

32.51 ppm ( $J_{\text{RhH}} = 155$  Hz) in its  $^{31}\text{P}$  NMR spectrum. Thus the coordination shift for this complex is 24.74 ppm. The corresponding  $^{31}\text{P}$  data for the complexes of 1 and 3 are respectively 14.8 ppm,  $J = 161$  Hz, and  $\Delta = 32.45$  ppm and 45.81 ppm,  $J = 148$  Hz, and  $\Delta = 18.73$  ppm. As is the case for the uncomplexed ligand the  $^{31}\text{P}$  NMR shift for the complex of 6 is approximately midway between those of 1 and 3. Again the  $^1\text{H}$  NMR spectra of the rhodium complex of 7 and other ligands show that a downfield shift of the ligand resonance occurs on complexation, although the magnitude is less than is found for the palladium derivatives.

The nickel(II) complexes of 1 and 3 are easily prepared. They are paramagnetic, indicating a tetrahedral structure which has been confirmed as described above, L-L = 1.

It is possible that the origin of the discrimination observed in reactions catalyzed by nickel and palladium complexes of 1 is the difference in structure, tetrahedral vs. square planar, of the two catalyst precursors in the catalytic cycle.

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**Registry No.** 1, 12150-46-8; 3, 84680-95-5; 6 (meso isomer), 95408-37-0; 6 (racemic isomer), 95464-04-3; 7, 95408-38-1; 8, 95408-39-2; 9, 95408-40-5; 10, 72954-06-4; 11, 83547-83-5; 12a, 12098-17-8; 12b, 95408-41-6; 13, 95408-42-7; Pd(1)Cl<sub>2</sub>, 72287-26-4; Pd(1)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, 95464-05-4; Ni(1)Br<sub>2</sub>, 67292-33-5; Mo(1)(C-O)<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>, 95408-44-9; Co(1)(CO)<sub>4</sub>, 67292-31-3; Mo(1)(CO)<sub>4</sub>, 67292-28-8; Pd(3)Cl<sub>2</sub>, 95408-45-0; Ni(3)Cl<sub>2</sub>, 95408-48-3; Ni(3)Br<sub>2</sub>, 95408-49-4; Pd(6)Cl<sub>2</sub>, 95408-46-1; [Rh(6)NBD]ClO<sub>4</sub>, 92269-95-9; Pd(7)Cl<sub>2</sub>, 95420-22-7; [Rh(7)NBD]ClO<sub>4</sub>, 92284-07-6; Pd(8)Cl<sub>2</sub>, 95408-47-2; [Rh(8)NBD]ClO<sub>4</sub>, 95408-51-8; Pd(9)Cl<sub>2</sub>, 95408-52-9; Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, 14220-64-5; Pd(COD)Cl<sub>2</sub>, 12107-56-1; K<sub>2</sub>PdCl<sub>4</sub>, 10025-98-6; ClPPh(CMe<sub>3</sub>)<sub>2</sub>, 29949-69-7; ClP(CMe<sub>3</sub>)<sub>2</sub>, 13716-10-4; ClPPh<sub>2</sub>, 1079-66-9; tetramethylethylene diamine dilithioferrocene, 65587-59-9.

**Supplementary Material Available:** Tables of final and isotropic thermal parameters, bond lengths and angles, and observed and calculated crystal structure amplitudes for all three compounds (114 pages). Ordering information is given on any current masthead page.

## Rotational Barriers in Substituted (Cycloheptatriene)Cr(CO)<sub>3</sub> Complexes

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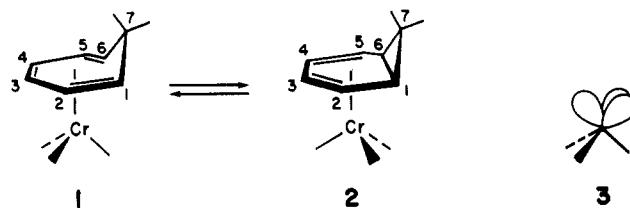
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The barriers of rotation about the cycloheptatriene-Cr axis have been determined for six (7-substituted cycloheptatriene)Cr(CO)<sub>3</sub> complexes. The barriers were determined from a complete line-shape analysis of the  $^{13}\text{C}$  spectra for the carbonyl region as a function of temperature. The values of  $\Delta H^*$  for the cycloheptatriene (CHT), 7-exo-MeCHT, 7-endo-MeOCHT, and 7,7-di-MeOCHT complexes are essentially identical ( $9.9 \pm 0.2$ ,  $10.4 \pm 0.5$ ,  $9.9 \pm 0.3$ , and  $9.9 \pm 0.4$  kcal/mol, respectively) and the values of  $\Delta S^*$  cluster around zero. On the other hand,  $\Delta H^*$  values for 7-exo-CNCHTCr(CO)<sub>3</sub> ( $8.9 \pm 0.2$  kcal/mol) and 7-exo-t-BuCHTCr(CO)<sub>3</sub> ( $10.9 \pm 0.3$  kcal/mol) are, respectively, slightly lower and higher than these values. This appears to be consistent with arguments concerning the electronic origin of these rotational barriers, namely, that the magnitude of the barrier is related to the cycloheptatriene-norcaradiene equilibrium. Estimates of the rotational barriers in three (1,6-methanoannulene)Cr(CO)<sub>3</sub> complexes are also consistent with this theory. Finally the barrier in (tropone)Cr(CO)<sub>3</sub> was found to be very small (~6 kcal/mol); extended Hückel molecular orbital calculations predict a barrier of 5.8 kcal/mol. A rationale why the barrier in this complex is much lower than the other cycloheptatriene complexes is given.

### Introduction

A theoretical study of the electronic origin for rotational barriers about the polyene-metal axis in (polyene)ML<sub>3</sub> complexes was undertaken some time ago.<sup>2</sup> One prediction<sup>2b</sup> from this body of work was that the ground state conformation of the Cr(CO)<sub>3</sub> group in (cycloheptatriene)Cr(CO)<sub>3</sub> complexes should be tied to the cycloheptatriene-norcaradiene equilibrium. Namely, if the ligand lies on the cycloheptatriene side of the equilibrium,

