The Crystal Structures of $MoMe_2(\eta^6\text{-}C_6H_6)(PPhMe_2)_2$ and $MoMe_2(\eta^6\text{-}C_6H_5Me)(PPhMe_2)_2$

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The crystal structure of $MoMe_2(\eta^6\text{-}C_6H_6)(PPhMe_2)_2$ and $MoMe_2(\eta^6\text{-}C_6H_5Me)(PPhMe_2)_2$ have been determined from three-dimensional *X*-ray diffraction data collected by counter methods. The former crystallizes in the monoclinic space group $P2_1/n$ with a = 8.108(4), b = 24.287(8), c = 11.961(5) Å, β = 96.59(4)°, and Z = 4 for D_c = 1.36 g cm^{-3}. The final R value was 0.035 based on 1 271 independent observed reflections. $MoMe_2(\eta^6\text{-}C_6H_5Me)(PPhMe_2)_2$ crystallizes in the triclinic space group $P\bar{1}$ with a = 9.128(2), b = 9.611(2), c = 14.842(3) Å, α = 105.44(3), β = 93.72(3), γ = 102.47(3)°, and Z = 2 for D_c = 1.35 g cm^{-3}. The R value was 0·019 for 3 586 observed reflections. The presence of the methyl group on the toluene ligand does not appreciably alter the electronic environment of the molybdenum atom. In the toluene derivative the two Mo–C(σ) bonds average 2.291(5) Å. The Mo–C(σ) lengths range from 2.250(2) to 2.344(2) Å, and are seen to vary in a pair-wise fashion such that the arene shows a tendency to act as a diene.

THE structural characterization of the metal–carbon sigma bond in organometallic complexes of titanium, zirconium, and hafnium has provided considerable information about the factors which govern the observed bond lengths. Study of compounds of the type $ZrR_2(\eta^5\text{-}C_5H_5)_2$ has shown the strong dependence of the Zr–C(σ) distance on the size of the group R: 2.280(4) Å in $Zr(CH_2SiMe_3)_2(\eta^5\text{-}C_5H_5)_2$ [1] *vs.* 2.388(12) Å in $Zr(CHPh_2)_2(\eta^5\text{-}C_5H_5)_2$.[2] An even more substantial difference has been found between the Zr–C(π) and Zr–C(σ) lengths. The former occur in the range 2.514(8) [3] to 2.58(3) Å,[4] while the latter vary from 2.251(6) [5] to 2.296(10) Å [1] in the absence of strong steric effects. This has been attributed to differences in *s*-, *p*-, and *d*-orbital energies.[6]

For the chromium group metals a wider range of compounds are available for crystallographic investigations. We have now studied two of the recently reported molybdenum compounds of the type $MoMe_2(\pi\text{-arene})(PR_3)_2$,[7] since they present the opportunity to compare metal–carbon (σ) and (π) bond lengths in the same molecule. These compounds, which were prepared from the reaction of $MoCl_3(PR_3)(C_4H_8O)_2$ and Me_2Mg in arene–tetrahydrofuran, were crystallized from light petroleum (b.p. 40—60 °C). The trimethylphosphine derivatives were extremely soluble and difficult to crystallize, so the dimethylphenylphosphine compounds were chosen for study.

EXPERIMENTAL

X-Ray Data Collection, Structure Determination, and Refinement for $MoMe_2(\eta^6\text{-}C_6H_6)(PPhMe_2)_2$.—*Crystal data.* $C_{24}H_{34}MoP_2$, $M = 480.4$, monoclinic, $a = 8.108(4)$, $b = 24.287(8)$, $c = 11.961(5)$ Å, $\beta = 96.59(4)°$, $U = 2\,339.8$ Å^3, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 6.92$ cm^{-1}, space group $P2_1/n$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.20 × 0.40 × 0.50 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the $\omega - 2\theta$ scan technique in a manner similar to that described previously.[8] All reflections in one independent quadrant out to $2\theta \leqslant 50°$ were measured; 1 271 were considered observed [$I \geqslant 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Full-matrix least-squares refinement was carried out using the Busing and Levy ORFLS program.† The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Mo, P, and C were taken from Cromer and Waber,[9] and the scattering for molybdenum was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[10] Scattering factors for hydrogen were from ref. 11.

