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Intra- vs. intermolecular configurations in the three-legged, piano-stool compounds (*o*, *m* and *p*-xylene)$Mo(CO)_3$

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Abstract

The three (η6-xylene)$Mo(CO)_3$ complexes have been prepared and crystallographically characterized to determine the rotational relationship of the arene ring to the undercarriage, as has been suggested by theoretical studies. In fact, no such relationship can be seen, especially when combined with eight examples of structures with $Z' > 1$, where both staggered and eclipsed forms are found.

Keywords: Molybdenum; Carbonyl complex; Xylene; Three-legged, piano-stool; X-ray crystal structure

1. Introduction

Three-legged piano-stool, η^6-(arene) complexes of transition-metal carbonyls are among the most fundamental of all organometallic compounds, as exemplified by η^6-(benzene)$Cr(CO)_3$. Nonetheless, despite a major effort recently to understand basic concerns such as the extent to which arene aromaticity is diminished by complexation, the pattern of C–C bond distances, and the rotational relationship of the aromatic system to the $M(CO)_3$ undercarriage, many aspects of these compounds remain controversial [1–6].

Many of the theoretical studies of these compounds sharpen their precision on structural work obtained from crystallographic characterizations. Attention is often focused on the ring/undercarriage rotational relationship; specifically, does the position of the $M(CO)_3$ group determine the C–C bond-distance pattern? One aspect that seems to be in broad agreement is the weakness of the barrier to ring rotation about the metal-centroid axis, which is probably less than 1.0 kcal mol^{-1} in fluid phases and less than 5.0 kcal mol^{-1} in the solid state where intermolecular crystal packing forces may impede rotation [1,4,6]. Thus, it would seem intuitive that in all likelihood the relative orientation of the aromatic ring to the $M(CO)_3$ group would be dominated in the solid state by intermolecular, and not intramolecular forces. In consequence, the observed solid-state ring orientations would seem to be of very limited value to theoretical understanding, despite a continued insistence that C–C distances are determined by rotational orientation [4,6].

Most structures studied both structurally and theoretically are either benzene or mesitylene derivatives possessing at least threefold molecular rotational symmetry. In an effort to obtain information about compounds of lower symmetry, we have prepared and crystallographically characterized the three (η^6-xylene)$Mo(CO)_3$ complexes, which possess only optimized mirror-plane symmetry. Of the nine possible group-6 (xylene)$M(CO)_3$ compounds, only the structures of the three Cr complexes have been previously determined: *ortho* [7], *meta* [8] and *para* [9]. Two of these were done at room-temperature with large crystallographic residuals. The current structures have *R*-factors in the range of 1.7–2.2%, were done at low temperature and have C–C bond distance precision of ±0.002–3 Å. Additionally,

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it will be of interest to compare these results with the homo-molecular structures of other methyl-substituted arene $M(CO)_3$ complexes.

2. Results and discussion

The three η^6-xylene molybdenum tricarbonyl complexes, (*ortho*-xylene)$Mo(CO)_3$ (**1-*o***),(*meta*-xylene)-$Mo(CO)_3$ (**1-*m***), and (*para*-xylene)$Mo(CO)_3$ (**1-*p***) have been prepared in moderate yields by refluxing $Mo(CO)_6$ with the respective xylene for 1 h. Cooling the solutions to −78 °C afforded high quality crystals.

The X-ray crystallographic structures of the three complexes were determined at low temperature with a C–C bond precision of ca. 0.003 Å. Although all three molecules possess idealized C_s symmetry, only the solid-state structure of **1-*m*** resides on a crystallographic mirror plane; the structures of **1-*o*** and **1-*p*** crystallize without imposed symmetry. The angles of rotation from a perfectly eclipsed structure are: **1-*o***, 21°; **1-m**, 0° and **1-*p***, 15° The structures are shown in two perspectives in Figs. 1 and 2, and unit-cell packing diagrams are shown in Fig. 3. While the structures of **1-m** and **1-*p*** are isomorphous with their Cr analogues [8,9], that of **1-*o*** is not. In **1-*o***(Cr), one of the underlying M-CO groups nearly bisects the ring C–C bond to which the methyl groups are bound, while in **1-*o***(Mo) the pattern is reversed by 180°, though in both structures they are staggered.