the ground state of the complex will be given by 1. On

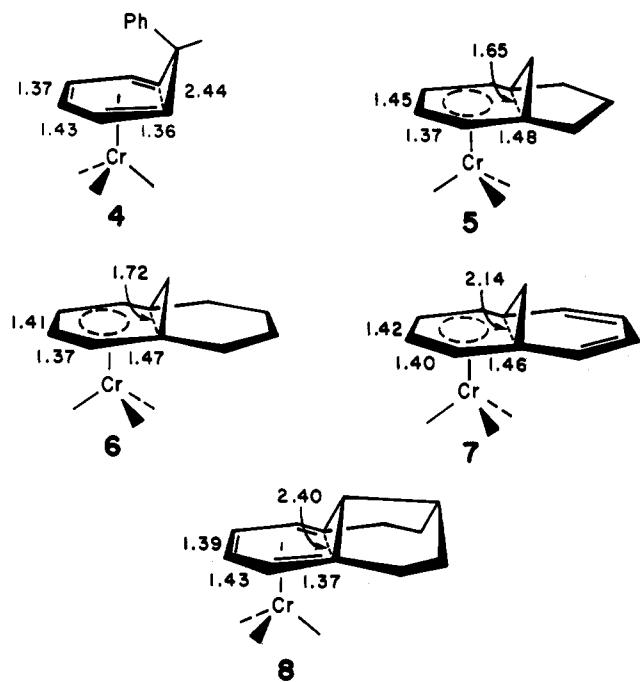


the other hand, if the ligand is forced to be at the norcaradiene extreme, then the Cr(CO)<sub>3</sub> group adopts the geometry shown in 2. There are a number of ways to view this pattern<sup>2b,e</sup> perhaps the easiest is to recall that there are three vacant hybrids in a Cr(CO)<sub>3</sub> fragment.<sup>2a</sup> They are hybridized away from the carbonyl ligands, and with use of a localized perspective shown in 3 they complete an

(1) Camille and Henry Dreyfus Teacher-Scholar, 1979-1984; Alfred P. Sloan Research Fellow, 1982-1984.

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Chart I



octahedron around chromium. The three acceptor orbitals on Cr(CO)<sub>3</sub> will overlap with the three  $\pi$  orbitals of the cycloheptatriene ligands optimally in conformation 1. At the norcaradiene structure the two  $\pi$  orbitals and to a lesser extent the C<sub>1</sub>-C<sub>6</sub>  $\sigma$  bond will overlap with 3 optimally in conformation 2. Substituents at C<sub>1</sub>, C<sub>6</sub>, and C<sub>7</sub> in particular will influence the norcaradiene-cycloheptatriene equilibrium.<sup>3</sup> For example,  $\pi$ -electron-withdrawing groups (e.g., CN, CO<sub>2</sub>R, etc.) substituted at C<sub>7</sub> cause the norcaradiene isomer to be stabilized relative to the cycloheptatriene form. Likewise, the introduction of a saturated or unsaturated bridging chain between C<sub>1</sub> and C<sub>6</sub> forces the C<sub>1</sub>-C<sub>6</sub> distance to decrease—the “Klammer effect”, thus favoring the norcaradiene side of the equilibrium.<sup>4</sup> Therefore, substitution of  $\pi$ -electron-withdrawing groups

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at C<sub>7</sub> on the cycloheptatriene ligand should lower the rotational barrier in 1 (the transition state, resembling 2 will be stabilized). In an extreme case of stabilizing a norcaradiene structure, 2 may become the ground state and a structure resembling 1 represents the transition state for Cr(CO)<sub>3</sub> rotation.<sup>2b</sup>

Some supporting evidence for this hypothesis can be given. The experimentally determined X-ray structures<sup>5</sup> of all (cycloheptatriene)Cr(CO)<sub>3</sub> complexes possess conformation 1. A typical example is (7-exo-phenylcycloheptatriene)Cr(CO)<sub>3</sub>, 4, in Chart I. Notice that a significant bond alternation remains in the cycloheptatriene ring mirroring the situation in the free ligand, namely, the C<sub>1</sub>-C<sub>2</sub>, C<sub>3</sub>-C<sub>4</sub>, and C<sub>5</sub>-C<sub>6</sub> bond lengths are considerably shorter than the C<sub>2</sub>-C<sub>3</sub> and C<sub>4</sub>-C<sub>5</sub> bonds. Likewise, the C<sub>1</sub>-C<sub>6</sub> distance at 2.44 Å is clearly nonbonding. These patterns are also found<sup>5</sup> in the other cycloheptatriene complexes. There are, however, three exceptional complexes, 5,<sup>6</sup> 6,<sup>7</sup> and 7,<sup>8</sup> in Chart I. Each have the Cr(CO)<sub>3</sub> group rotated by 60° in comparison to 4. The averaged C-C bond lengths of the coordinated ring now alternate in the opposite sense, namely, C<sub>1</sub>-C<sub>2</sub>, C<sub>3</sub>-C<sub>4</sub>, and C<sub>5</sub>-C<sub>6</sub> distances are longer than those for C<sub>2</sub>-C<sub>3</sub> and C<sub>4</sub>-C<sub>5</sub>. The C<sub>1</sub>-C<sub>6</sub> distance of 1.65 Å in 5 is certainly much shorter than the 2.4 Å typical of cycloheptatriene complexes. Steric interactions between the alkyl chain substituted at C<sub>1</sub> and C<sub>6</sub> do not force the Cr(CO)<sub>3</sub> unit to adopt the opposite orientation. This is evidenced by 8<sup>9</sup> which has the orientation of the Cr(CO)<sub>3</sub> group and C-C bond alternation consistent with the other (cycloheptatriene)Cr(CO)<sub>3</sub> complexes. Evidently tying C<sub>10</sub> to C<sub>7</sub> forces the C<sub>1</sub>-C<sub>6</sub> distance to increase in 8. Thus, structures 5-7 are consistent with the simplified model presented by 2; however, it is important to note that a large amount of electron density must be transmitted from the C<sub>1</sub>-C<sub>6</sub>  $\sigma$  bond to the Cr atom. In other words, a three-center-two-electron bonding situation exists between C<sub>1</sub>, C<sub>6</sub>, and Cr.<sup>8</sup> It is certainly debatable whether any significant bonding is retained between C<sub>1</sub> and C<sub>6</sub> in 7. We will come back to this point later. It is also interesting to note that the C<sub>1</sub>-C<sub>6</sub> distance in (2,7-methanoaza[10]annulene)Cr(CO)<sub>3</sub><sup>10</sup> and (anti-1,6,8,13-bis(methano[14]annulene)Cr(CO)<sub>3</sub> is 2.17 and 2.36 Å, respectively. These are values between those for 7 and 8. The conformation of the Cr(CO)<sub>3</sub> in both cases lies between that observed for the normal cycloheptatriene complexes and the series in 5-7. Likewise, there is no clear C-C bond alternation in the sense of 1 or 2 for the com-

