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Dynamic Processes in the Solid State. *X*-Ray Structural Characterization and Dynamic Behaviour of $[Mo(C_6H_5Me)(CO)_3]$†

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The structure of $[Mo(C_6H_5Me)(CO)_3]$ has been determined by single-crystal *X*-ray diffractometry. The complex shows a staggered orientation of the tricarbonyl group with respect to the arene atoms, differing from $[Cr(C_6H_5Me)(CO)_3]$ where the tricarbonyl group is eclipsed. The dynamic behaviour evidenced by ^{13}C cross-polarization magic angle spinning n.m.r. spectroscopy in the solid state is explored by means of atom–atom pairwise potential-energy calculations and thermal motion analysis.

The compounds $[Mo(C_6H_5Me)(CO)_3]$ and $[Cr(C_6H_5Me)(CO)_3]$ have been reported to show very similar dynamic behaviour under ^{13}C magic angle spinning (m.a.s.) cross polarization (c.p.) n.m.r. experimental conditions in the solid state.[1] For both species it was suggested that the tricarbonyl groups undergo reorientation around the co-ordination axes while the arene ligands remain static. From linewidth analysis, rotational barriers of *ca.* 15 and 17 kcal mol^{-1} for the complexes of Cr and Mo were estimated.

The similarity of the spectral features of the two derivatives had led to the conclusion that the two species would be isostructural in the solid state.[1] This expectation prompted us to undertake the structural characterization of $[Mo(C_6H_5Me)(CO)_3]$ by single-crystal *X*-ray diffraction.

In this paper we show that the two complexes possess different rotameric conformations in the solid: while the chromium species is eclipsed[2] the molybdenum one is almost staggered, the CO groups being rotated by *ca.* 28° with respect to the ring C atoms.

We have previously investigated[3,4] the molecular fragment reorientational motions in solid $[Cr(C_6H_5Me)(CO)_3]$, in the related species $[Cr(C_6H_6)_2]$ and $[Cr(C_6H_6)(CO)_3]$, and in crystals of the *cis* and *trans* isomers of $[Fe_2(C_5H_5)_2(CO)_4]$ by means of thermal motion analysis and atom–atom pairwise potential-energy calculations. These methods are here applied to investigate the dynamic behaviour of the molybdenum complex in the solid state.

Experimental

X-Ray Structure Determination.—Crystal data and details of measurements are summarized in Table 1. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with Mo-K_α radiation, and reduced to F_o; no decay correction was necessary. An absorption correction was applied by the Walker and Stuart method[5] (correction range in ω and θ: 0.89—1.0). The structure was solved by direct methods, which afforded the position of the Mo atom; all remaining atoms, including the H atoms, were located by subsequent Fourier difference syntheses. The refinement was by least-squares calculations, the function minimized being $\Sigma w(F_o - KF_c)^2$. The weighting scheme employed was $w = K/[\sigma^2(F) + |g|F^2]$ where both K and g were refined (1.6 and 0.0006, respectively). For all calculations the SHELX[6] package of crystallographic programs was used. All atoms were allowed to vibrate anisotropically, except the H atoms which were treated isotropically. No geometrical constraints were applied to the H(phenyl) atoms, while the methyl group was refined as a rigid body after location of the H(Me) atoms from the Fourier synthesis. Fractional atomic co-ordinates are reported in Table 2. Thermal motion analysis, based on the *T*, *L*, *S* approach,[7] was performed by using the THMA11 program.[8]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 1. Crystal data and details of measurements for $[Mo(C_6H_5Me)(CO)_3]$

Formula (*M*)	$C_{10}H_8MoO_3$ (272.1)
Space group	$P2_1/c$
a/Å	6.212(1)
b/Å	12.098(1)
c/Å	13.717(3)
β/°	101.83(1)
Z	4
U/Å^3	1 009.0
F(000)	528
D_c/g cm^{-3}	1.79
μ(Mo-K_α)/cm^{-1}	11.4
Reflections measured	3 673
Reflections observed [$I > 2.0\sigma(I)$]	3 029
$R(R')$	2.9 (3.2)
Crystal size (mm)	0.1 × 0.1 × 0.08
Scan range (°)	$2.5 < \theta < 35$
Scan method	ω—2θ
Scan interval (°)	1.1 + 0.35 tan θ
Prescan speed (° min^{-1})	5
Prescan accept, $\sigma(I)/I$	0.5
Required final $\sigma(I)/I$	0.01
Background measurement time	Peak time
Max. time for measurement (s)	120
Collected octants	$\pm h, +k, +l$

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† Tricarbonyl(η-toluene)molybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: cal = 4.184 J.

