are due to the geometrical constraints and probably to the packing effects and may explain the observation that the angle between the normals to the Cp ligand planes (128.0°) differs by about 3° from the Cp1-Zr-Cp2 (centroids) angle (131.2°).

We are currently trying to extend this reaction to other main-group derivatives. Reaction of the dimetallacycles with various electrophilic reagents leading to new heterocyclic systems will be reported in due time.

Supplementary Material Available: Tables of the anisotropic thermal parameters, hydrogen atom coordinates, complete bond distances and angles, and least-squares planes (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Experimental Observation of the Barrier to Rotation around the Metal-Arene Bond in [1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]molybdenum Tricarbonyl

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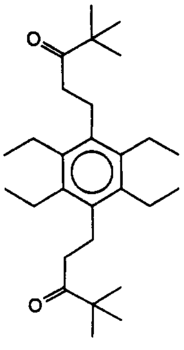
Summary: The barrier to rotation about the metal-arene bond in **1-Mo** is deduced from variable-temperature ^{13}C NMR studies. The dynamic stereochemistry of **1-Mo** is compared to that of **1-Cr** and the free arene **1**. The results indicate that the tripod rotation barrier is primarily steric in nature.

The debate over the magnitude of the barrier to rotation about the metal-arene bond in (hexaethylbenzene)chromium tricarbonyl has been settled by studies on desymmetrized analogues.[1,2] It has also been demonstrated that the alkyl groups on the arene and the metal tripod mesh complementarily;[3] the motion of the alkyl groups gate the motion of the tripod.[1] In order to better understand the physical nature of this barrier we have investigated the periodic effect of substituting chromium by molybdenum. Herein we report the experimental observation of the barrier to rotation about the molybdenum-arene bond in [1,4-bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]molybdenum tricarbonyl, 1-Mo.



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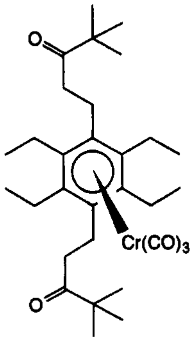
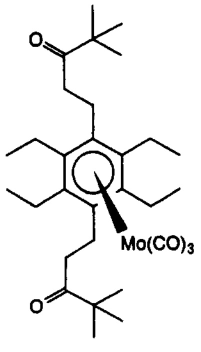


1-Cr



1-Mo

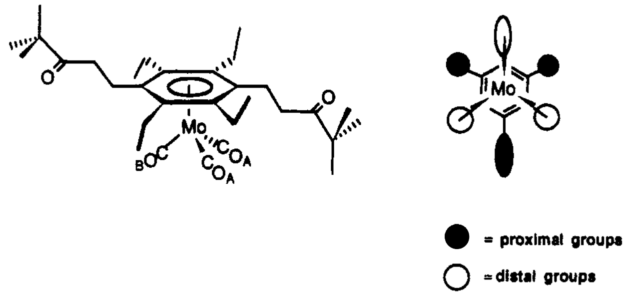


Figure 1. Structure of 1-Mo (Chem 3-D) and projection down the Mo-arene bond.

Synthesis of 1-Mo was accomplished by reaction of 1[4] with tris(acetonitrile)tricarbonylmolybdenum[5] in dioxane for 5 h at reflux under an atmosphere of argon. The product was purified by chromatography on silica gel (31% yield).

The symmetry analysis is the same as for the chromium compound. The static symmetry of 1-Mo is C_s and should give rise to two types of carbon monoxide sites in a ratio of 2:1 as well as two nonequivalent oxopentyl arms in a ratio of 1:1 (Figure 1). Tripod rotation produces a dynamic symmetry of $C_s \times C_3$, rendering the carbon monoxide sites equivalent but leaving the oxopentyl arms nonequivalent. Alkyl group rotation introduces yet greater dynamic symmetry and renders the oxopentyl arms equivalent. Thus independent probes for the tripod and for the ethyl group motion are established.

The ^{13}C NMR spectrum of 1-Mo shows one signal each for the methyl carbons of the *tert*-butyl groups, the tertiary carbon of the *tert*-butyl group, and the carbon monoxide carbon at room temperature. At -80 °C both the methyl carbon signal of the *tert*-butyl groups and the tertiary carbon signal of the *tert*-butyl group carbon have split into two peaks ($\delta\nu$ = 9.2, 14.3 Hz), respectively, of equal intensity whereas the carbon monoxide carbon signal remains a sharp singlet. At -140 °C in $CDCl_2F$[6] the carbon monoxide signal also splits into two peaks ($\delta\nu$ = 130 Hz)

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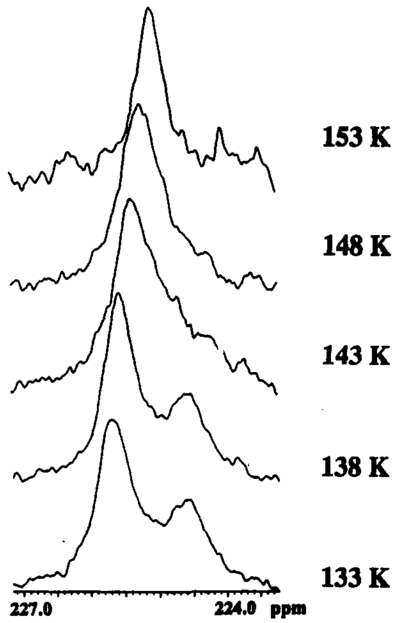