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Table I. Activation Energies for the (Cycloheptatriene)Cr(CO)<sub>3</sub> Complexes

compound <sup>a</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$\Delta G^\ddagger_{220}$ , kcal/mol
CHTCr(CO) <sub>3</sub> , 9	9.9 ± 0.2	-0.7 ± 1.1	10.1 ± 0.05
<i>exo</i> -MeCHTCr(CO) <sub>3</sub> , 10	10.4 ± 0.5	+0.6 ± 2.1	10.3 ± 0.06
<i>endo</i> -MeOCHTCr(CO) <sub>3</sub> , 11	9.9 ± 0.3	-0.5 ± 1.2	10.0 ± 0.08
di-MeOCHTCr(CO) <sub>3</sub> , 12	9.9 ± 0.4	0.0 ± 2.1	9.9 ± 0.16
<i>exo</i> -CNCHTCr(CO) <sub>3</sub> , 13	8.9 ± 0.2	-2.4 ± 1.1	9.4 ± 0.11
<i>exo</i> - <i>t</i> -BuCHTCr(CO) <sub>3</sub> , 14	10.9 ± 0.3	+0.5 ± 1.3	10.8 ± 0.13

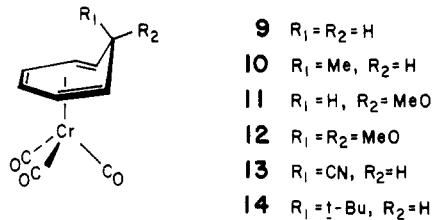
<sup>a</sup> CHT = cycloheptatriene.

plexed carbons of the ligand.

Our purpose in this work was to measure the barrier of rotation about the Cr-cycloheptatriene bond in a series of (7-substituted cycloheptatriene)Cr(CO)<sub>3</sub> compounds. With the proviso that some semblance of norcaradiene character is retained in the transition state for rotation (2),  $\pi$ -electron-withdrawing substituents should lower the rotational barrier. Likewise, if the norcaradiene structure can be destabilized, then the rotational barrier should increase. In addition, we shall present some evidence for rotational barriers in the (1,6-methanoannulene)Cr(CO)<sub>3</sub> series. Only the rotational barrier for (cycloheptatriene)Cr(CO)<sub>3</sub> itself has been reported previously by Kreiter and co-workers.<sup>12</sup>

## Results and Discussion

The (cycloheptatriene)Cr(CO)<sub>3</sub> complexes given in 9–14 were prepared by standard routes.<sup>13</sup> Compounds 9 and



11 were prepared by direct reaction of the cycloheptatriene with (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub>. The other complexes were prepared by nucleophilic addition to the appropriate (tropylium)Cr(CO)<sub>3</sub><sup>+</sup>. The <sup>1</sup>H NMR data for these complexes were in agreement with previously reported values.<sup>14</sup> A listing of the <sup>1</sup>H and <sup>13</sup>C chemical shifts are available as supplementary material. Some care was taken to ensure the stereochemical integrity of the monosubstituted ligand complexes. The most reliable criterion is the magnitude of the vicinal H<sub>1</sub>(H<sub>6</sub>)-H<sub>7</sub> coupling constants.<sup>15</sup> The coupling to an exo H<sub>7</sub> proton (R<sub>1</sub> in 9) is much smaller, typically ~2 Hz, than that to an endo proton (R<sub>2</sub> in 9) which is normally ~8 Hz. Likewise in this closely related series of complexes the exo protons are shielded by ~2 ppm with respect to the endo protons. Attempted preparation of (*endo*-methylcycloheptatriene)- or (*endo*-*tert*-butylcycloheptatriene)Cr(CO)<sub>3</sub> (R<sub>1</sub> = H; R<sub>2</sub> = Me or *t*-Bu) by the direct reaction of the ligand with (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub> afforded ~5% and ~50%, respectively, of the exo products

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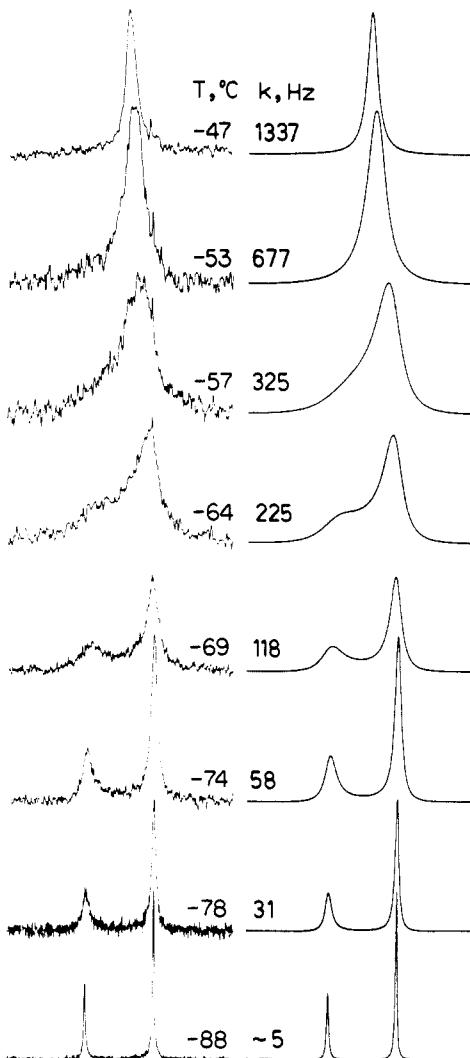


Figure 1. Experimental (left) and calculated (right) spectra of the carbonyl region in (7,7-dimethoxycycloheptatriene)Cr(CO)<sub>3</sub>.

10 and 14. Consequently, these compounds were not used for the NMR studies. In our hands 7-cyanocycloheptatriene reacts with (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub> to give exclusively the exo product 13; no trace of the desired endo product was observed.

Variable-temperature <sup>13</sup>C NMR studies were carried out on compounds 9–14 at 25.158 MHz using a Varian XL-100 spectrometer. Operating conditions were maintained in as uniform a manner as possible for the entire series of compounds. The solvent employed for each compound was a 50:50 (v/v) mixture of acetone-*d*<sub>6</sub> and methylene chloride and care was taken to use the same concentration for each sample. Other experimental details are given in the Experimental Section. Low-temperature spectra show two resonances in the carbonyl region with a peak area ratio of ~1:2 which is consistent with the static structure exemplified by 1. At higher temperatures the two peaks broaden and coalesce, and ultimately a single, sharp res-

onance is observed where rotation of the Cr(CO)<sub>3</sub> group with respect to the cycloheptatriene is rapid on the NMR time scale.<sup>16</sup> Rate constants for the rotation process were found by a least-squares fitting of the *total* line shape from computed spectra to the experimental ones using a local program.<sup>17</sup> A typical set of spectra, for (7,7-dimethoxy-cycloheptatriene)Cr(CO)<sub>3</sub>, 12, are shown in Figure 1. Activation energies for 9–14 were determined from least-squares fits to Eyring plots. The values of the activation energies are reported in Table I, and the error limits were determined by realistic methods.<sup>18</sup>

