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Crystal structures of $(\eta^6\text{-C}_7\text{H}_8)\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{W}$). Comparisons among a homologous series of cycloheptatriene complexes and experimental evidence for a boat conformation of the coordinated ring

Fred J. Hadley¹, Thomas M. Gilbert and Robin D. Rogers

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115 (USA)

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Abstract

Single crystal X-ray diffraction studies of the η^6 -cycloheptatriene complexes $(\eta^6\text{-C}_7\text{H}_8)\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$, **1**; $\text{M} = \text{W}$, **3**) are described. Complex **1** crystallizes in the monoclinic space group $P2_1/n$, $a = 12.189(9)$ Å, $b = 6.946(2)$ Å, $c = 12.355(3)$ Å, $\beta = 114.10(7)^\circ$, $Z = 4$. Data were collected in the ω - 2θ mode and refined to $R = 0.032$ and $R_w = 0.043$. Complex **3** is isostructural, with $a = 12.223(9)$ Å, $b = 7.079(3)$ Å, $c = 12.390(9)$ Å, $\beta = 113.90(8)^\circ$, $Z = 4$, $R = 0.042$ and $R_w = 0.056$. The bond distance and angle data indicate that both molecules adopt the “staggered” structure with the unique carbonyl ligand centered under the open side of the polyene ring, and that in both cases the ring adopts a cycloheptatriene structure rather than a norcaradiene one. The cycloheptatriene ligand is slightly non-planar, the metal is shifted toward the “closed” end of the ring, and the six-membered pseudo-ring carbon-carbon bonds exhibit three different sets of values rather than two.

1. Introduction

We have been investigating the “parent” cycloheptatriene compounds $(\eta^6\text{-C}_7\text{H}_8)\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}$, **1**; $\text{M} = \text{Mo}$, **2**; $\text{M} = \text{W}$, **3**) as starting materials for the preparation of new $(\eta^6\text{-arene})$ chromium, -molybdenum, and -tungsten tricarbonyl compounds [1]. In the course of this work, we noted that, of these three, only the molybdenum compound **2** had been studied by single crystal X-ray diffraction [2]; the structures of **1** and **3** remained undetermined. In fact, a search of the Cambridge Structural Database (CSD) [3] revealed that, while structural reports of several chromium and molybdenum compounds with derivatized cycloheptatriene rings exist, no $(\eta^6\text{-cycloheptatriene})$ tungsten compounds of any type have been structurally characterized.

We have therefore determined the structures of **1** and **3**, with particular emphasis on obtaining bonding and non-bonding distances sufficiently precise to allow comparisons between **1**, **2** and **3**, on determining the

relative orientations of the ligands, and on evaluating the planarity of the cycloheptatriene ring. Several features of the structures are notable, and we report them below.

2. Experimental details

Compounds **1** and **3** were prepared by literature methods [4,5]. They were crystallized from pentane as deep red air-stable chunks. Features of the data collection and refinement are given in Table 1. In the case of **3**, the position of the tungsten was determined using SHELXS [6], difference Fourier syntheses were used in combination with SHELX to determine the positions of other atoms [7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to “ride” on that atom with an isotropic temperature factor fixed at 5.5 \AA^2 . The refinement of **1** employed the coordinates determined for **3** as a starting model. Positional parameters are given in Tables 2 and 3, and bond distances appear in Table 4. ORTEP drawings of the molecules appear in Figs. 1 and 2. Tables of calculated hydrogen atom positions, anisotropic thermal parameters, and observed and cal-

Correspondence to: Prof. T.M. Gilbert or Professor R.D. Rogers.

¹ Permanent address: Department of Chemistry, Rockford College, Rockford, IL, USA.

TABLE 1. Summary of data collection and refinement parameters for **1** and **3**