Whether in a given compound in the solid state the ring/undercarriage relationship is staggered or eclipsed appears essentially random. In the isomorphous structures of the (benzene)$M(CO)_3$ compounds Cr [10], Mo [11], W [12], they are perfectly staggered. In (toluene)$M(CO)_3$, M = Cr is eclipsed [13] and M = Mo is staggered [14]. All (mesitylene)$M(CO)_3$ structures are eclipsed Cr [15] Mo [16], W [17]. In (pentamethylbenzene)$Cr(CO)_3$ the structure is staggered [18], and in (hexamethylbenzene)$M(CO)_3$, both Cr [19] and Mo [16] are staggered. As observed crystallographically and as supported by theory, the C–C bond distances in the staggered configuration for (benzene)$M(CO)_3$ alternate between long (ca. 1.42 Å) and short (ca. 1.40 Å) distances with the carbonyl groups lying under the middle of the longer distances [2,4,19]. As revealed in Fig. 4, to the extent possible in substituted complexes limited to C_s symmetry, this relationship is preserved.

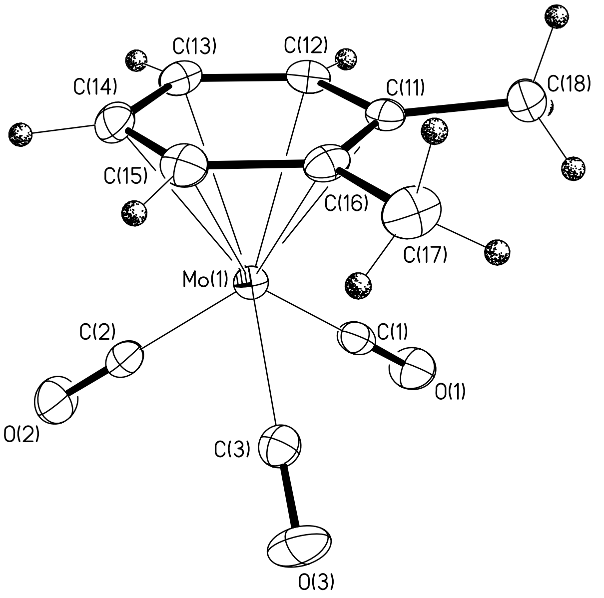

Fig. 1a. Molecular ORTEP drawing of **1-*o***.

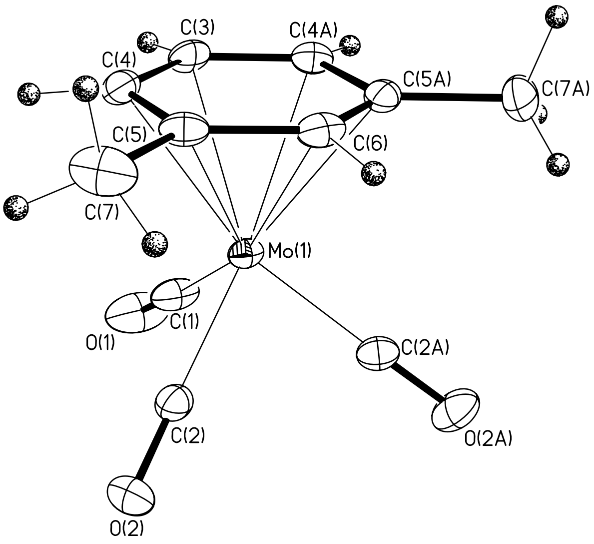

Fig. 1b. Molecular ORTEP drawing of **1-*m***.

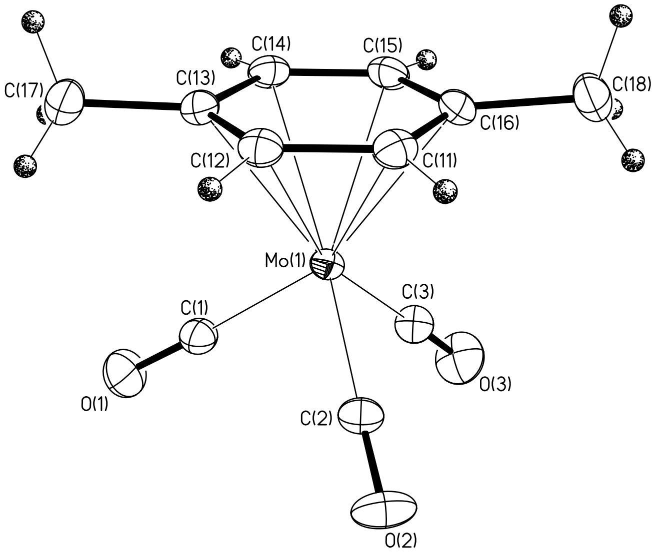

Fig. 1c. Molecular ORTEP drawing of **1-*p***.