It can be seen from Table I that the values for  $\Delta S^*$  in all compounds cluster around zero. The  $\Delta H^*$  values for 9, 11, and 12 are identical. In an earlier study<sup>12d</sup> of 9 in acetone-*d*<sub>6</sub> a  $\Delta H^*$  value of 9.9 kcal/mol was also found. Furthermore, the value of  $\Delta H^*$  in 10 is statistically no different than the others.<sup>19</sup> One would not expect 9–12 to be different based on the model outlined in the Introduction; i.e.,  $\pi$ -donor groups like MeO have no influence on the cycloheptatriene–norcaradiene equilibrium for the parent ligands.<sup>4</sup> The barriers for 9–12 also demonstrate that there are no direct steric effects between endo substituents and the Cr(CO)<sub>3</sub> group during the course of rotation. Finally, we believe that since the barriers in 9–12 are essentially identical, a  $\Delta H^*$  value of 9.9 kcal/mol (or  $\Delta G^*$  of 10.1 kcal/mol) is a reliable estimate for the rotational barrier in a “standard” (cycloheptatriene)Cr(CO)<sub>3</sub> complex.

As detailed in the Introduction, a  $\pi$ -electron-withdrawing group substituted at C<sub>7</sub> should lower the rotational barrier. The  $\Delta H^*$  determined for *exo*-CHCHTCr(CO)<sub>3</sub>, 13, was  $8.9 \pm 0.2$  kcal/mol which does appear to be slightly lower than the “standard” values of 9–12. However, this difference is certainly small enough so that caution is warranted.

Two approaches were taken to define more clearly the role of substituents at C<sub>7</sub> on the rotational barrier. The obvious approach was to substitute two CN groups at C<sub>7</sub>. In this context it should be noted that no detectable concentration of the norcaradiene isomer has been observed for the 7-cyanocycloheptatriene<sup>9e,20</sup> ligand itself, whereas the 7,7-dicyano compound exists solely on the norcaradiene side of the equilibrium.<sup>21</sup> Unfortunately the reaction of 7,7-dicyanonorcaradiene with either (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub> or the more sensitive (NH<sub>3</sub>)<sub>3</sub>Cr(CO)<sub>3</sub> in THF, dioxane, or Et<sub>2</sub>O at a variety of temperatures did not lead to any complex consistent with a (7,7-dicyanocycloheptatriene)Cr(CO)<sub>3</sub> formulation. Normally mixtures of products were obtained wherein the 7,7-dicyanonorcaradiene ligand was  $\sigma$  bonded via a cyano nitrogen to the chromium. Interestingly, the reaction of (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub> with 7,7-dicyanonorcaradiene with either a 2:1 mixture of dioxane and Et<sub>2</sub>O at 9 °C or with Et<sub>2</sub>O at 0 °C led to the

(16) This exchange between the two types of carbonyls has been ascribed to rotation of the M(CO)<sub>3</sub> group with respect to a polyene in all (polyene)M(CO)<sub>3</sub> complexes; see ref 2f and references therein. There is very good evidence for this rather than other permutational mechanisms from work on related (butadiene)FeL<sub>3</sub> complexes, see: Van-Catledge, F. A.; Ittel, S. D.; Jesson, J. P. *J. Organomet. Chem.* 1979, 168, C25. Bischofberger, P.; Hansen, H.-J. *Helv. Chim. Acta* 1982, 65, 721. Howell, J. A. S.; Dixon, D. T.; Kola, J. C. *J. Organomet. Chem.* 1984, 266, 69.

(17) Reynolds, S. D. Ph.D. Thesis, University of Houston, 1983.

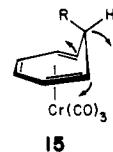
(18) Sandstrom, J. “Dynamic NMR Spectroscopy”; Academic Press: New York, 1982; pp 108–115. An equivalent formulation may be found in: Heinzer, J.; Öth, J. F. M. *Helv. Chim. Acta* 1981, 64, 258.

(19) A  $\Delta H^*$  of  $10.0 \pm 0.5$  kcal/mol was also found for *exo*-MeOCHTCr(CO)<sub>3</sub>. However, the number of data points and accuracy of measurement was lower than that for the cases reported in Table I.

(20) Wehner, R.; Günther, H. *J. Am. Chem. Soc.* 1975, 97, 923.

(21) Ciganek, C. *J. Am. Chem. Soc.* 1971, 93, 2207. Hall, G. E.; Roberts, J. D. *Ibid.* 1971, 93, 2203. Fritchi, C. J., Jr. *Acta Crystallogr.* 1966, 20, 27.

production of a crystalline product which was identical with authentic (benzene)Cr(CO)<sub>3</sub> by its <sup>1</sup>H NMR and mass spectrum. Evidently the  $\pi$  complex once formed undergoes rearrangement to (benzene)Cr(CO)<sub>3</sub> and dicyanocarbene. The reverse reaction of a carbene with (arene)Cr(CO)<sub>3</sub> compounds leading to cycloheptatriene complexes is known.<sup>5b,c</sup> Photolysis of dicyanodiazomethane with (benzene)Cr(CO)<sub>3</sub> at  $-30$  °C in THF leads to the consumption of the former reactant; however, only unreacted (benzene)Cr(CO)<sub>3</sub> was isolated. An alternative approach is to note that if bonding between C<sub>1</sub> and C<sub>6</sub> stabilizes the transition state for rotation, then the magnitude of the barrier should be sensitive to steric effects induced by exo substituents. A sterically bulky group, R in 15, will interact with the  $\pi$ -electron density associated with the cycloheptatriene ligand. This should cause the C<sub>7</sub> group to move in the direction indicated by the arrow in 15 which



15

in turn forces the C<sub>1</sub>–C<sub>6</sub> distance to increase.<sup>22</sup> Elongating the C<sub>1</sub>–C<sub>6</sub> distance destabilizes the norcaradiene structure 2, and therefore, one might expect an increase of the rotational barrier over that observed for (cycloheptatriene)Cr(CO)<sub>3</sub> itself. This motivated our determination of the barrier in *exo*-*t*-BuCHTCr(CO)<sub>3</sub>, 14. The  $\Delta H^*$  value of  $10.9 \pm 0.3$  kcal/mol is marginally larger than the standard value for 9, 11, and 13. What one can say with considerably more certainty is that the rotational barrier in 7-*exo*-CNCHTCr(CO)<sub>3</sub>, 13, is smaller than that observed for 7-*exo*-*t*-BuCHTCr(CO)<sub>3</sub>, 14. This can be seen more graphically by noting that the chemical shift difference between the two carbonyl resonances in the rate-limiting spectra for 13 and 14 are very similar (282 and 287 Hz, respectively). However, the coalescence temperature<sup>23</sup> for 13 is 25 K lower than that observed for 14 (213 and 238 K, respectively). The results in Table I, particularly for 13 and 14, appear to support the theoretical model for rotational barriers in (cycloheptatriene)Cr(CO)<sub>3</sub> complexes as outlined in the Introduction. On the other hand, the differences in the barriers for the compounds in Table I are disappointingly small and further work is certainly needed to make a more definitive assessment. What is also clear from this study and is consistent with the structural results in Chart I is the direct interaction between C<sub>1</sub> and C<sub>6</sub> at the transition state for rotation is smaller than that for a norcaradiene ligand itself. Consequently the ability of substituents to modify the cycloheptatriene–norcaradiene equilibrium appear to have a diminished impact on rotational barriers in (cycloheptatriene)Cr(CO)<sub>3</sub> complexes.