	1	3
Formula	$\text{C}_{10}\text{H}_8\text{CrO}_3$	$\text{C}_{10}\text{H}_8\text{O}_3\text{W}$
Formula weight	228.17	360.02
Space group	$P2_1/n$	$P2_1/n$
T , K	293	293
a , Å ^a	12.189(9)	12.223(9)
b , Å	6.946(2)	7.079(3)
c , Å	12.355(3)	12.390(9)
β , °	114.10(7)	113.90(8)
V , Å ³	954.8	980.1
Z	4	4
D_{calc} , g cm ⁻³	1.59	2.44
μ_{calc} , cm ⁻¹	12.2	124
Diffractometer/scan	Enraf-Nonius CAD-4/ ω -2 θ	Enraf-Nonius CAD-4/ ω -2 θ
Relative transmission factors, %	83/100	54/100
Radiation	Mo-K α ($\lambda = 0.71073$)	Mo-K α ($\lambda = 0.71073$)
Decay of standard reflections	$\pm 2\%$	$\pm 1\%$
Reflections measured	1915	1953
2 θ range,	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
h, k, l range	+14, +8, ± 14	+14, +8, ± 14
Observed reflections ^b	1466	1456
Parameters	127	127
Weights	$[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0013F_o^2]^{-1}$
R ^c	0.032	0.042
R_w	0.043	0.056
GOF ^d	1.0	1.26

^a Least-squares refinement of $(\sin \theta)/\lambda$ values for 25 reflections with $\theta > 20^\circ$.

^b Corrected for Lorentz/polarization effects and absorption (empirical ψ scan); $F_o \geq 5\sigma(F_o)$.

^c $R = \Sigma \|F_o| - |F_c| \| / \Sigma |F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2\}^{1/2}$.

^d $\text{GOF} = [\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$; N_o = number of observations, N_v = number of variables

culated structure factors are available as supplementary material from the authors.

3. Structural results and discussion

Compounds **1** and **3** are entirely isostructural with each other, and with the molybdenum compound **2**

(which was refined in the non-standard space group $P2_1/a$). The higher precision of the distances and angles for the chromium compound *vs.* the tungsten compound probably reflects a combination of the greater domination of the structure factors by contributions from the metal in the tungsten complex (a greater "heavy atom" effect) and the difficulty in accounting

TABLE 2. Final fractional coordinates for **1**

Atom	x	y	z	B_{eq} ^a
Cr	0.28517(3)	0.10848(5)	0.53287(3)	1.94
O(1)	0.2584(2)	-0.0364(4)	0.2956(2)	4.98
O(2)	0.4712(2)	-0.1897(3)	0.6614(2)	4.90
O(3)	0.0845(2)	-0.1750(3)	0.4815(2)	3.77
C(1)	0.2713(2)	0.0241(4)	0.3865(2)	2.86
C(2)	0.3990(3)	-0.0783(4)	0.6108(3)	2.95
C(3)	0.1608(2)	-0.0630(4)	0.5051(2)	2.60
C(4)	0.3407(3)	0.2267(4)	0.7238(2)	3.35
C(5)	0.2234(3)	0.2650(4)	0.6527(3)	3.32
C(6)	0.1797(3)	0.3613(4)	0.5421(3)	2.91
C(7)	0.2435(3)	0.4112(4)	0.4751(2)	2.80
C(8)	0.3662(3)	0.3749(4)	0.5010(3)	2.80
C(9)	0.4524(3)	0.3109(4)	0.6066(3)	2.88
C(10)	0.4462(3)	0.3373(5)	0.7240(3)	3.47

^a $B_{\text{eq}} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

TABLE 3. Final fractional coordinates for **3**

Atom	x	y	z	B_{eq}^a
W	0.28742(3)	0.09525(5)	0.53313(3)	1.51
O(1)	0.261(1)	-0.038(2)	0.2848(9)	4.36
O(2)	0.4790(9)	-0.215(1)	0.662(1)	4.61
O(3)	0.0767(8)	-0.189(1)	0.4741(8)	3.52
C(1)	0.274(1)	0.017(2)	0.3771(9)	2.42
C(2)	0.404(1)	-0.105(1)	0.608(1)	2.76
C(3)	0.155(1)	-0.084(1)	0.498(1)	2.41
C(4)	0.343(1)	0.224(2)	0.729(1)	3.10
C(5)	0.229(1)	0.262(1)	0.662(1)	2.82
C(6)	0.184(1)	0.362(2)	0.551(1)	2.69
C(7)	0.248(1)	0.415(1)	0.482(1)	2.48
C(8)	0.372(1)	0.379(1)	0.510(1)	2.26
C(9)	0.457(1)	0.308(2)	0.610(1)	2.81
C(10)	0.455(1)	0.326(2)	0.730(1)	3.08

$$^a B_{\text{eq}} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}].$$

for all the absorption effects with an empirical absorption correction. In both **1** and **3** the bond and angle esds are better than those for the molybdenum com-