The position of the molybdenum atom was deduced by the inspection of a Patterson map, and the subsequent calculation of Fourier maps allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.093$. Conversion into anisotropic thermal parameters and further refinement gave $R_1 = 0.045$. The hydrogen atoms of the phenyl groups and the benzene ring were placed at calculated positions 1.00 Å from the bonded carbon atoms and their parameters were not refined. Those of the methyl groups were located on a difference Fourier map and their positional co-ordinates were varied. Additional cycles of refinement led to final values of $R_1 = 0.035$ and $R_2 = \{\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2\}^{\frac{1}{2}} = 0.036$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.4e Å^{-3}. The standard deviation of an observation of unit weight was 2.05. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F\text{-}|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 1_c. The observed and calculated structure factor amplitudes and thermal

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† Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distances and angles with estimated standard deviations, by W. R. Busing, K. O. Martin, and H. A. Levy), FOURIER (Fourier synthesis, D. J. Hodgson's version of Dellaca and Robinson's program), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and BPL (least-squares planes, by W. E. Hunter).

TABLE 1

Atomic positions in fractional co-ordinates for $MoMe_2(\eta^6\text{-}C_6H_6)(PPhMe_2)_2$

Atom	x/a	y/b	z/c
Mo	0.306 4(1)	0.359 43(3)	0.300 56(7)
P(1)	0.400 5(3)	0.294 9(1)	0.162 1(2)
P(2)	0.356 9(3)	0.448 7(1)	0.210 2(2)
C(1)	0.097(1)	0.363 0(4)	0.153 9(8)
C(2)	0.590(1)	0.364 5(4)	0.335 7(8)
C(3)	0.251(1)	0.242 6(4)	0.107 2(9)
C(4)	0.571(1)	0.247 9(4)	0.213 3(9)
C(5)	0.475(1)	0.320 4(4)	0.031 6(7)
C(6)	0.370(1)	0.323 0(4)	−0.069 1(8)
C(7)	0.426(2)	0.344 6(4)	−0.166 3(8)
C(8)	0.586(2)	0.363 2(5)	−0.162(1)
C(9)	0.692(1)	0.361 2(5)	−0.063(1)
C(10)	0.636(1)	0.339 4(4)	0.031 6(9)
C(11)	0.560(1)	0.483 2(4)	0.239 7(10)
C(12)	0.325(1)	0.457 9(4)	0.056 9(8)
C(13)	0.218(1)	0.503 0(4)	0.252 0(8)
C(14)	0.071(1)	0.516 5(4)	0.187 4(8)
C(15)	−0.033(1)	0.557 2(5)	0.221 0(9)
C(16)	0.006(2)	0.584 5(4)	0.323 0(10)
C(17)	0.150(2)	0.570 3(5)	0.388 6(9)
C(18)	0.256(1)	0.529 7(4)	0.354 7(8)
C(19)	0.127(2)	0.395 9(5)	0.412 7(9)
C(20)	0.289(2)	0.396 0(5)	0.472 5(9)
C(21)	0.374(2)	0.346 5(6)	0.497 0(8)
C(22)	0.316(2)	0.297 6(5)	0.444 3(10)
C(23)	0.154(2)	0.296 7(5)	0.384 7(10)
C(24)	0.058(1)	0.345 0(6)	0.378 9(9)

TABLE 2

Atomic positions in fractional co-ordinates for $MoMe_2(\eta^6\text{-}C_6H_5Me)(PPhMe_2)_2$