The theory developed for rotational barriers in (cycloheptatriene)Cr(CO)<sub>3</sub> complexes can also be tested by compounds 5, 6, and 7 in Chart I. Since the ground-state geometry is now given by that shown in 2, a shorter C<sub>1</sub>–C<sub>6</sub> distance should yield a larger rotational barrier. Provided that the C<sub>1</sub>–C<sub>6</sub> distances in 5–7 are not set by packing

(22) Some tentative support for this can be cited from the structures of two very similar structures. In (*endo*-7-phenyl-3-ethylcycloheptatriene)Cr(CO)<sub>3</sub> the dihedral angle of the planes defined by C<sub>1</sub>–C<sub>2</sub>–C<sub>5</sub>–C<sub>6</sub> and C<sub>1</sub>–C<sub>7</sub>–C<sub>6</sub> was  $56.3^\circ$  and the corresponding C<sub>1</sub>–C<sub>6</sub> distance was  $2.39$  Å,<sup>5b</sup> whereas in (*exo*-7-phenylcycloheptatriene)Cr(CO)<sub>3</sub> the corresponding angle was  $45.7^\circ$  and the C<sub>1</sub>–C<sub>6</sub> distance enlarges to  $2.44$  Å.<sup>5a</sup>

(23) We have defined the coalescence temperature for two exchanging nuclei with unequal populations in the manner given by: Chanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* 1970, 74, 961.

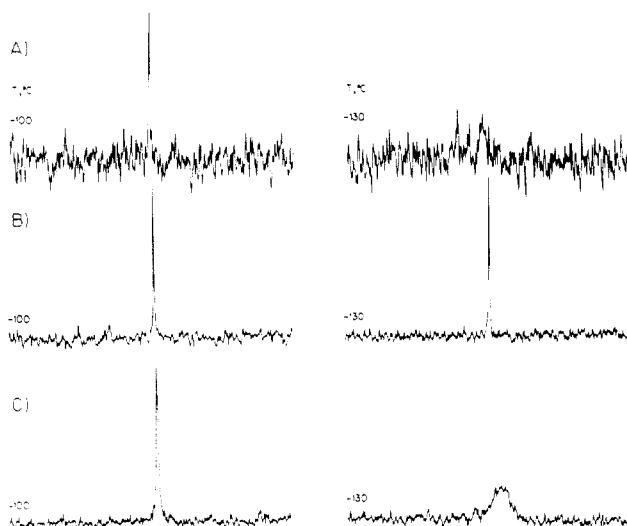
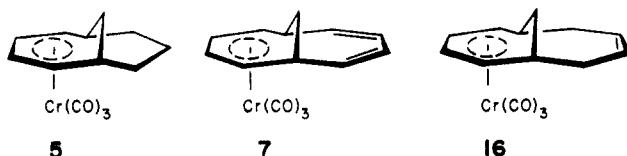


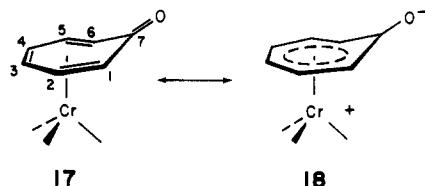
Figure 2. Spectra of the carbonyl region at  $-100$  and  $-130$   $^{\circ}\text{C}$  for 5 (A), 7 (B), and (tropone)Cr(CO)<sub>3</sub> (C).

effects, and we have no reason to suspect that this is the case, the rotational barriers should decrease in the order  $5 > 6 > 7$ . Some information concerning this argument was derived from NMR studies on 5, 7, and 16. No



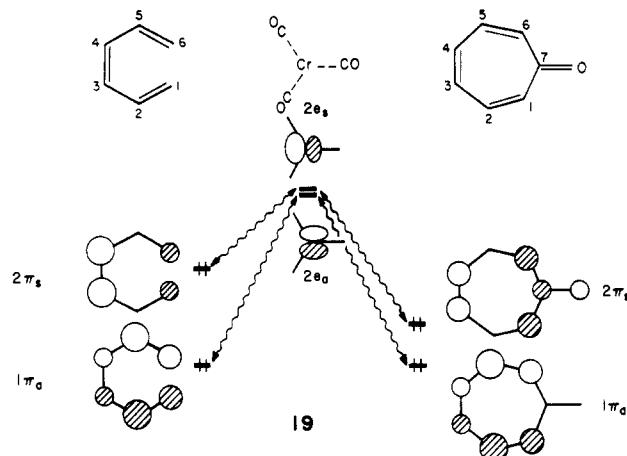
broadening of the carbonyl signal was observed down to  $-120$   $^{\circ}\text{C}$  for 5, 7, or 16 at 25.158 MHz using a 1:1 solvent mixture of CD<sub>2</sub>Cl<sub>2</sub>/CHClF<sub>2</sub>. At 53.5 MHz on a Varian XL-200 spectrometer a single, sharp resonance was observed for the three compounds at  $-100$   $^{\circ}\text{C}$ . This is shown in parts A and B of Figure 2 for 5 and 7, respectively. Upon cooling to lower temperatures the carbonyl resonance for 5 broadens and at  $-130$   $^{\circ}\text{C}$  it merges into the base line (the other resonances in 5 remain narrow), whereas the carbonyl signals for 7 and 16 do not show any broadening. This is also illustrated in parts A and B of Figure 2 for 5 and 7, respectively. Making the assumption that the chemical shift difference between the two types of carbonyls will not vary much for 5, 7, and 16 requires that the barrier in 5 is larger than that for 7 and 16. On the basis of the chemical shift differences between the carbonyl carbons in 9–14, a value for  $\Delta G^*$  of  $\sim 6$ – $7$  kcal/mol can be estimated for 5. Extended Hückel calculations (computational details are given in the Experimental Section) on (cycloheptatriene)Cr(CO)<sub>3</sub> with a geometry identical to that in 5 (a C<sub>1</sub>–C<sub>6</sub> distance of 1.65  $\text{\AA}$ ) predicted a ground-state conformation analogous to 2 and a rotational barrier of 5.6 kcal/mol which is in reasonable agreement with the estimate from our NMR studies.

