(12)
C(16)-C(11)-P(1)	117.7(12)
C(13)-C(12)-C(11)	123(2)
C(12)-C(13)-C(14)	119(2)
C(15)-C(14)-C(13)	120(2)
C(16)-C(15)-C(14)	121(2)
C(15)-C(16)-C(11)	119(2)
C(26)-C(21)-C(22)	118.1(13)
C(26)-C(21)-P(1)	122.8(11)

C(22)-C(21)-P(1)	119.0(11)
C(23)-C(22)-C(21)	119.5(14)
C(24)-C(23)-C(22)	120(2)
C(25)-C(24)-C(23)	121(2)
C(24)-C(25)-C(26)	120(2)
C(25)-C(26)-C(21)	121.5(14)
C(36)-C(31)-C(32)	120(2)
C(36)-C(31)-P(1)	120.2(12)
C(32)-C(31)-P(1)	119.9(13)
C(33)-C(32)-C(31)	119(2)
C(32)-C(33)-C(34)	121(2)
C(35)-C(34)-C(33)	118(2)
C(34)-C(35)-C(36)	122(2)
C(31)-C(36)-C(35)	120(2)
C(42)-C(41)-C(46)	118.5(13)
C(42)-C(41)-P(1)	119.2(11)
C(46)-C(41)-P(1)	122.2(12)
C(43)-C(42)-C(41)	120.2(14)
C(42)-C(43)-C(44)	119(2)
C(45)-C(44)-C(43)	122(2)
C(44)-C(45)-C(46)	118(2)
C(45)-C(46)-C(41)	121(2)
C(61)-P(2)-C(71)	105.3(13)
C(61)-P(2)-C(81)	113.0(10)
C(71)-P(2)-C(81)	113.2(10)
C(61)-P(2)-C(51)	109.1(12)
C(71)-P(2)-C(51)	111.2(12)
C(81)-P(2)-C(51)	105.1(10)
C(51)-P(2)-C(8)	124.6(10)
C(52)-C(51)-C(56)	120.0
C(52)-C(51)-P(2)	117.4(11)
C(56)-C(51)-P(2)	122.3(11)
C(53)-C(52)-C(51)	120.0
C(52)-C(53)-C(54)	120.0
C(55)-C(54)-C(53)	120.0
C(54)-C(55)-C(56)	120.0
C(55)-C(56)-C(51)	120.0
C(62)-C(61)-C(66)	120.0
C(62)-C(61)-P(2)	120(2)
C(66)-C(61)-P(2)	120(2)
C(61)-C(62)-C(63)	120.0
C(62)-C(63)-C(64)	120.0
C(65)-C(64)-C(63)	120.0
C(66)-C(65)-C(64)	120.0
C(65)-C(66)-C(61)	120.0
C(72)-C(71)-C(76)	120.0
C(72)-C(71)-P(2)	119(2)
C(76)-C(71)-P(2)	120(2)
C(73)-C(72)-C(71)	120.0
C(74)-C(73)-C(72)	120.0
C(73)-C(74)-C(75)	120.0
C(76)-C(75)-C(74)	120.0
C(75)-C(76)-C(71)	120.0
C(82)-C(81)-C(86)	120.0

C(82)-C(81)-P(2)	121.1(4)
C(86)-C(81)-P(2)	118.9(4)
C(81)-C(82)-C(83)	120.0
C(84)-C(83)-C(82)	120.0
C(83)-C(84)-C(85)	120.0
C(86)-C(85)-C(84)	120.0
C(85)-C(86)-C(81)	120.0
Cl(2A)-C(1)-Cl(2B)	36.5
Cl(2A)-C(1)-Cl(1)	111.4
Cl(2B)-C(1)-Cl(1)	100.6
Cl(2B)-Cl(2A)-C(1)	72.9
Cl(2A)-Cl(2B)-C(1)	70.6
C(6)-C(3)-C(7)	117.8
C(6)-C(3)-Cl(3A)	165.7
C(7)-C(3)-Cl(3A)	53.6
C(6)-C(3)-Cl(3B)	80.0
C(7)-C(3)-Cl(3B)	120.6
Cl(3A)-C(3)-Cl(3B)	94.8
C(6)-C(3)-O(1)	74.4
C(7)-C(3)-O(1)	50.4
Cl(3A)-C(3)-O(1)	101.8
Cl(3B)-C(3)-O(1)	137.4
C(6)-C(3)-C(5)	43.5
C(7)-C(3)-C(5)	108.3
Cl(3A)-C(3)-C(5)	124.6
Cl(3B)-C(3)-C(5)	45.4
O(1)-C(3)-C(5)	94.2
C(6)-C(3)-C(8)	159.3
C(7)-C(3)-C(8)	43.8
Cl(3A)-C(3)-C(8)	21.5
Cl(3B)-C(3)-C(8)	116.3
O(1)-C(3)-C(8)	84.9
C(5)-C(3)-C(8)	140.3
C(8)-Cl(3A)-C(7)	82.5
C(8)-Cl(3A)-C(3)	117.5
C(7)-Cl(3A)-C(3)	53.1
C(8)-Cl(3A)-Cl(3B)	163.2
C(7)-Cl(3A)-Cl(3B)	84.8
C(3)-Cl(3A)-Cl(3B)	45.7
C(5)-Cl(3B)-C(3)	74.9
C(5)-Cl(3B)-C(6)	50.6
C(3)-Cl(3B)-C(6)	29.4
C(5)-Cl(3B)-Cl(3A)	103.9
C(3)-Cl(3B)-Cl(3A)	39.5
C(6)-Cl(3B)-Cl(3A)	68.3
Cl(4A)-C(4)-Cl(4B)	111.4
C(6)-C(5)-Cl(3B)	78.7
C(6)-C(5)-C(3)	25.8
Cl(3B)-C(5)-C(3)	59.8
C(3)-C(6)-C(5)	110.7
C(3)-C(6)-O(1)	76.2
C(5)-C(6)-O(1)	117.0
C(3)-C(6)-Cl(3B)	70.7
C(5)-C(6)-Cl(3B)	50.7