TABLE 4. Bond distances (\AA) and angles (deg) for **1** ($\text{M} = \text{Cr}$), **2** ($\text{M} = \text{Mo}$), ^a and **3** ($\text{M} = \text{W}$)

	1	2	3
M-C1	1.842(3)	1.99(2)	1.95(1)
M-C2	1.856(3)	1.99(2)	1.96(1)
M-C3	1.846(7)	1.95(2)	1.96(1)
M-C4	2.323(3)	2.47(2)	2.41(1)
M-C5	2.202(4)	2.37(2)	2.31(1)
M-C6	2.206(3)	2.31(2)	2.33(1)
M-C7	2.212(3)	2.31(2)	2.348(9)
M-C8	2.208(3)	2.33(2)	2.33(1)
M-C9	2.334(3)	2.43(2)	2.42(1)
M-C10	2.858(3)	2.96(2)	2.96(1)
M-Cent ^b	1.61	1.76	1.74
C4-C5	1.364(4)	1.35(2)	1.33(2)
C5-C6	1.415(4)	1.45(2)	1.44(2)
C6-C7	1.391(5)	1.38(2)	1.42(2)
C7-C8	1.418(5)	1.40(3)	1.43(2)
C8-C9	1.373(4)	1.34(2)	1.35(2)
C9-C10	1.495(5)	1.51(2)	1.50(2)
C4-C10	1.498(5)	1.54(3)	1.54(2)
C4-C9	2.431(5)	2.52	2.48(2)
C1-O1	1.149(3)	1.19(2)	1.15(1)
C2-O2	1.146(3)	1.13(3)	1.18(2)
C3-O3	1.155(3)	1.13(3)	1.15(1)
C1-M-C2	92.1(1)		90.9(5)
C1-M-C3	82.7(1)		82.4(5)
C2-M-C3	91.6(1)		90.6(5)
Cent-M-C1	128.9		127.7
Cent-M-C2	120.4		122.1
Cent-M-C3	129.3		130.5

^a Ref. 3. Atom labels for **2** have been changed to conform with those in this paper. ^b Cent is the calculated centroid of the six-membered pseudo-ring defined by C4-C9.

pound, partly reflecting the improvements in diffractometer technology since 1960.

In 1978, Albright *et al.* [8] reported a theoretical study of the orientation of 1,6-methano(annulene)- $\text{Cr}(\text{CO})_3$ compounds for which the coordinated section of the annulene formally corresponded to an η^6 -cycloheptatriene ring. The study concluded that the position of the carbonyl ligands with respect to the methano carbon (corresponding to C10 in **1-3**) depends upon the proximity of the two neighboring ring carbons (C4 and C9) to each other. If these two are close ($< ca. 2.1 \text{ \AA}$), the ring formally approaches a norcaradiene limiting structure, and the eclipsed form **B**, with the unique carbonyl lying under the closed side of the polyene, is predicted. If the two atoms are

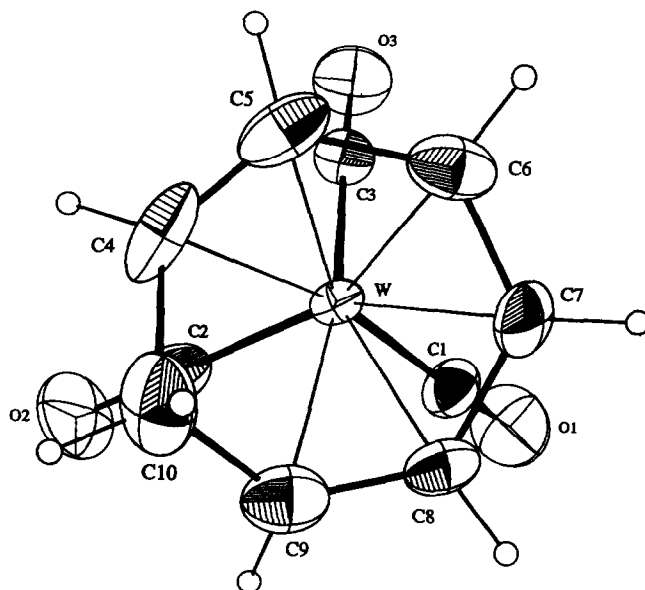


Fig. 1. ORTEP drawing of $(\eta^6\text{-C}_7\text{H}_8)\text{W}(\text{CO})_3$, **3**, showing the staggered orientation of the carbonyl ligands.