The work that we have described has focused on how factors relating to the cycloheptatriene–norcaradiene equilibrium influence the rotational barriers in Cr(CO)<sub>3</sub> complexes. Other electronic factors can also modify the barrier. One example is provided by (tropone)Cr(CO)<sub>3</sub>. The ground-state geometry<sup>24</sup> is indicated by 17. <sup>13</sup>C spectra at 53.5 MHz for temperatures of  $-100$  and  $-130$   $^{\circ}\text{C}$  are shown in Figure 2C. The considerable broadening at  $-130$   $^{\circ}\text{C}$  implies a  $\Delta G^*$  of  $\sim 6$  kcal/mol. This is considerably



smaller than the value of 10.1 kcal/mol for (cycloheptatriene)Cr(CO)<sub>3</sub> itself (see Table I). Extended Hückel calculations on (cycloheptatriene)Cr(CO)<sub>3</sub> gave an activation energy for rotation of 10.2 kcal/mol. For (tropone)Cr(CO)<sub>3</sub> (using the experimental geometry) we obtained a 5.8 kcal/mol barrier.

The rationale behind this lowering of the rotational barrier in (tropone)Cr(CO)<sub>3</sub> certainly does not lie in the cycloheptatriene–norcaradiene isomerism. The norcaradiene isomer of tropone is energetically inaccessible. Perhaps the most simple way to view this result is by invoking a significant contribution of the dipolar resonance structure 18 to the bonding in the complex. One argument that can be cited in favor of 18 is that the C<sub>7</sub> carbon in (tropone)Cr(CO)<sub>3</sub> is only bent 28.5° out of the plane of the other six ring carbons,<sup>24</sup> whereas a value of 50° is typical for other cycloheptatriene complexes.<sup>5</sup> Atypical reactivity and spectroscopic data for (tropone)Cr(CO)<sub>3</sub> have also been interpreted in this vein.<sup>25</sup> One would not expect a large barrier for a (cycloheptatrienyl)Cr(CO)<sub>3</sub><sup>+</sup> complex even though it is perturbed by an oxanion substituent.<sup>2a</sup> Thus, the abnormally small rotational barrier is a reflection of the intervention of resonance structure 18 in (tropone)Cr(CO)<sub>3</sub>. An alternative (but equivalent) molecular orbital description of this phenomenon can also be advanced. The major bonding between a hexatriene or cycloheptatriene ligand and Cr(CO)<sub>3</sub> is derived between the interaction of the empty 2e set on Cr(CO)<sub>3</sub> and the two highest filled  $\pi$  orbitals on the triene ligand.<sup>2a</sup> This is shown in a diagrammatic fashion on the left side of 19. Notice that the



2e orbitals are left-right asymmetric.<sup>2a</sup> The 2e<sub>a</sub> orbital is more heavily weighted on the right side of Cr(CO)<sub>3</sub>, toward the symmetry unique carbonyl, while the 2e<sub>g</sub> function is more concentrated on the left side. The overlap between 2e<sub>a</sub> and 1 $\pi_a$  of the triene is approximately equal in the conformation where the unique carbonyl lies between C<sub>1</sub> and C<sub>6</sub> (the ground-state geometry) and where the unique carbonyl eclipses the C<sub>3</sub>–C<sub>4</sub> bond (the transition state for rotation).<sup>2a</sup> In other words, the bonding molecular orbital formed between 2e<sub>a</sub> and 1 $\pi_a$  stays at approximately the

Table II. Parameters Used in the Extended Hückel Calculations

orbital	$H_{ii}$ , eV	$\xi_1$	$\xi_2$	$C_1^a$	$C_2^a$
Cr 3d	-11.22	4.95	1.60	0.4876	0.7205
	4s	-8.66	1.70		
	4p	-5.24	1.70		
C 2s	-21.40	1.625			
	2p	-11.40	1.625		
O 2s	-32.30	2.275			
	2p	-14.80	2.275		
H 1s	-13.60	1.30			

<sup>a</sup> Contraction coefficients used in the double- $\xi$  expansion.

same energy during the rotation. The  $2\pi_s$  orbital, however, overlaps to a greater extent with  $2e_g$  at the ground-state geometry because there is more electron density concentrated at  $C_3$  and  $C_4$  than at  $C_1$  and  $C_6$  in  $2\pi_s$ .<sup>2a</sup> Therefore, the  $2\pi_s + 2e_g$  bonding molecular orbital rises in energy during rotation. The  $1\pi_a$  orbital of tropone, on the right side of 19, is identical (to a first approximation) with that in the triene. A major change occurs in  $2\pi_g$ . The CO  $\pi^*$  orbital mixes heavily into this orbital. Electron density from especially  $C_3$  and  $C_4$  is redistributed to  $C_7$  and O. The overlap between  $2e_g$  and  $2\pi_g$  becomes more equalized in the ground- and transition-state geometries; therefore, the bonding combination of  $2e_g$  and  $2\pi_g$  does not rise as high in energy upon rotation as it does in the cycloheptatriene complex. Furthermore, the mixing of CO  $\pi^*$  character stabilizes  $2\pi_g$ . Using a perturbation theory argument, as the energy gap between  $2e_g$  and  $2\pi_g$  increases, any overlap differential between the fragment orbitals in different conformations becomes less energetically important; again this leads to a smaller barrier for (tropone)Cr(CO)<sub>3</sub>. The  $2\pi_g$  orbital becomes degenerate with  $1\pi_a$  in the cycloheptatrienyl cation, and the rotational barrier in (cycloheptatrienyl)Cr(CO)<sub>3</sub><sup>+</sup> is extremely small.<sup>2a</sup> The situation for tropone is consequently intermediate between that for cycloheptatriene and the cycloheptatrienyl cation as implicated by resonance structure 18.

## Experimental Section

**Preparation of the Chromium Complexes.** The unsubstituted complex 9, the *endo*-MeO complex 11, and (tropone)Cr(CO)<sub>3</sub>, 17, were synthesized by reaction of the appropriate ligand with tris(acetonitrile)chromium tricarbonyl.<sup>13a,17</sup> 13 and 14 were prepared by reacting the appropriate Grignard reagent with (tropylium)chromium tricarbonyl tetrafluoroborate.<sup>13b,c,17</sup> The *exo*-methyl complex 10 was generated by an S<sub>N</sub>2 displacement of the methoxy group on (*endo*-methoxycycloheptatriene)chromium tricarbonyl using methylmagnesium iodide.<sup>13c</sup> The dimethoxy complex 12 was synthesized by the reaction of sodium methoxide and (methoxytropylium)chromium tricarbonyl tetrafluoroborate.<sup>13b</sup> All reactions were performed under inert-atmosphere conditions. Complexes 5, 7, and 16 were graciously donated by Professor E. Vogel.