Atom	x/a	y/b	z/c
Mo	−0.004 98(2)	0.194 24(2)	0.256 51(1)
P(1)	0.236 97(7)	0.319 73(7)	0.361 61(4)
P(2)	0.014 39(6)	0.360 77(7)	0.148 96(4)
C(1)	−0.053 1(3)	0.400 6(3)	0.345 3(2)
C(2)	0.170 1(3)	0.120 9(3)	0.168 7(2)
C(3)	0.394 3(3)	0.233 7(4)	0.354 7(2)
C(4)	0.215 7(3)	0.336 3(3)	0.485 5(2)
C(5)	0.343 4(2)	0.512 5(3)	0.363 3(2)
C(6)	0.317 7(3)	0.633 2(3)	0.423 6(2)
C(7)	0.388 9(4)	0.777 9(3)	0.419 1(2)
C(8)	0.486 8(4)	0.803 2(4)	0.354 9(3)
C(9)	0.516 3(4)	0.686 5(5)	0.295 8(3)
C(10)	0.444 8(3)	0.539 8(4)	0.298 9(2)
C(11)	0.078 5(3)	0.564 3(3)	0.189 5(2)
C(12)	0.127 6(3)	0.342 1(4)	0.052 2(2)
C(13)	−0.173 8(2)	0.333 9(2)	0.084 3(2)
C(14)	−0.268 9(3)	0.419 9(3)	0.115 3(2)
C(15)	−0.414 0(3)	0.392 0(4)	0.067 0(2)
C(16)	−0.465 0(3)	0.278 8(4)	−0.011 1(3)
C(17)	−0.373 6(4)	0.192 3(4)	−0.041 7(2)
C(18)	−0.228 8(3)	0.219 0(3)	0.005 0(2)
C(19)	−0.180 8(4)	−0.000 1(3)	0.160 1(2)
C(20)	−0.262 2(3)	0.089 2(3)	0.213 0(2)
C(21)	−0.242 2(3)	0.115 8(3)	0.309 4(2)
C(22)	−0.129 4(3)	0.073 8(3)	0.356 5(2)
C(23)	−0.053 3(3)	−0.024 1(3)	0.305 3(2)
C(24)	−0.090 2(4)	−0.066 1(3)	0.208 6(2)
C(25)	0.048 1(4)	−0.093 5(3)	0.354 4(2)

parameters are given in Supplementary Publication No. SUP 22521. (36 pp.) *

X-Ray Data Collection, Structure Determination, and Refinement for $MoMe_2(\eta^6\text{-}C_6H_5CH_3)(PPhMe_2)_2$.—*Crystal Data.* $C_{25}H_{36}MoP_2$, M 494.5, triclinic, $a = 9.128(2)$, $b = 9.611(2)$, $c = 14.842(3)$ Å, $\alpha = 105.44(3)$, $\beta = 93.72(3)$, $\gamma = 102.47(3)°$, $U = 1\,215.1$ Å^3, $Z = 2$, $D_c = 1.35$ g cm^{-3}; $\mu(\text{Mo-}K_\alpha) = 6.70$ cm^{-1}, space group $P\bar{1}$. The lattice parameters were determined as above based on 15 reflections with $2\theta \geqslant 30°$.

A crystal of dimensions 0.20 × 0.25 × 0.30 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. The data collection procedure was the same as given above. All reflections in one independent hemisphere out to $2\theta \leqslant 50°$ were measured; 3 586 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the methods described above. Refinement with isotropic temperature factors gave $R_1 = 0.064$. The employment of anisotropic thermal parameters led to 0.044, and addition of the hydrogen atoms followed by further refinement gave final values of $R_1 = 0.019$ and $R_2 = 0.022$. The standard deviation of an observation of unit weight was 0.60. A final difference Fourier showed no

TABLE 3

Comparison of bond lengths (Å) and angles (°)