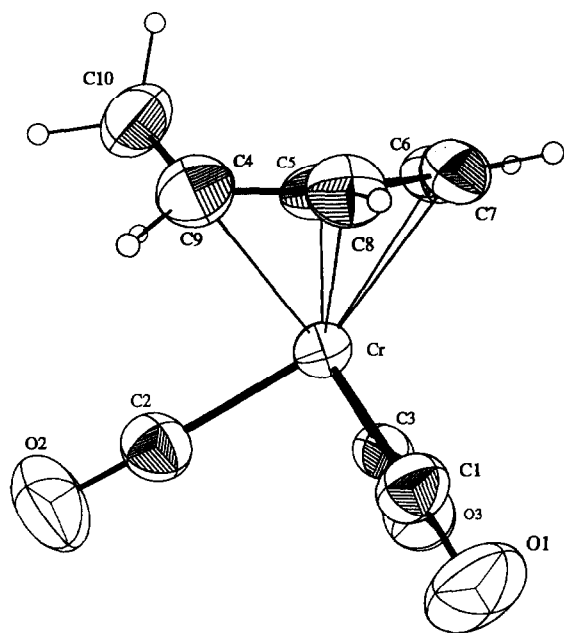


Fig. 2. ORTEP drawing of $(\eta^6\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3$, **1**, showing the flattened boat conformation of the cycloheptatriene ring.

farther apart (the cyclohexatriene limit), the staggered structure **A**, with the unique carbonyl lying under the open side of the polyene, is favored.

The data presented in Table 4 and Figs. 1 and 2 demonstrate that the parent $(\eta^6\text{-cycloheptatriene})\text{metal}$ tricarbonyls **1–3** corroborate this view. All three exhibit C4–C9 distances greater than 2.4 Å, and also exist in the staggered orientation, with a unique carbonyl (C2–O2) lying under the open side of the cycloheptatriene ligand, between C9 and C4 and nearly directly under C10. Thus the theoretical arguments expressed for the chromium compounds apply equally well to the molybdenum and tungsten homologues, implying that such

“heavy metal” factors as relativistic effects do not affect the bonding significantly.

The carbonyl ligands exhibit similar, typical distances and appear only slightly non-linear. Interestingly, consistently distinct bond angles associated with these ligands are observed. For example, in each case, the unique carbonyl C2–O2 displays a smaller ring centroid–metal–carbonyl carbon bond angle (Cent–M–C2) and larger carbonyl carbon–metal–carbonyl carbon bond angles (C1–M–C2 and C2–M–C3) than those of the similar carbonyl ligands (C1–O1 and C3–O3; angle C1–M–C3) residing nearer the “closed” end of the ring. One might describe the former observation as the similar carbonyls “bending away” from the ring–metal moiety, and the latter observation as either a “squeezing together” of carbonyls C1–O1 and C3–O3 or equally as a “spreading out” of carbonyl C2–O2. We interpret the angular differences as indicating that steric repulsion exists between the carbonyl ligands and the cycloheptatriene ring carbons. The carbonyl ligands C1–O1 and C3–O3 lying beneath the metal-bound carbons at the closed end of the ring are repelled more significantly, thus pushed away from the ring, increasing their Cent–M–C angles and decreasing the C–M–C angles. The unique carbonyl, oriented below the open end of the ring and, in particular, below the methano carbon C10 (which lies above the ring plane, away from the metal and the carbonyl) experiences less repulsion and therefore exhibits a more acute Cent–M–C angle.

Turning to the cycloheptatriene ring, we note that, as expected, the centroid of the six-membered pseudo-ring (defined by carbon atoms C4–C9) is closer to the metal for Cr than for Mo or W, and that the latter two are equidistant from this point, reflecting the relative bonding radii [9] of these metal atoms. As previously observed in several instances [2,10–13] the metals do not lie perpendicularly under the centroid, but in fact shift slightly toward the closed side of the ring, thereby increasing the M–C4 and M–C9 distances approximately 0.1 Å over those for the other carbons. The distortion is not significant enough to warrant the term “ring slip”, but does provide an indication that the bonding in these compounds differs from that present in an $(\eta^6\text{-arene})\text{metal}$ tricarbonyl, where the metal generally lies directly below the centroid.