O(1)-C(6)-Cl(3B)	132.7
C(3)-C(6)-C(7)	37.2
C(5)-C(6)-C(7)	105.0
O(1)-C(6)-C(7)	44.3
Cl(3B)-C(6)-C(7)	90.9
C(7)-O(1)-C(6)	72.3
C(7)-O(1)-C(3)	45.8
C(6)-O(1)-C(3)	29.4
C(3)-C(7)-Cl(3A)	73.3
C(3)-C(7)-O(1)	83.8
Cl(3A)-C(7)-O(1)	149.7
C(3)-C(7)-C(8)	98.6
Cl(3A)-C(7)-C(8)	35.9
O(1)-C(7)-C(8)	134.7
C(3)-C(7)-C(6)	25.0
Cl(3A)-C(7)-C(6)	97.6
O(1)-C(7)-C(6)	63.4
C(8)-C(7)-C(6)	123.0
Cl(3A)-C(8)-C(7)	61.6
Cl(3A)-C(8)-C(3)	41.0
C(7)-C(8)-C(3)	37.6
Cl(3A)-C(8)-P(2)	92.6(4)
C(7)-C(8)-P(2)	84.8(4)
C(3)-C(8)-P(2)	113.5(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table 4S. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[PPh_4]_3[Mo_3I_{12}]\cdot 3/2CH_2Cl_2\cdot 1/2Et_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Mo(1)	60(2)	32(1)	95(2)	-25(1)	-55(2)	21(1)
Mo(2)	35(1)	28(1)	30(1)	-2(1)	-9(1)	5(1)
I(1)	58(1)	40(1)	39(1)	-11(1)	-3(1)	10(1)
I(2)	40(1)	35(1)	25(1)	2(1)	-5(1)	5(1)
I(3)	34(1)	42(1)	46(1)	-2(1)	-7(1)	-2(1)
I(11)	41(1)	37(1)	43(1)	-2(1)	-7(1)	-4(1)
I(12)	41(1)	35(1)	34(1)	8(1)	-7(1)	0(1)
I(13)	35(1)	34(1)	27(1)	-3(1)	-5(1)	0(1)
P(1)	26(2)	32(2)	21(2)	4(2)	-1(2)	1(2)
C(11)	35(10)	33(10)	26(9)	-3(7)	-10(7)	4(7)
C(12)	38(10)	31(10)	48(11)	6(8)	-8(8)	-1(8)
C(13)	49(12)	33(10)	66(14)	-3(9)	-13(10)	-1(9)
C(14)	52(12)	48(12)	45(12)	-12(9)	-7(9)	1(10)
C(15)	20(9)	55(12)	52(12)	-22(10)	2(8)	10(9)
C(16)	34(10)	41(10)	24(9)	4(7)	-2(7)	-1(8)
C(21)	28(8)	28(8)	12(8)	2(6)	-4(6)	7(7)
C(22)	35(10)	48(11)	27(10)	-8(8)	4(7)	9(8)
C(23)	72(13)	40(10)	29(10)	0(8)	-23(9)	35(10)
C(24)	52(12)	52(12)	49(12)	-18(10)	-10(10)	13(10)
C(25)	40(11)	82(14)	21(10)	-3(9)	13(8)	16(10)
C(26)	29(9)	47(10)	29(10)	5(8)	2(7)	18(8)
C(31)	18(8)	29(9)	25(9)	3(7)	7(7)	2(7)
C(32)	34(10)	46(11)	38(10)	-6(9)	-4(8)	4(8)
C(33)	39(11)	37(10)	59(13)	-4(10)	1(9)	-10(8)
C(34)	45(11)	60(13)	36(11)	-17(10)	1(9)	-17(9)
C(35)	45(11)	61(13)	29(10)	-7(10)	-7(8)	3(9)
C(36)	43(10)	38(10)	20(9)	4(8)	-3(7)	-7(8)
C(41)	18(8)	28(8)	25(8)	-5(7)	-7(7)	9(6)
C(42)	36(10)	46(10)	17(8)	3(8)	5(7)	0(8)
C(43)	44(10)	37(10)	20(9)	3(7)	2(8)	-22(8)
C(44)	24(9)	28(9)	58(12)	-6(9)	15(8)	-10(7)
C(45)	30(10)	41(10)	43(11)	-7(9)	3(8)	4(8)
C(46)	39(10)	32(9)	33(10)	-6(8)	-7(8)	0(8)
P(2)	33(5)	61(6)	25(5)	4(4)	-2(4)	-12(4)
Cl(1)	71(9)	93(10)	162(15)	-37(10)	-9(9)	-27(8)
Cl(2A)	158(23)	158(29)	99(18)	-37(18)	-37(19)	-45(21)
Cl(2B)	297(97)	110(48)	76(39)	-73(38)	18(47)	-78(55)