Bond	$MoMe_2(\eta^6\text{-}C_6H_6)$-$(PPhMe_2)_2$	$MoMe_2(\eta^6\text{-}C_6H_5Me)$-$(PPhMe_2)_2$
Mo–C(19)	2.26(1)	2.250(2)
Mo–C(20)	2.26(1)	2.282(3)
Mo–C(21)	2.37(1)	2.341(2)
Mo–C(22)	2.28(1)	2.257(2)
Mo–C(23)	2.27(1)	2.308(2)
Mo–C(24)	2.35(1)	2.344(2)
Mo–Cent	1.82	1.816
Mo–C(1)	2.30(1)	2.296(2)
Mo–C(2)	2.29(1)	2.286(2)
Mo–P(1)	2.463(3)	2.467(1)
Mo–P(2)	2.477(3)	2.476(1)
P(1)–C(3)	1.83(1)	1.836(3)
P(1)–C(4)	1.84(1)	1.834(2)
P(1)–C(5)	1.84(1)	1.843(2)
P(2)–C(11)	1.85(1)	1.835(3)
P(2)–C(12)	1.84(1)	1.828(2)
P(2)–C(13)	1.84(1)	1.839(2)
C(19)–C(20)	1.42(2)	1.424(4)
C(20)–C(21)	1.40(2)	1.389(4)
C(21)–C(22)	1.40(1)	1.400(4)
C(22)–C(23)	1.42(1)	1.434(4)
C(23)–C(24)	1.40(1)	1.396(4)
C(24)–C(19)	1.40(1)	1.415(4)
C(23)–C(25)		1.511(4)
Angle		
C(1)–Mo–C(2)	140.7(3)	142.4(1)
C(1)–Mo–P(1)	76.7(2)	76.8(1)
C(1)–Mo–P(2)	77.2(3)	77.3(1)
C(1)–Mo–Cent	109.9	108.5
C(2)–Mo–P(1)	77.0(2)	78.2(1)
C(2)–Mo–P(2)	79.6(3)	80.1(1)
C(2)–Mo–Cent	109.2	109.1
P(1)–Mo–P(2)	100.6(1)	100.2(1)
P(1)–Mo–Cent	130.4	130.7
P(2)–Mo–Cent	129.0	129.0
Mo–P(1)–C(3)	116.0(4)	119.3(1)
Mo–P(1)–C(4)	116.6(3)	114.4(1)
Mo–P(1)–C(5)	120.9(3)	120.2(1)
C(3)–P(1)–C(4)	97.5(5)	98.5(1)
C(3)–P(1)–C(5)	101.5(5)	99.9(1)
C(4)–P(1)–C(5)	100.5(5)	100.8(1)
Mo–P(2)–C(11)	120.3(3)	122.7(1)
Mo–P(2)–C(12)	122.2(3)	120.7(1)
Mo–P(2)–C(13)	111.8(3)	111.0(1)
C(11)–P(2)–C(12)	98.9(5)	98.2(2)
C(11)–P(2)–C(13)	100.5(5)	100.4(1)
C(12)–P(2)–C(13)	99.2(5)	99.8(1)
C(24)–C(19)–C(20)	118(1)	117.8(3)
C(19)–C(20)–C(21)	120(1)	119.3(3)
C(20)–C(21)–C(22)	120(1)	121.6(3)
C(21)–C(22)–C(23)	118(1)	119.5(3)
C(22)–C(23)–C(24)	120(1)	117.3(3)
C(23)–C(24)–C(19)	121(1)	122.6(3)
C(25)–C(23)–C(22)		121.2(3)
C(25)–C(23)–C(24)		121.1(3)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

feature greater than 0.2 e Å^{-3}. Unit weights were used, and no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was observed. The final values of the positional parameters are listed in Table 2. The observed and calculated structure factor amplitudes and thermal parameters are given in SUP 22521.

DISCUSSION

The molecular structure and atom-numbering scheme for $MoMe_2(\eta^6-C_6H_6)(PPhMe_2)_2$ and $MoMe_2(\eta^6-C_6H_5CH_3)(PPhMe_2)_2$ are shown in Figures 1 and 2, respectively. The two molecules crystallize in different space groups and reside in different packing environments, as shown in Figures 3 and 4. The close equivalence of related bond lengths and angles therefore allows the inference that (1) crystal packing does not exert a major effect upon the molecular parameters, and (2) the presence of the methyl group on the toluene ligand does not appreciably alter the electronic environment of the molybdenum atom. Since the structure of the toluene derivative is much more accurately determined than that of the benzene complex, the discussion will focus on the former. A comparison of the bond lengths and angles for both compounds is given in Table 3.

The two Mo–C(σ) bonds average 2.291(5) Å, and their difference, 0.010(3) Å = 3.3σ,* has no chemical significance. Previous structural studies have established the range of Mo–C(σ) lengths from 2.244(9) [12] to 2.414(4) Å [13] for 18-electron situations. In $MoMe_2(\eta^6-C_6H_5CH_3)(PPhMe_2)_2$ the average falls on the short end of the range, and even further so when compared to Mo–C(σ) bonds to alkyl ligands: 2.383(10) Å in $[Mo(CO)_3(CH_3)]_2$(azulene) [14] and 2.397(19) Å in $Mo(CO)_3(C_2H_5)(\eta^5$-