Figure 2. Variable-temperature ^{13}C NMR of 1-Mo in the region of the carbon monoxide (bound) carbons. The molybdenum tripod rotation barrier is 6.7 kcal/mol.

now of intensity 2:1 (Figure 2). The coalescence temperatures for the methyl carbon signal of the *tert*-butyl groups and the tertiary carbon signal of the *tert*-butyl groups are −55 and −50 °C, respectively; whereas the coalescence temperature for the carbon monoxide signal is −130 °C. On the basis of the above data and the Gutowsky–Holm approximation,[7] the free energies of activation (ΔG^{*}) for the various dynamic processes are estimated as follows: free arene ethyl group = 11.3 ± 0.5 kcal mol^{-1};[1] complexed arene ethyl group = 11.4 ± 0.5 kcal mol^{-1};[8] molybdenum tricarbonyl tripod = 6.7 ± 0.5 kcal mol^{-1}.[10]

Unlike the chromium case, where the rate of tripod rotation is closely linked to the rate of ethyl group rotation (k_{tripod} is ca. 50 k_{ethyl} at T_c), the molybdenum tricarbonyl fragment is rapidly rotating long after the ethyl groups have stopped (k_{tripod} is ca. $10^4 k_{ethyl}$ at T_c). Although the ethyl groups set up a sterically varigated environment for the metal tripod there is no evidence for gating behavior in 1-Mo.

The decrease in ΔG^{*} with change in metal (Cr = 9.5 ± 0.5 kcal/mol^{-1}; Mo = 6.7 ± 0.5 kcal mol^{-1}) supports a steric-based barrier. The X-ray geometry of (hexaethylbenzene)molybdenum tricarbonyl[9] shows a Mo to ring-center distance of 1.88 Å and a Mo to CO distance of 1.95 Å. These are both roughly 0.16 Å longer than the corresponding distances in the chromium complex. Thus moving the metal tripod away from the arene core manifests a smaller steric demand and a lower barrier.

One anomaly in the series is the high value for the ethyl group rotation in the chromium complex (11.8 kcal mol^{-1}) as compared to the free ligand (11.3 kcal mol^{-1}) and the molybdenum complex (11.4 kcal mol^{-1}). The difference is just outside of the error limits and may be of questionable significance. Nonetheless, one speculation is that the transition state for the ethyl group rotation requires a certain amount of out-of-plane distortion and that the more tightly bound chromium stiffens this potential compared to the weakly bound molybdenum or the free arene.

Experimental Procedure

[1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene]molybdenum Tricarbonyl (1-Mo). To a stirred solution containing 1,4-bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethylbenzene[1] (0.5 g, 1.2 mm) and 50 mL of dry dioxane was added 1.5 equiv of tris(acetonitrile)tricarbonylmolybdenum[5] (2.0 g, 6.6 mm). The reaction mixture was heated to reflux for 5 h; the color changed from yellow to brown to black. The solution was filtered hot under argon, and the solvent was evaporated, yielding a yellow-brown solid. The molybdenum complex was isolated by column chromatography on silica gel. Initially, the column was eluted with hexanes, yielding starting material, followed by 20% ethyl acetate/80% hexanes, yielding the product (0.220 g, 0.38 mm, 31.2% yield). Mp: 132 °C dec. ^1H NMR (499.8 MHz, $CDCl_3$, 25 °C, TMS): δ 1.18 (18 H, s), 1.23 (12 H, t, J = 7 Hz), 2.34 (8 H, q, J = 7 Hz), 2.62 (4 H, m), 2.77 (4 H, m). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3/CD_2Cl_2$, −80 °C, $CDCl_3$): δ 14.5 (q), 19.7 (t), 22.9 (t), 23.2 (t), 23.7 (q), 25.8 (q), 25.9 (q), 36.3 (t), 43.6 (s), 43.7 (s), 47.3 (t), 110.7 (s), 114.5 (s), 119.6 (s), 121.3 (s), 214.3 (s), 215.4 (s), 224.3 (s). IR (KBr): ν (cm^{-1}) 1930, 1845 (Mo–CO), 1700 (C═O). FABMS (high resolution) found 729.1478 (calcd for $C_{31}H_{46}O_5Cr$ (M + Cs^+) 729.1454).

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Registry No. 1, 132541-63-0; 1-Mo, 138857-10-0.

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[7] (a) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 97. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. (c) The GHA gives one temperature kinetics; the dominant error comes from the determination of the temperature of coalescence. We assume a possible error of 10 °C which leads to ca. 0.5 kcal mol^{-1} error. From extensive experience with the method we find this to be a generous error limit.

[8] The barrier to ethyl group rotation (ΔG^{*}) was determined from the coalescence behavior of the $C_{(q)}$ and $C_{(me)}$ ^{13}C signals of the *tert*-butyl group. The reported value was the average of the value determined for the two different sets of exchanging nuclei.

[9] Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

[10] The barrier to rotation of the metal tripod is given as the average of the barriers to exchange for CO_A to CO_B (6.8 ± 0.5 kcal mol^{-1}) and CO_B to CO_A (6.6 ± 0.5 kcal mol^{-1}); the population of CO_A equals twice that of CO_B.