**NMR Parameters and Conditions.** Room-temperature <sup>1</sup>H NMR spectra were recorded on Varian T-60 and Varian FT-80A spectrometers. The room-temperature <sup>13</sup>C spectra were recorded on the FT-80A, as well as a Varian XL-100 spectrometer equipped with a Nicolet 1180 data acquisition system. The variable-temperature spectra for all the cycloheptatriene complexes were recorded on the Varian/Nicolet XL-100/1180 system. The sample temperature was measured before and after the acquisition of a spectrum using a digital thermometer equipped with a platinum resistance thermoprobe and calibrated at -80.0 °C and 0.0 °C. If the two readings differed by more than 0.5 °C, the spectrum was rerun. Temperatures were measured by immersing the thermoprobe to a preset distance into a "blank" NMR tube (containing 3.0 mL of acetone-*d*<sub>6</sub>) such that the blank was in exactly the same position as an actual sample. The thermoprobe was held in place by a specially constructed rig such that the NMR

tube would spin freely, duplicating the conditions of the real sample. The system was allowed to equilibrate for 15 min before a temperature measurement was made. Samples were then allowed to equilibrate for 15 min before a spectrum was acquired.

The samples were prepared by dissolving 0.400 ± 0.005 g of the complex and 20.0 ± 0.1 mg of tris(acetylacetone)chromium(III) in 4.0 ± 0.1 mL of a dried, deoxygenated 50:50 (v/v) mixture of acetone-*d*<sub>6</sub> and methylene chloride. The NMR samples were deoxygenated and sealed under nitrogen.

All spectra were acquired by using 4K data points, with a spectral width of 600 Hz, giving a digital resolution of just under 0.3 Hz. The pulse width and pulse delay, 1.71 and 0.1 s, respectively, were chosen to give a recovery period greater than 4T<sub>1</sub>. Broadening of the signals due to  $T_2$  relaxation and viscosity effects, which were minor, were monitored by observing the width at half-height of the acetone carbonyl peak and subtracted out of the experimentally observed carbonyl peaks.

The variable-temperature spectra of 5, 7, 16, and 17 were acquired on a Varian XL-200 NMR spectrometer equipped with a feedback regulated variable-temperature controller. The measurement accuracy is ±5 °C, with a repeatability of ±1 °C, which was sufficient for these spectra.

The samples were prepared by dissolving 0.20 ± 0.01 g of the complex and 20.0 ± 0.1 mg of tris(acetoacetone)chromium in 4.0 ± 0.1 mL of a 50:50 (v/v) mixture of dried, deoxygenated CD<sub>2</sub>Cl<sub>2</sub>/CHF<sub>2</sub>Cl. The samples were prepared under inert atmosphere and sealed.

The spectra were acquired by using a spectral width of 15 kHz and 18K data points, giving a spectral resolution of 1.7 Hz. A pulse acquisition delay and acquisition time of 0.9 and 0.6 s, respectively, gave a recovery period of approximately 4T<sub>1</sub>. Full spectra were obtained for the cases where broadening was observed to ensure that the other resonances remained sharp at the experimental temperature.

**Line-Shape Calculations.** The rate of rotation for a given compound at a measured temperature was determined a least-squares fit to the total line-shape analysis. The theoretical spectrum was calculated by one or both of two methods: either an in-house two-site exchange program, 17, based on the modified Bloch equations,<sup>26,27</sup> or a packaged routine provided with our Nicolet 1180 system NTCHXCH. Both methods gave identical results.

The activation enthalpy,  $\Delta H^*$ , and entropy,  $\Delta S^*$ , of rotation for a given compound were calculated from the slope and y intercept, respectively, of the line fit by the least-squares method to an Eyring plot. The reported errors were calculated by accepted methods,<sup>18,28</sup> and an error of ±1.0° was assumed for the temperature measurement.

**Molecular Orbital Calculations.** The molecular orbital calculations were carried out by using the extended Hückel method<sup>29</sup> with the modified Wolfsberg-Helmholz formula.<sup>30</sup> The parameters in Table II were taken from previous work.<sup>2a,b</sup> The experimental geometries were used for (cycloheptatriene)Cr(CO)<sub>3</sub>,<sup>5b</sup> a ("norcaradiene")Cr(CO)<sub>3</sub>,<sup>6</sup> and (tropone)Cr(CO)<sub>3</sub>.<sup>24</sup>

**Acknowledgment.** We wish to thank Professor E. Vogel for samples of 5, 7, and 16 and the patience he has shown us. Partial financial support of this work was derived from the Robert A. Welch Foundation and, at an early stage, the Research Corp. We wish to thank the Analytical Research labs at Exxon Research and Engineering (Baytown) for generous donation of time and assistance on their Varian XL-200 spectrometer.

**Registry No.** 5, 95388-83-3; 7, 12087-00-2; 9, 12125-72-3; 10, 12146-40-6; 11, 31760-96-0; 12, 32679-04-2; 13, 12146-34-8; 14, 80915-85-1; 16, 95388-84-4; 17, 32648-85-4; (CH<sub>3</sub>CN)<sub>3</sub>Cr(CO)<sub>3</sub>,

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(29) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* 1962, 36, 2179, 3489; 1962, 37, 2872. Hoffmann, R. *Ibid.* 1963, 29, 1397.

(30) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

16800-46-7; (B)  $\text{CrCO}_3$  (B = benzene), 12082-08-5; CHT, 544-25-2; MeCH<sub>2</sub>T, 4281-04-3; MeOCH<sub>2</sub>T, 1714-38-1; CNCHT, 13612-59-4; t-BuCH<sub>2</sub>T, 17635-75-5; (tropylum)chromium tricarbonyl tetrafluoroborate, 12170-19-3; (methoxytropylum)chromium tricarbonyl tetrafluoroborate, 32826-06-5; tropone, 539-80-0; di-

cyanocarbene, 1884-65-7; 7,7-dicyanonorcaradiene, 95388-85-5.

**Supplementary Material Available:** Listings of the <sup>13</sup>C and <sup>1</sup>H spectra for 9-14 and their derived rate constants (2 pages). Ordering information is given on any current masthead page.