One is forced to conclude that there is little or no correlation between the rotational orientation of the ring and the legs it stands on. This is further supported by a review of the Cambridge Structural Database for all (arene)$M(CO)_3$ structures with more than one molecule in the crystallographic asymmetric unit: eight structures were

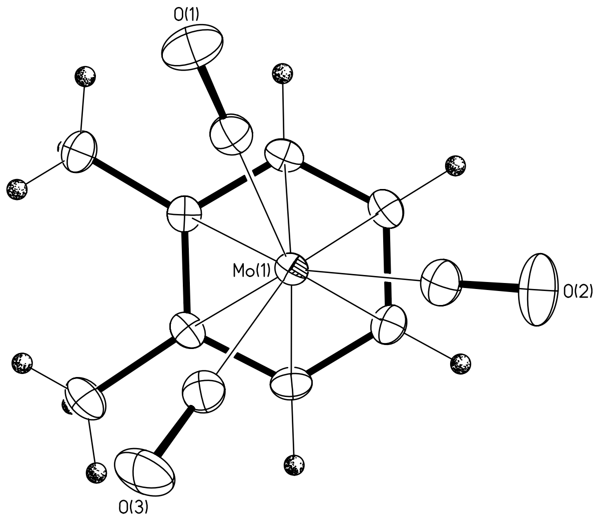

Fig. 2a. Centroid view of rotational orientation for **1-*o***.

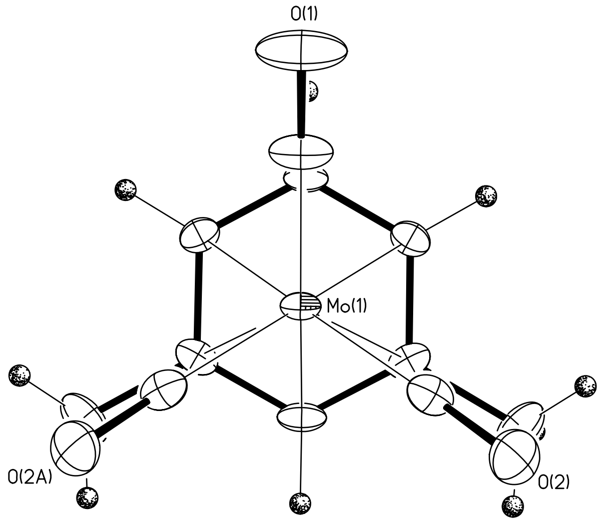

Fig. 2b. Centroid view of rotational orientation for **1-*m***.

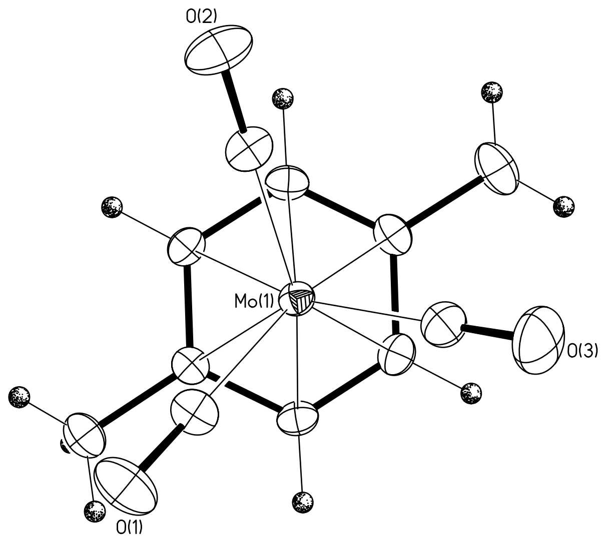

Fig. 2c. Centroid view of rotational orientation for **1-*p***.