Table 5S. Hydrogen atom and interstitial solvent coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[PPh_4]_3[Mo_3I_{12}]\cdot 3/2CH_2Cl_2\cdot 1/2Et_2O$.

	x	y	z	U(eq)
H(12)	4740(15)	11183(12)	1437(11)	51
H(13)	3473(16)	12668(14)	1233(12)	62
H(14)	1364(17)	12418(15)	1456(11)	60
H(15)	585(14)	10674(14)	1906(11)	53
H(16)	1908(14)	9175(13)	2058(9)	44
H(22)	5721(15)	7444(13)	2989(10)	48
H(23)	5208(17)	6593(13)	4428(10)	58
H(24)	3515(17)	7206(15)	5391(12)	62
H(25)	2211(16)	8514(16)	4931(10)	67
H(26)	2507(14)	9141(13)	3489(10)	49
H(32)	4481(14)	6563(14)	2297(11)	50
H(33)	4095(15)	5298(15)	1612(12)	59
H(34)	3584(16)	5863(16)	320(11)	57
H(35)	3430(15)	7694(15)	-228(11)	56
H(36)	3803(14)	8960(13)	452(9)	44
H(42)	5939(14)	10139(13)	2424(9)	45
H(43)	7999(14)	10667(13)	1870(9)	44
H(44)	9257(14)	10143(12)	634(11)	52
H(45)	8551(14)	9032(13)	-24(11)	50
H(46)	6506(14)	8488(12)	528(10)	43
H(52)	-28(28)	42(25)	6337(17)	36
H(53)	-1154(29)	-1321(23)	6202(21)	46
H(54)	-1181(31)	-1468(24)	4849(25)	45
H(55)	-82(33)	-252(29)	3630(20)	62
H(56)	1045(29)	1111(25)	3765(17)	38
H(62)	-731(28)	2329(34)	6197(21)	70
H(63)	-1518(19)	2834(29)	7517(22)	59
H(64)	-224(35)	2808(36)	8364(16)	76
H(65)	1856(32)	2276(40)	7891(24)	226
H(66)	2642(18)	1770(32)	6571(26)	24
H(72)	3314(26)	3473(32)	4544(26)	67
H(73)	3211(37)	5239(29)	3757(33)	191
H(74)	1516(47)	5812(21)	3244(30)	136
H(75)	-76(33)	4619(34)	3519(27)	110
H(76)	26(27)	2852(29)	4306(27)	79
H(82)	3995(12)	1891(12)	3856(6)	64
H(83)	5910(13)	974(15)	3668(8)	109
H(84)	6245(14)	-417(16)	4764(10)	58
H(85)	4664(15)	-889(12)	6049(9)	56
H(86)	2748(12)	29(8)	6237(7)	67
C(1)	1206(9)	2367(9)	7576(6)	47(13)
Cl(1)	-508(10)	2205(10)	8263(7)	112(5)
Cl(2A)	1509(8)	1800(7)	6695(6)	134(11)
Cl(2B)	1050(8)	2580(7)	6551(6)	164(37)
C(3)	3220(14)	4009(11)	3769(7)	11(22)
Cl(3A)	3268(11)	2988(10)	4408(6)	67(11)
Cl(3B)	3008(15)	4820(9)	4462(9)	110(19)
C(4)	-1002(14)	3799(17)	4626(9)	57(41)
Cl(4A)	-484(11)	3200(13)	5408(8)	75(12)
Cl(4B)	-334(18)	5201(16)	4128(10)	73(12)
C(5)	2184(17)	5208(10)	4002(9)	55(20)
C(6)	2999(17)	4609(12)	3473(8)	87(30)
O(1)	2389(16)	3626(14)	3188(6)	83(18)
C(7)	2564(13)	3207(11)	3947(6)	173(63)
C(8)	3371(11)	2408(10)	4241(6)	43(17)