Table 2. Fractional atomic co-ordinates for $[Mo(C_6H_5Me)(CO)_3]$

Atom	*x*	*y*	*z*
Mo	0.681 33(2)	0.271 89(2)	0.499 99(1)
C(1)	0.618 8(4)	0.164 3(2)	0.637 9(1)
C(2)	0.814 3(4)	0.225 6(2)	0.669 2(2)
C(3)	0.819 9(5)	0.337 8(2)	0.663 2(2)
C(4)	0.628 1(7)	0.397 3(3)	0.625 1(2)
C(5)	0.431 7(5)	0.340 2(3)	0.592 3(2)
C(6)	0.428 3(4)	0.223 3(3)	0.598 9(2)
C(7)	0.619 8(4)	0.039 5(2)	0.649 5(1)
C(8)	0.833 4(4)	0.154 3(2)	0.442 7(2)
O(8)	0.919 4(5)	0.085 8(2)	0.408 9(2)
C(9)	0.456 1(4)	0.266 8(2)	0.377 6(2)
O(9)	0.319 2(4)	0.263 1(2)	0.307 8(2)
C(10)	0.848 3(4)	0.372 4(2)	0.432 4(2)
O(10)	0.945 4(4)	0.431 3(2)	0.391 8(2)

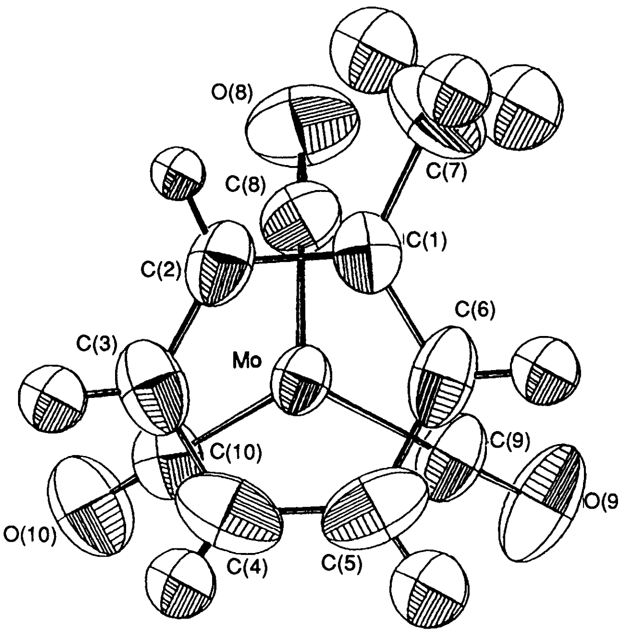


Figure 1. ORTEP drawing of $[Mo(C_6H_5Me)(CO)_3]$ showing the atomic labelling scheme

Table 3. Relevant bond distances (Å) and angles (°) for $[Mo(C_6H_5Me)(CO)_3]$

Mo–C(1)	2.393(2)	Mo–C(9)	1.954(2)
Mo–C(2)	2.366(2)	Mo–C(10)	1.951(2)
Mo–C(3)	2.366(2)	C(8)–O(8)	1.135(3)
Mo–C(4)	2.364(3)	C(9)–O(9)	1.144(3)
Mo–C(5)	2.344(3)	C(10)–O(10)	1.149(3)
Mo–C(6)	2.351(3)	C(2)–H(1)	0.96(3)
C(1)–C(2)	1.413(3)	C(3)–H(2)	0.96(4)
C(2)–C(3)	1.360(4)	C(4)–H(3)	0.83(4)
C(3)–C(4)	1.398(5)	C(5)–H(4)	0.93(5)
C(4)–C(5)	1.394(5)	C(6)–H(5)	0.99(4)
C(5)–C(6)	1.418(5)	C(7)–H(6)	0.92
C(1)–C(6)	1.391(4)	C(7)–H(8)	0.92
C(1)–C(7)	1.518(4)	C(7)–H(9)	0.92
Mo–C(8)	1.960(3)		
C(1)–C(2)–C(3)	122.5(2)	C(2)–C(1)–C(7)	120.4(2)
C(2)–C(3)–C(4)	120.4(2)	Mo–C(8)–O(8)	179.3(2)
C(3)–C(4)–C(5)	119.2(3)	Mo–C(9)–O(9)	177.7(2)
C(4)–C(5)–C(6)	119.8(3)	Mo–C(10)–O(10)	179.4(2)
C(5)–C(6)–C(1)	120.9(2)	C(8)–Mo–C(9)	87.2(1)
C(6)–C(1)–C(2)	117.2(2)	C(8)–Mo–C(10)	85.1(1)
C(6)–C(1)–C(7)	122 4(2)	C(9)–Mo–C(10)	88.2(2)