## Metal Alkoxides: Models for Metal Oxides. 8.<sup>1</sup> Monocarbonyl Adducts of Ditungsten Hexaalkoxides ( $\text{M}\equiv\text{M}$ ) ( $\text{RO} = t\text{-BuO}$ , $i\text{-PrO}$ , and $t\text{-BuCH}_2\text{O}$ ) and the Dimer $[\text{W}_2(\text{O}-i\text{-Pr})_6(\mu\text{-CO})]_2$

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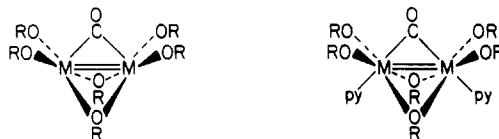
Addition of 1 equiv of carbon monoxide to a near saturated solution of  $\text{W}_2(\text{O}-t\text{-Bu})_6$  in hexanes, with or without added pyridine (py), cooled to 0 °C leads to the precipitation of  $\text{W}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  as a red microcrystalline compound.  $\text{W}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  is isomorphous and isostructural with its molybdenum analogue and contains a central  $\text{W}_2(\text{O}-t\text{-Bu})_2(\mu\text{-CO})$  unit: W-W = 2.526 (1) Å, W-C = 1.997 (15) Å, and C-O = 1.25 (1) Å ( $\mu\text{-CO}$ ). Each tungsten atom is in a square-based pyramidal geometry with the  $\mu\text{-CO}$  ligand occupying the apical position. The molecule has mirror symmetry. Addition of CO (1 equiv) to hexane/pyridine solutions, ca. 6:1, of  $\text{W}_2(\text{OR})_6(\text{py})_2$  yields under comparable conditions  $\text{W}_2(\text{OR})_6(\text{py})_2(\mu\text{-CO})$  compounds, where R =  $i\text{-Pr}$  and  $t\text{-BuCH}_2$ , as finely divided crystalline precipitates. Crystals of  $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\text{CO})$  have been reexamined and shown to be identical with those previously studied (Chisholm, Huffman, Leonelli, Rothwell *J. Am. Chem. Soc.* 1982, 104, 7030) and have been shown to dissolve in toluene- $d_8$  to give  $[\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-CO})]_2$  and pyridine (2 equiv). This transformation appears irreversible, and all attempts to recrystallize  $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-CO})$  yield only  $[\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})(\mu\text{-CO})]_2$ , previously characterized by Cotton and Schwotzer (*J. Am. Chem. Soc.* 1983, 105, 4955). Solution <sup>1</sup>H and <sup>13</sup>C NMR and IR spectral data indicate that  $\text{W}_2(\text{OCH}_2-t\text{-Bu})_6(\text{py})_2(\mu\text{-CO})$  is present in hydrocarbon solutions, while addition of  $i\text{-PrOH}$  (>6 equiv) to  $\text{W}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  yields  $[\text{W}_2(\text{O}-i\text{-Pr})_6(\mu\text{-CO})]_2$ , which is closely related to the Cotton and Schwotzer pyridine adduct. These findings are understandable in terms of steric control in the binding of pyridine to the ditungsten center and the nucleophilic properties of the  $\text{W}_2(\mu\text{-CO})$  oxygen atom. In the solid state, molecules of  $[\text{W}_2(\text{O}-i\text{-Pr})_6(\mu\text{-CO})]_2$  are centrosymmetric and contain an essentially planar central  $[\text{W}_2(\mu\text{-CO})]_2$  unit with W-W = 2.657 (1) Å, W-C = 1.95 (1) Å (averaged), W-O = 1.97 (1) Å, and C-O = 1.35 (1) Å. Each tungsten atom is in a distorted trigonal-bipyramidal environment and NMR studies show that, while the central  $[\text{W}_2(\mu\text{-CO})]_2$  unit is rigid on the NMR time scale, scrambling of the terminal OR ligands occurs at two of the symmetry-related tungsten atoms. The reaction sequence  $\text{W}\equiv\text{W} + \text{C}\equiv\text{O} \rightarrow \text{W}_2(\mu\text{-CO}) \rightarrow [\text{W}_2(\mu\text{-CO})]_2$  represents a stepwise reduction in M-M and C-O bond order from 3 to 2 to 1 and is suggestive of a model for the reaction pathway of  $\text{C}\equiv\text{O}$  on a metal oxide leading ultimately to carbide,  $\text{C}^4-$ , and oxide,  $\text{O}^{2-}$ . Differences in the binding of CO to the ( $\text{W}\equiv\text{W}$ )<sup>6+</sup> and ( $\text{Mo}\equiv\text{Mo}$ )<sup>6+</sup> units in  $\text{M}_2(\text{OR})_6$  compounds are related to the greater reducing power ( $\pi$ -back-bonding) of the ditungsten center. Crystal data for  $\text{W}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  at -162 °C: a = 17.660 (2) Å, b = 9.182 (13) Å, c = 19.307 (5) Å, Z = 4, and space group *Cmc2*<sub>1</sub>. Crystal data for  $[\text{W}_2(\text{O}-i\text{-Pr})_6(\mu\text{-CO})]_2$  at -162 °C: a = 12.085 (2) Å, b = 17.224 (4) Å, c = 13.027 (3) Å, β = 99.25 (1)°, Z = 2, and space group *P2*<sub>1</sub>/n.

### Introduction

Kelly<sup>2</sup> first discovered that hydrocarbon solutions of  $\text{Mo}_2(\text{O}-t\text{-Bu})_6$  and  $\text{C}\equiv\text{O}$  react rapidly at room temperature and 1 atm according to the stoichiometry shown in eq 1.



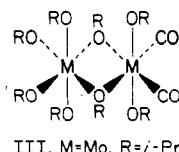
The first step in (1) is the reversible formation of  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$ , I. Carbonylation of  $\text{Mo}_2(\text{O}-i\text{-Pr})_6$  proceeds similarly to give  $\text{Mo}(\text{CO})_6$ , and in the presence of pyridine an initial carbonyl adduct,  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-CO})$ , has been isolated and characterized.<sup>3</sup> The latter compound adopts the structure shown in II which is closely related to I having Mo-N bonds trans to the Mo-C bond, thereby completing octahedral coordination of each molybdenum atom.



I. M=Mo or W, R=t-Bu

II. M=Mo or W, R=i-Pr or  $\text{CH}_2-t\text{-Bu}$

In the case of the carbonylation of  $\text{Mo}_2(\text{O}-i\text{-Pr})_6$ , the oxidized form of molybdenum is  $\text{Mo}_2(\text{O}-i\text{-Pr})_8(\text{CO})_2$  which is believed to have the edge-shared bioctahedral structure shown in III.<sup>4</sup>



III. M=Mo, R=i-Pr

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(2) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* 1979, 101, 7645.

(3) Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Rothwell, I. P. *J. Am. Chem. Soc.* 1982, 104, 7030.

(4) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* 1979, 101, 7615.