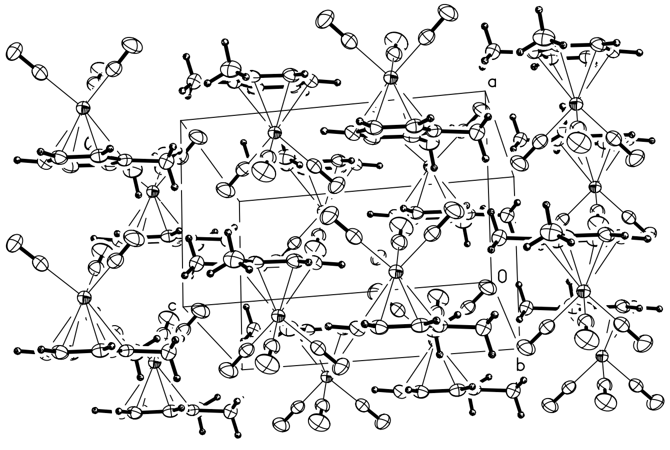

Fig. 3a. Unit-cell packing diagram for **1-*o*.**

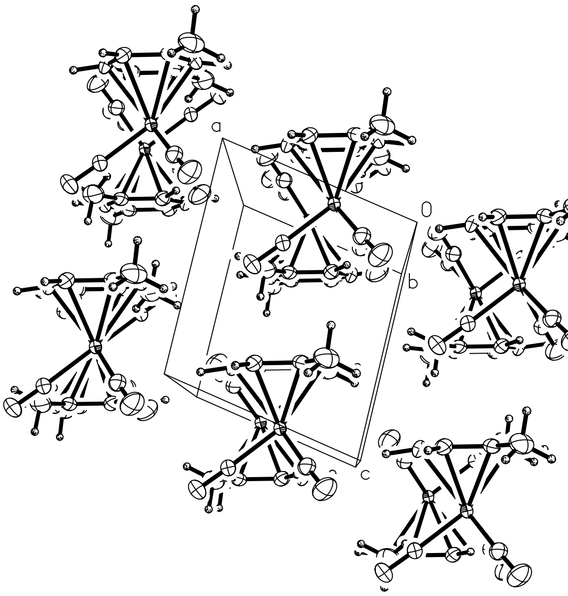

Fig. 3b. Unit-cell packing diagram for **1-*m*.**

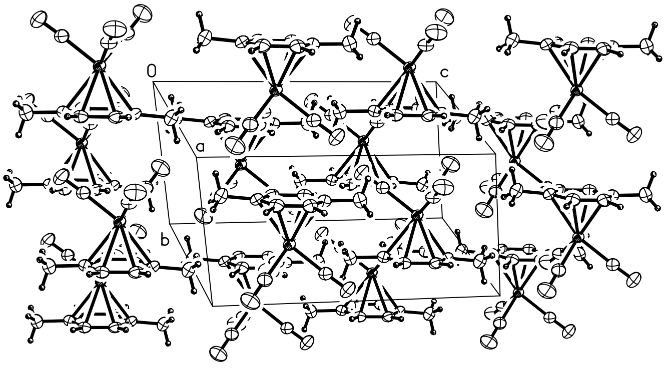

Fig. 3c. Unit-cell packing diagram for **1-*p*.**

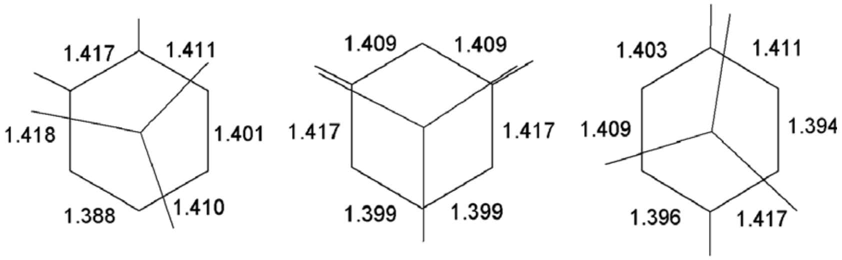

Fig. 4. Aromatic C–C bond distances (Å) for **1-*o***, **1-*m***, and **1-*p***. All esds are approximately 0.003 Å.