Potential-energy-barrier Calculations.—The calculations of the potential-energy barriers associated with the arene and tricarbonyl group reorientations in the solid state were based on a Buckingham potential of the type (1) where index i

$$\text{p.e.} = \Sigma_i\Sigma_j(Ae^{-Br_{ij}} - Cr_{ij}^{-6}) \quad (1)$$

encompasses all atoms of the reference molecule, j the atoms of the surrounding molecules distributed according to space-group symmetry, and r_{ij} represents the atom–atom intermolecular distance.[9] The values of coefficients A—C used in this work were taken from ref. 10. For the Mo atom such coefficients are not available; values for the corresponding noble gas (Xe) were used.[10] In all calculations a 10-Å cut-off distance was used. Ionic contributions were not considered. All calculations were performed by using a slightly modified version of the computer program OPEC.[11] The methyl group was treated as a Cl atom centred on the C(Me) position. This is necessary to take into account the almost free rotational motion of the CH_3 groups in the solid and is justified by the similarity of the bulk of the CH_3 and Cl groups.[10a] Arene and tricarbonyl reorientations were performed around the co-ordination axis. The potential energy was calculated at 10° rotational steps for complete rotations of the fragments between ±180°. Relative potential-energy profiles (ΔE) were calculated as p.e. − p.e.$_{\text{min.}}$, where p.e.$_{\text{min.}}$ is the value corresponding to the observed structure (0° rotation). Allowance for 'co-operation'[12] of the molecules surrounding the reorienting fragment did not appreciably change the results.

Two models for the reorientational processes are discussed herein: (*a*) rigid-body reorientation of either the C_6H_5Me ligand or the $Mo(CO)_3$ group, and (*b*) independent simultaneous reorientation of the two fragments.

Results and Discussion

Structural Characterization of $[Mo(C_6H_5Me)(CO)_3]$.—The molecular structure of $[Mo(C_6H_5Me)(CO)_3]$ is shown in Figure 1 together with the atomic labelling scheme. The most relevant bond distances and angles are reported in Table 3. The $(CO)_3$ group is tilted on the average by 28° with respect to the C atoms of the arene ligand. As mentioned above this is the main structural difference from $[Cr(C_6H_5Me)(CO)_3]$ where the $(CO)_3$ group was found to be almost perfectly eclipsed.[2] The Mo atom appears to be slightly displaced from the exact centre of the aromatic ring showing Mo–C(toluene) distances in the range 2.344(3)—2.393(2) Å, the longest being from the atom bearing the methyl group [C(1)]. The average Mo–C(toluene) and Mo–C(CO) distances [2.365(3) and 1.955(2) Å] are as expected longer than in the chromium derivative [2.213(5) and 1.824(4) Å].

To our knowledge, the $[M(C_6H_5Me)(CO)_3]$ pair (M = Cr or Mo) represents the only case in the family of $[M(\text{arene})(CO)_3]$ complexes[13] in which two different conformations are found for the same arene.

Thanks to the good quality of the diffraction data, all H atoms could be directly located from the Fourier map (see Experimental section), showing that two of the methyl group H atoms lie on the molybdenum side of the arene plane, while the remaining H atoms are strictly coplanar with the carbon ring (average elevation 0.03 Å, maximum elevation 0.5 Å). No out-of-plane bending can be detected for the Me group (C-atom elevation 0.05 Å).