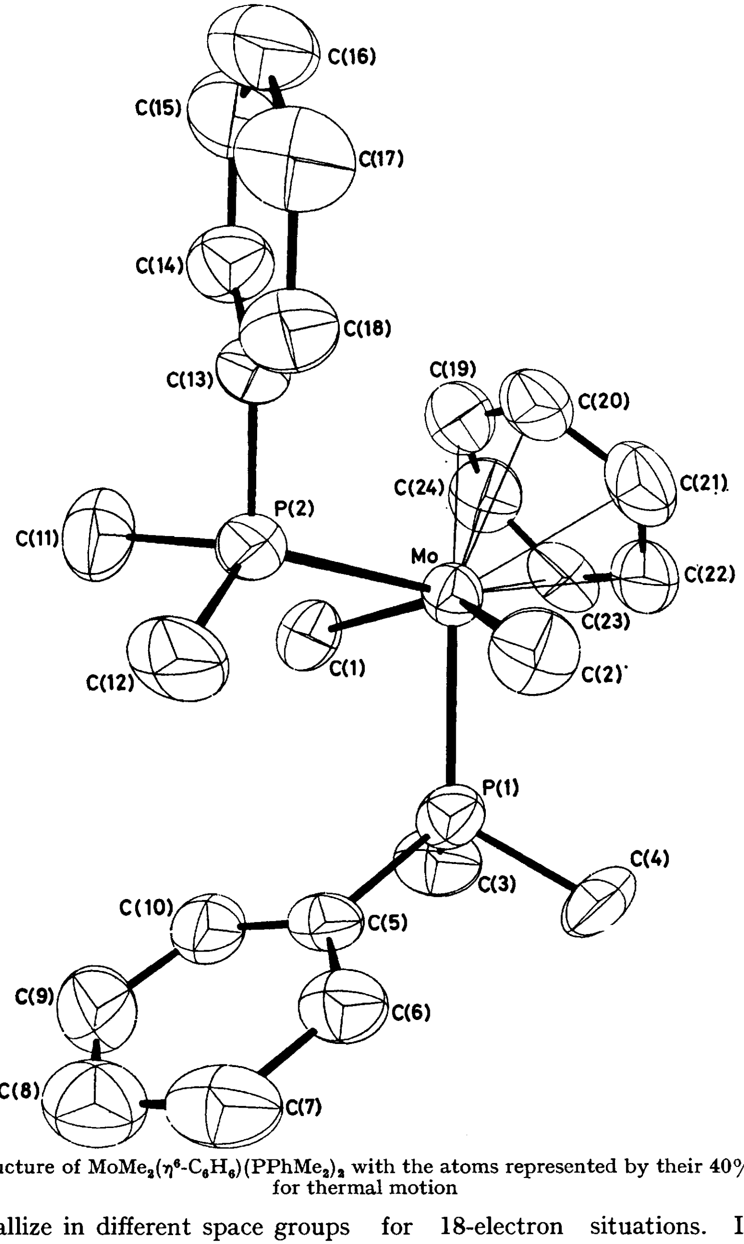

FIGURE 1 Molecular structure of $MoMe_2(\eta^6-C_6H_6)(PPhMe_2)_2$ with the atoms represented by their 40% probability ellipsoids for thermal motion

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* The standard deviation of the difference is given by σ(difference) = $(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$.