Prior structural determinations [10–13] have demonstrated that the pseudo-ring carbon–carbon bond distances conform to an alternating “single bond–double bond” pattern. Closer inspection of the data for the homologous **1–3**, however, reveals that this apparently oversimplifies the general situation. This is particularly evident in the chromium complex, owing to the small esds, but the molybdenum and tungsten complexes exhibit the same features.

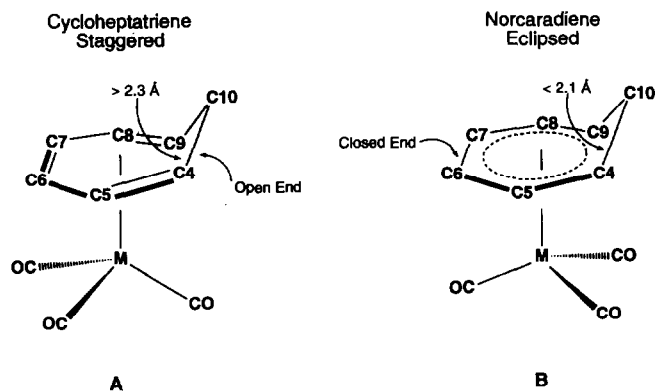


TABLE 5. Least-squares planes data for 1 and 3

	1 Deviation	3 Deviation
<i>Plane 1</i>	$(-0.0049)X + (-0.9104)Y + (-0.4136)Z = -4.7809$	$(-0.0120)X + (-0.8983)Y + (-0.4392)Z = -5.0131$
C4	-0.031	-0.041
C5	0.063	0.062
C6	-0.030	-0.021
C7	-0.039	-0.035
C8	0.063	0.045
C9	-0.027	-0.009
M	1.605	1.745
C10	-0.738	-0.715
<i>Plane 2</i>	$(0.0363)X + (-0.9318)Y + (-0.3613)Z = -4.3961$	$(0.0233)X + (-0.9186)Y + (-0.3945)Z = -4.6830$
C4	-0.002	-0.015
C5	0.001	0.012
C8	-0.001	-0.011
C9	0.002	0.014
C6	-0.171	-0.142
C7	-0.180	-0.159
<i>Plane 3</i>	$(-0.0564)X + (-0.8775)Y + (-0.4762)Z = -5.0868$	$(-0.0501)X + (-0.8691)Y + (-0.4921)Z = -5.2722$
C5	-0.002	-0.001
C6	0.004	0.002
C7	-0.004	-0.002
C8	0.002	0.001
C4	-0.211	-0.192
C9	-0.204	-0.145
<i>Angles between planes</i>		
Plane 2/Plane 3	9.0°/171.0°	7.6°/172.4°

For 1–3, the C4–C5 and C8–C9 bonds average 1.351 (15, 16, 6) Å [14*], identical to the double-bond length in free cycloheptatriene [15] while the C5–C6 and C7–C8 bonds average 1.426 (17, 18, 6) Å, slightly longer than the single-bond length in free cycloheptatriene, but comparable to the distance observed for the single bonds of metal-coordinated substituted η^6 -cycloheptatrienes. The unusual aspect of the pseudo-ring system is the C6–C7 bond length, which averages 1.397 (15, 21, 3) Å. This distance is longer than the corresponding distance in free cycloheptatriene and longer than the other double bonds in the pseudo-ring at a 95% confidence level [16]; indeed, it approaches the single-bond length observed in the pseudo-ring. This phenomenon is curious, as one might expect the C6–C7 bond to be the most double bond-like, because it lies between two other double bonds.

We cannot be certain that the above observations represent a general feature of $(\eta^6\text{-cycloheptatriene})\text{metal tricarboxyl complexes}$, since an inspection of reported structures gives varied results. In sev-

eral cases, the bonds appear to correspond to this pattern, but the esds are too large to assess this with certainty. In a few cases, the C6–C7 bond is observed to be shorter than the C8–C9 and C4–C5 bonds. However, the fact that we discerned this pattern by comparing a homologous series of compounds supports the possibility. It does not seem likely that the pattern should occur only in the parent species; in particular, the presence of some other moiety in the *exo* position at C10 (the most common substitution site and stereochemistry for these systems) should have little effect on the bonding in the pseudo-ring. The question then arises as to the cause of this result. One possible explanation holds that the observed shift of the metal toward this bond populates an orbital containing a significant amount of antibonding character localized on this bond. This view requires that the π and π^* orbitals on C6 and C7 be decoupled somewhat from those on C4, C5, C8, and C9.