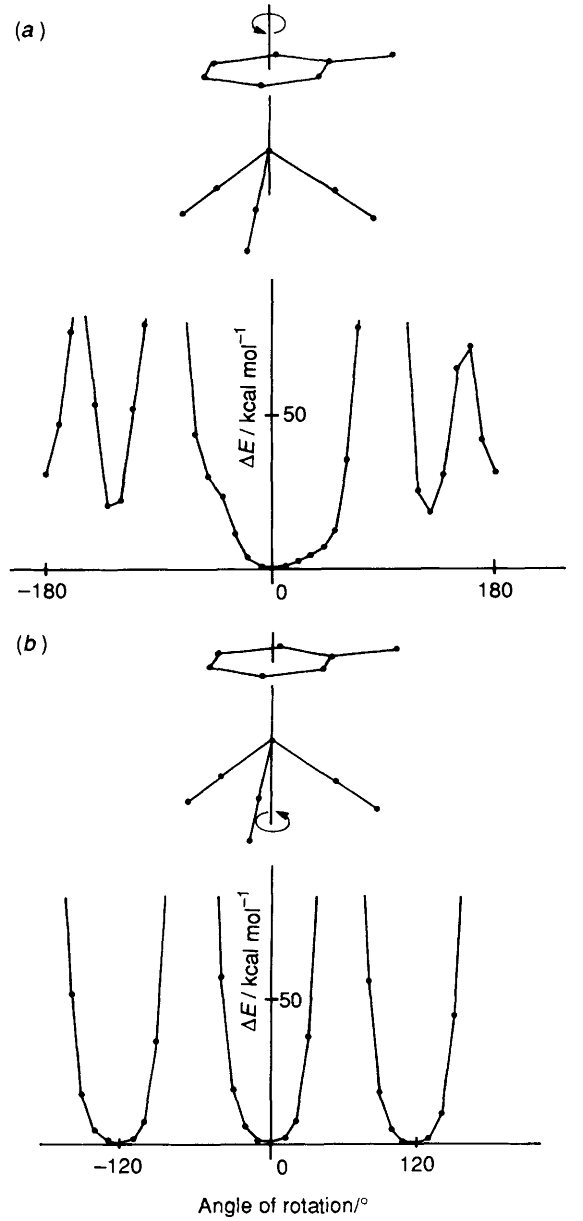


Figure 2. Relative potential energy *vs.* angle of rotation for reorientation of the toluene ligand (*a*) and of the Mo(CO)$_3$ group (*b*)

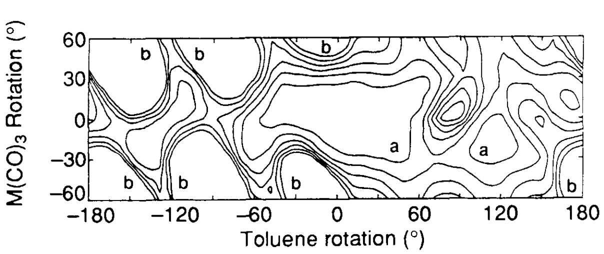


Figure 3. Topographic map for the combined rotations of the toluene ligand and of the Mo(CO)$_3$ group. Relative potential-energy levels (ΔE/kcal mol^{-1}) are drawn at 15 kcal mol^{-1} steps, the minimum being set at 0 kcal mol^{-1} for the original orientations of the two fragments: a, $\Delta E < 15$ kcal mol^{-1}; b, $\Delta E > 90$ kcal mol^{-1}

Solid-state Dynamic Behaviour of [Mo(C$_6$H$_5$Me)(CO)$_3$].—In order to investigate the nature of the solid-state dynamic behaviour of [Mo(C$_6$H$_5$Me)(CO)$_3$], reorientations of the two fragments around the co-ordination axis were performed as described above. The results of the C$_6$H$_5$Me and Mo(CO)$_3$ independent rotations [model (*a*)] are shown in Figure 2(*a*) and (*b*), respectively, from which the following deductions can be made: (1) as previously observed for [Cr(C$_6$H$_5$Me)(CO)$_3$],[3] complete reorientation of the two fragments is prohibited by the high energy barriers on both sides of the p.e. wells; (2) minima of $\Delta E = 0$ are seen [Figure 2(*b*)] at ±120° rotation of the M(CO)$_3$ group corresponding to the three-fold symmetry of the fragment; and (3) both fragments (but especially C$_6$H$_5$Me) lie in rather flat p.e. wells (but see also below).