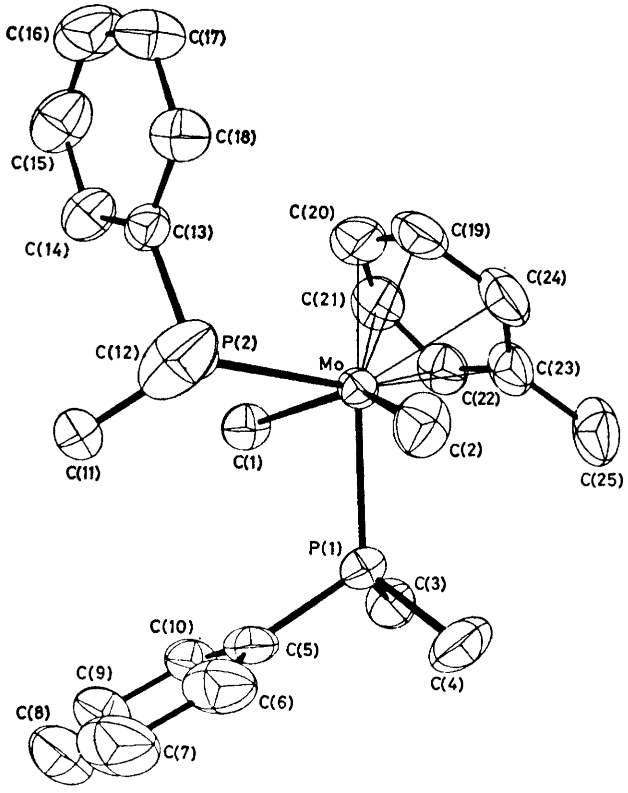


FIGURE 2 Molecular structure of $MoMe_2(\eta^6-C_6H_5Me)(PPhMe_2)_2$

C_5H_5).[15] The distance in the π-arene complex is, in fact, similar to the 2.288(9) Å value in the σ-perfluoropropyl compound $Mo(CO)_3(C_3F_7)(\eta^5-C_5H_5)$.

The Mo–C(π) bond distances in the toluene compound range from 2.250(2) to 2.344(2) Å, and are seen to vary in a pair-wise fashion. The bonds to C(20) and C(23) are short, those to C(19) and C(22) intermediate, and the ones to C(21) and C(24) long. With the aid of the ring-numbering scheme given in (I), it may be seen that the arene shows a tendency to act as a diene (II). The results of the best-plane calculations for the six-membered ring (Table 4) show that it is only planar to 0.08 Å, and C(21) and C(24) are displaced 0.07 and 0.08 Å in the direction away from the molybdenum atom. The same pattern is also shown for the benzene complex. It should be noted, however, that the contribution of (II) does not produce a localization of the bonding electron density in the rings themselves.

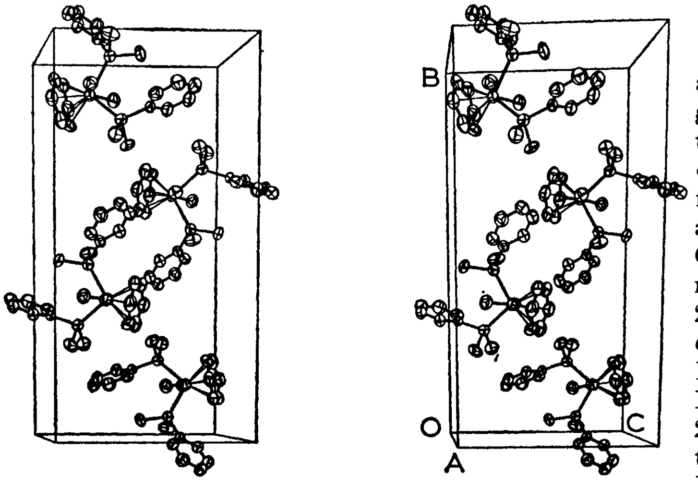


FIGURE 3 Stereoscopic view of the unit-cell packing in $MoMe_2(\eta^6-C_6H_6)(PPhMe_2)_2$

TABLE 4

Least-squares planes

Plane *	Equation of plane
A	$0.492\,4X + 0.168\,6Y - 0.853\,9Z + 2.377\,6 = 0$
B	$0.554\,3X + 0.832\,2Y - 0.012\,4Z + 1.568\,3 = 0$

Deviation of atoms from plane (Å)

Atom	Plane A	Plane B
C(19)	0.04	0.06
C(20)	0.04	0.02
C(21)	−0.09	−0.07
C(22)	0.05	0.06
C(23)	0.03	0.02
C(24)	−0.08	−0.08
C(25)		−0.09
Mo	1.820	1.816

* The atoms of the six-membered ring were used to compute the planes. Plane A is associated with $MoMe_2(\eta-C_6H_6)(PPhMe_2)_2$, and Plane B, $MoMe_2(\eta-C_6H_5Me)(PPhMe_2)_2$.