It is well documented that free cycloheptatriene in the vapor phase exists in a boat conformation [15], and it is presumed that this conformation decouples the π/π^* orbitals of the three double bonds. However, when coordinated to a metal center, the six-membered pseudo-ring is routinely described as planar within the

* Reference number with asterisk indicates a note in the list of references.

esds of the atomic positions, which argues for greater interaction between the orbitals. Interestingly, though, several workers have noted that the carbon atoms corresponding to C4, C6, C7, and C9 lie above the plane, while C5 and C8 lie below the plane; in other words, the ring maintains a boat conformation (although a greatly flattened one). Presumably this was felt to be artifactual.

We believe our least-squares planes data (Table 5) confirm the presence of a flattened boat conformation for the coordinated ring. The six members of the pseudo-ring (C4–C9) are coplanar within 0.06 Å for both **1** and **3**. However, this again appears to oversimplify the actual situation. Examining the chromium data closely, we find that atoms C4/C5/C8/C9 are planar with 0.002 Å, while C6 and C7 lie 0.17 Å and 0.18 Å above this plane. The obtuse angle between the C4/C5/C8/C9 and C5/C6/C7/C8 planes is 171.0°. Similar values occur in **3**: the C4/C5/C8/C9 unit is planar within 0.01 Å, and C6 and C7 lie 0.14 Å and 0.16 Å above the plane forming an obtuse plane angle of 172.4°. The deviation of the pseudo-ring from planarity is small [17*], but the trend is evident: the coordinated cycloheptatriene ring exists in a flattened boat conformation. An ORTEP drawing of **1** oriented to show this conformation appears in Fig. 2.

The non-planarity could give rise to a molecular orbital containing greater C6/C7 π^* character than C4/C5 or C8/C9 π^* character. Since the metal shifts from the exact centroid toward the closed side of the pseudo-ring (i.e. the C6/C7 π bond), this orbital could be populated sufficiently to increase the C6–C7 bond length. From a Dewar–Chatt–Duncanson perspective [18], the system would formally mimic a metallacyclopropane with chelating olefin arms. One might equally describe the ring as η^4/η^2 -bound rather than as η^6 -bound, with the C6/C7 bond acting independently of the C4/C5 and C8/C9 bonds. Such speculation requires further theoretical and experimental study. We note, however, that previous diffraction studies have tended to minimize comment on the planarity of the pseudo-ring. The results here suggest that more careful evaluation of this detail is required.

The features involving the bridgehead carbon C10 are unexceptional. This essentially sp^3 carbon lies nearly 3 Å from the metal and is not involved in ring-to-metal bonding. It lies 0.74 Å above the six-membered pseudo-ring plane in **1** and 0.72 Å above in **3**.

4. Conclusion

It appears that the nature of the interaction between an η^6 -cycloheptatriene ring and a metal may be

more subtle than previously thought. Our data suggest that coordination of chromium tricarbonyl or tungsten tricarbonyl fragments causes the ring to flatten considerably from the boat conformation of the free ligand, but that this conformation is not entirely lost. In addition, metal coordination disrupts the conjugation of the linked olefin fragments, and results in significant lengthening of the “closed end” double bond. This bond distance approaches that of a ring single bond, suggesting the possibility of depressed reactivity at C6/C7, and therefore the potential for regiospecific substitution of the hydrogen atoms bonded to C4, C5, C8, and C9. We plan to explore this issue.

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- Estimated errors of averaged bond distances and angles are reported as follows: average esd = $[\sum(\text{esd})]/N$, standard deviation of the distances or angles = $[\sum(x_i - \bar{x})^2/N]^{1/2}$, N = number of values averaged.
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- A reviewer noted that the data in Table 5 do not include esd's associated with the deviations from the plane. Our computer

program does not currently calculate these errors, but our experience has been that they are approximately the same as the associated bond length esd's (*i.e.* the esd's of the M–C bonds). Thus likely esd's for atoms C6 and C7 from plane 2 are *ca.* 0.003 Å for **1** and *ca.* 0.01 Å for **3**, while the esd for the angle between

the planes is *ca.* 0.1° for **1** and *ca.* 0.5° for **3**. The observed deviations are clearly significantly larger than the esd's.

18 D.M.P. Mingos, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon, New York, 1982, pp. 1–88.