In order to investigate the possibility of an independent and simultaneous motion of the two fragments [model (*b*)] the following procedure was adopted: (*a*) the tricarbonyl group was rotated between −60 and +60°, (*b*) at each rotational step of the tricarbonyl group full reorientation (±180°) of the toluene group was performed, and (*c*) each set of p.e. values was 'normalized' by subtracting the value of p.e.$_{,\text{min.}}$ for the 0°, 0° rotation. The resulting three-dimensional plot of p.e. against toluene rotation (abscissa) and Mo(CO)$_3$ rotation (ordinate) is shown in Figure 3. It can be seen that the combined rotations of the two fragments define a wide 'crater' surrounded by high-potential walls (the activation energy of *ca.* 15 kcal mol^{-1} has been taken as a reference to draw the first isopotential curve). Within the 15 kcal mol^{-1} borderline the toluene fragment easily moves in the angular interval ±60°, while tricarbonyl motion is more restricted (*ca.* ±30°).

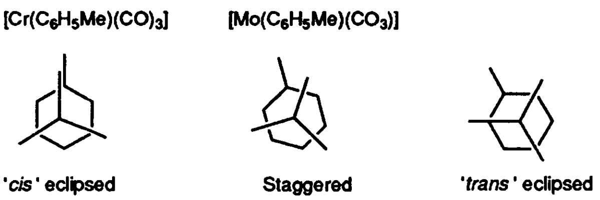
Although some more complicated motion [say coupled rotational/translational motion of the surrounding molecules to 'give way' to the reorienting fragment(s)] cannot be confidently ruled out, there appear to be no reasons for a preferential tricarbonyl group full-scale rotation with respect to toluene reorientation. Rather this latter fragment appears to sit in a flatter p.e. well than that of the CO ligands.

Finally the thermal motion analysis results can be discussed. Mean-square librational amplitudes obtained from the atomic anisotropic displacement parameters (a.d.p.s) for a rigid-body libration of the entire molecule are $L_1 = 47.8$, $L_2 = 12.6$, and $L_3 = 11.4°^2$. These values clearly indicate a strongly anisotropic motion ($L_1 \gg L_2 = L_3$) around an axis that is nearly coincident with the co-ordination axis (6.8°). With the THMA11 program it is also possible to introduce non-rigid librational modes, *i.e.* the C$_6$H$_5$Me and (CO)$_3$ groups librating in addition to the rigid-body motion.[14] In this way the mean-square librational amplitudes about the co-ordination axis, obtained as the sum of the rigid-body and additional motion components, are 57.2 and 41.9°^{2} for the C$_6$H$_5$Me and (CO)$_3$ groups, respectively.

Although speculations based on a.d.p.s obtained at only one temperature must be taken with great caution, the relationship between the mean-square librational amplitudes lends further support to the idea that the C$_6$H$_5$Me group has more librational freedom then Mo(CO)$_3$, this latter sitting in a steeper p.e. well as shown by p.e. calculations.

In conclusion, while we find no support for the full reorientational motion of the Mo(CO)$_3$ unit proposed on the basis of the m.a.s. n.m.r. experiment,[1] we have clear indications that the crystal packing does not oppose extensive 'swinging' of the two fragments around the co-ordination axis. A ±15° torsional motion of the two fragments in opposite rotameric directions (see Scheme) is enough to bring about interconversion between the limiting '*trans*' and '*cis*' conformations (the latter being the one observed for the chromium analogue). Such motion can be totally uncorrelated in the crystal so yielding, on the n.m.r. time-scale,[15] a complex mixture of all different rotameric conformations available for [Mo(C$_6$H$_5$Me)(CO)$_3$]. As the temperature decreases the swinging freedom also decreases, freezing out the more stable conformation.

In this respect the apparent contradiction between the



Scheme.

conformational difference shown by the derivatives of Cr and Mo and the extremely similar m.a.s. n.m.r. spectral features can be rationalized by an identical 'exchange' mechanism based on large-amplitude librational motions of the molecular fragments in the crystals of the two species. However, the possibility of a phase transition on decreasing the temperature should also be examined for a full assessment of the phenomenon.

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