Concerning the origin of the nonplanarity of the π-arenes, it might be expected, on purely electronic grounds, that the long Mo–C(π) bonds would be *trans* to the more strongly π-bonding phosphine ligands. The opposite is true: in the toluene complex P(1) is symmetrically situated under C(19) and C(20) at 3.497(3) and 3.460(3) Å, while P(2) is 3.530(3) and 3.536(3) Å from C(22) and C(23), respectively. The closest intramolecular nonbonding approaches, are C(1) • • • C(21), 2.737(4) Å, and C(2) • • • C(24), 2.756(4) Å. The corresponding H • • • H hydrogen separations are: H(6)[C(2)] • • • H(29)[C(24)], 2.41 Å; H(5)[C(2)] • • • H(29)[C(24)], 2.51 Å; H(2)[C(1)] • • • H(32)[C(21)], 2.44 Å; H(1)[C(1)] • • • H(32)[C(21)], 2.45 Å. Thus, there are four interactions at the 2.4 Å sum of the H • • • H van der Waals radii.[16] If C(21) and C(24) were brought into the plane of the other four ring-carbon

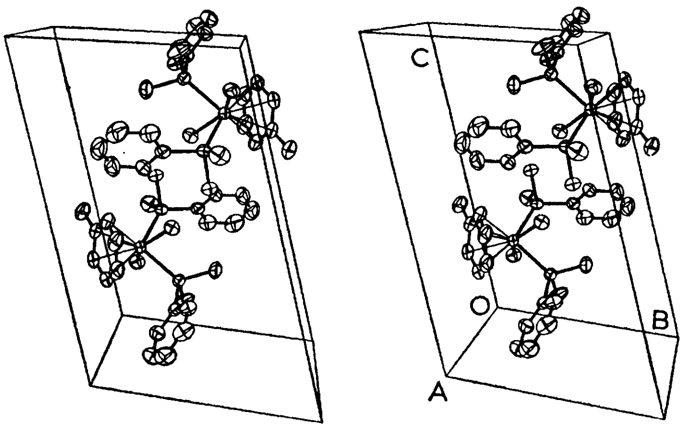
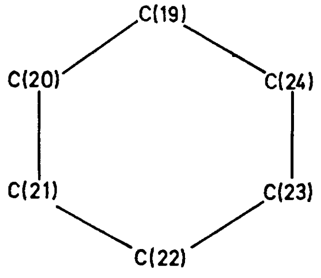


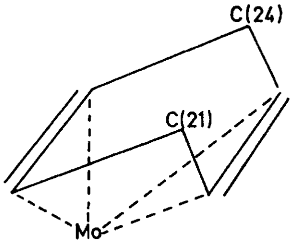
FIGURE 4 Unit-cell packing in $MoMe_2(\eta^6-C_6H_5Me)(PPhMe_2)_2$

atoms a significant steric repulsion between these hydrogen atoms would result.

The average Mo–C(π) distances, 2.297 Å in MoMe$_2$(η^6-C$_6$H$_5$CH$_3$)(PPhMe$_2$)$_2$, and 2.298 Å in MoMe$_2$(η^6-C$_6$H$_6$)(PPhMe$_2$)$_2$, are shorter than that found in cyclopentadienylmolybdenum complexes: 2.332 Å in Mo(CO)$_2$(η^5-C$_5$H$_5$)(PPh$_3$)[C(CN)$_2$C(CN)$_2$CH$_3$],[13] and 2.358 Å in [Mo(CO)$_3$(CH$_3$)(azulene)]$_2$.[14] The reason for the closer approach of the π-arenes may lie in the absence of the strongly π-bonding carbonyl groups. With reference to a well-studied series of chromium compounds, it is seen that the Cr–C(π) distance in Cr(CO)$_3$(η^6-C$_6$H$_6$) is 2.22 Å,[17] while the Cr–C(π) length in Cr(CO)$_2$(η^5-C$_5$H$_5$)(NO) is 2.188(5) Å.[18] However, the replacement of the three carbonyl groups by another benzene molecule reduces the Cr–C(π) length to the 2.14 Å found in Cr(η^6-C$_6$H$_6$)$_2$.[17]



(I)



(II)

Although Mo–P bond lengths have been reported over a wide range (2.3—2.6 Å), they cluster around *ca.* 2.47 Å,[19] and the 2.472(5) Å average in MoMe$_2$(η^6-C$_6$H$_5$CH$_3$)(PPhMe$_2$)$_2$ may therefore be considered normal. In both compounds the P–Mo–P angles are close to 100° which is consistent with the low values of $J_{\mathrm{P-P'}}$, *ca.* 20 Hz, found for these complexes and with the appearance of the phosphine methyl resonances as ' filled-in ' doublets.[7]

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