found in which both eclipsed and staggered orientations were found for the same compound in the same crystal [20]. Therefore, in the solid state, the rotational orientation must be dominated by intermolecular forces. In an examination of these intermolecular forces present in (η^6-arene)Cr(CO)$_3$, it was concluded that an important factor is the weakly attractive interaction between the oxygen atom of the carbonyl group and π-electron cloud of the arene [2]. In accord with this observation, all of the current complexes crystallize in similar packing arrangements, as shown in Fig. 3. The molecules stack in head-to-tail columns, i.e., with the three CO groups roughly equidistant from the arene ring. The ranges of the shortest and average intermolecular distances between the carbonyl oxygen atoms and the arene systems is very similar in the Cr systems reported, and in the Mo compounds reported herein, confirming that the interactions are not much affected by the size of the metal atom. The stacking in the case of **1-*p*** is slightly offset and this is reflected in a wider range of C–O···(arene) distances, 3.19 = 3.65 Å, as compared to ranges of 3.24 = 3.47 Å for **1-*o***, and 3.20–3.35 Å for **1-*m***.

Table 1
Crystallographic data for compounds **1-*o***, **1-*m***, and **1-*p***

Compound	**1-*o***	**1-*m***	**1-*p***
Empirical formula	$C_{11}H_{10}MoO_3$	$C_{11}H_{10}MoO_3$	$C_{11}H_{10}MoO_3$
Formula weight	286.13	286.13	286.13
Crystal system	Triclinic	Monoclinic	Triclinic
Lattice parameters			
a (Å)	6.800(3)	6.1446(5)	6.2038(17)
b (Å)	7.430(3)	12.8938(10)	6.9163(19)
c (Å)	11.114(4)	7.0516(6)	13.183(4)
α (°)	94.153(7)	90	80.933(5)
β (°)	92.649(7)	100.3470(10)	81.866(4)
γ (°)	106.311(6)	90	75.982(4)
V (Å^3)	536.2(4)	549.59(8)	538.8(3)
Space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
Z, Z'	2, 1	2, 0.5	2, 1
ρ_{calc} (g cm^{-3})	1.772	1.729	1.764
μ (Mo Kα) (mm^{-1})	1.205	1.176	1.199
Temperature (K)	211(2)	150(2)	218(2)
$2\theta_{max}$ (°)	52.52	56.40	56.72
Reflections collected	2738	3466	4441
Reflections/parameters	1531/136	1333/76	2731/137
R indices ($I > 2\sigma I$)			
R	0.0193	0.0174	0.0212
wR_2	0.0587	0.0519	0.0549
R indices (all data)			
R	0.0197	0.0180	0.0219
wR_2	0.0591	0.0524	0.0554
Largest peak final difference in map (e Å^{-3})	0.357	0.369	0.512

3. Experimental

3.1. General methods

The procedure is adapted from one described in the literature [21]. Molybdenum hexacarbonyl, Mo(CO)$_6$, (2.0 g, 7.56 mmol) was refluxed in 50 mL of the appropriate xylene for 1 h in a nitrogen-flushed flask and room-temperature condenser. The reaction flask was then stoppered and cooled slowly to room temperature, and further to −78 °C, which caused the yellow product to precipitate from solution in a form suitable for diffraction experiments. For other analytical work, the crude product was redissolved in CH_2Cl_2 to remove small quantities of elemental Mo. Elemental analysis: Calc. for $C_{11}H_{10}MoO_3$: C, 46.17; H, 3.52.

(*o*-Xylene)Mo(CO)$_3$: yield: 66%, m.p. 108–110 °C. Found: C, 45.56; H, 3.33%.
(*m*-Xylene)Mo(CO)$_3$: yield: 47%, m.p. 110–112 °C. Found: C, 45.77; H, 3.42%.
(*p*-Xylene)Mo(CO)$_3$: yield: 43%, m.p. 111–113 °C. Found: C, 46.01; H, 3.31%.

3.2. Crystallographic methods

Crystallographic data are collected in Table 1. All data were collected at low temperature on a Bruker platform diffractometer equipped with an APEX detector. In all cases the centrosymmetric alternative space groups were favored by the statistical distribution of normalized structure factors and confirmed by the results of refinement.

All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as idealized contributions. All software was contained in libraries distributed by Bruker-AXS (Madison, WI).

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre,CCDC nos. 611100 (**1-*o***), 611101 (**1-*m***), and 611102 (**1-*p***). Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, or by e-mail: deposit@ccdc.ac.uk or at http://www.ccdc.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.014.

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