cence temperature for **5** was estimated to be −84 °C, which gives a rough estimate of the barrier for N–N rotation of $\Delta G^{\ddagger} \simeq 9.2$ kcal/mol.[21,22] A similar phenomenon has been observed in the chemistry of the amino-substituted Fischer carbenes $(CO)_5W{=}C(NR_2)R'$, where the barrier for rotation of the C–N bond is high enough that two isomers are observed at room temperature ($\Delta G^{\ddagger} > 25$ kcal/mol).[22a]

Preliminary experiments on the reactivity of **5** provide a comparison with the behavior of the non-heteroatom-stabilized complex $(CO)_5W{=}NPh$. The reaction of $(CO)_5W{=}NPh$ with aldehydes has been found to yield phenylimines (Scheme I).[6] Likewise, when an excess of benzaldehyde was added to the reaction mixture after formation of **5** and the mixture was left at room temperature in the dark for 12 h, the hydrazone $Me_2NN{=}CHPh$[23] was formed in 85% yield (based on initial **5**) by ^1H NMR spectroscopy.

Although $(CO)_5W{=}NPh$ (**1**) reacts rapidly with PPh_3 to produce the phosphine ylide **9** (Scheme I),[2] $(CO)_5W{=}NNMe_2$ did not react with PPh_3 at room temperature. The lack of reactivity of **5** toward PPh_3 as compared to that of **1** implies a reduced electrophilicity at the nitrene nitrogen. This situation has a parallel in the chemistry of Fischer carbenes: while PPh_3 readily reacts (−78 °C) with the highly electrophilic $(CO)_5W{=}CHPh$ to give a phosphine ylide,[8] heteroatom-stabilized Fischer carbenes such as $(CO)_5W{=}C(OMe)Me$ do not form ylides with PPh_3 even at room temperature.[24]

In conclusion, we have prepared the low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (**5**) by photochemical metathesis of $(CO)_5W{=}C(p\text{-Tol})Ph$ with the triazene $PhN{=}NNMe_2$. Spectroscopic evidence is consistent with a bent terminal hydrazido ligand in **5**. As in the Fischer carbenes, the heteroatom-containing substituent results in increased stability and decreased electrophilicity of **5** as compared to $(CO)_5W{=}NPh$.

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Supplementary Material Available: Experimental procedures for the generation of $(CO)_5W{=}NNMe_2$ and trapping with benzaldehyde, ^1H NMR spectra of **5**, **5**-[^{15}N], and **5**-[^{15}N]$_2$, ^{15}N NMR spectra of **5**-[^{15}N] and **5**-[^{15}N]$_2$, the ^{13}C NMR spectrum of **5**-[^{13}C] and the IR spectrum of **5** (9 pages). Ordering information is given on any current masthead page.

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[21] The rate constant for the exchange was calculated to be 104.04 s^{-1} by using $k = (\pi)\Delta\nu/2^{1/2}$.

[22] (a) Kreiter, C. G.; Fischer, E. O. *Proceedings of the XXXIII International Congress of Pure and Applied Chemistry*; Butterworths: London, 1971; Vol. 6, pp 151–168. (b) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237–258. (c) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760–762.

[23] Authentic $Me_2NN{=}CHPh$ was synthesized by combining 1,1-dimethylhydrazine with benzaldehyde in toluene-d_8 at room temperature in the presence of 4-Å molecular sieves.

[24] Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262–1276.

Computational Evidence for a Nonplanar η^3-Cyclopentadienyl Ligand in Dicarbonylbis(cyclopentadienyl)chromium and the Pathway for the $\eta^5 \leftrightarrow \eta^3$ Ring Interchange

Michael S. Lawless and Dennis S. Marynick*

Department of Chemistry, University of Texas at Arlington, Arlington, Texas 76019-0065

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Summary: The geometry of $(Cp)_2Cr(CO)_2$ (Cp = cyclopentadienyl) was completely optimized with the use of the partial retention of diatomic differential overlap (PRDDO) method and found to contain an η^5-Cp and a nonplanar η^3-Cp ring. The pathway for the interconversion of the two bonding modes was also calculated and shown to be facile via a $(\eta^3\text{-}Cp)_2Cr(CO)_2$ complex in which both Cp rings are planar.

There are many ways in which a cyclopentadienyl (Cp) ligand is capable of bonding to a metal atom.[1] A systematic molecular orbital study of some of the various binding modes has recently been published.[2] In almost every case, the cyclopentadienyl ring is planar; however, nonplanar Cp coordination has been observed in a few organometallic systems. The first definitive proof of a nonplanar Cp ring was provided when the X-ray crystal structure of $(Cp)_2W(CO)_2$ revealed an η^3-Cp ring in which two carbon atoms were bent out of the plane of the other three by an angle of 20°.[3] A similar η^3-bonding mode has been suggested[4] for $(Cp)_2Cr(CO)_2$ on the basis of infrared spectral data, but this structure has not been confirmed by X-ray crystallography. More recently it has been shown that the Cp ligands in $(Cp)_2Cr(CO)_2$ are not bound to the metal in the same manner and that the interchange of bonding modes occurs with an activation energy of 13.5 kcal/mol.[5] While the authors imply an η^3-Cp ligand, in reality any bonding mode that is not the same for both ligands could account for the observed NMR spectra. In this communication, we present the first molecular orbital study in which an *optimized* geometry for a nonplanar η^3-Cp ligand is calculated and shown to represent the minimum energy conformation on the potential energy surface. We also present a simple rationale for the bent

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[1] For example, in a review article (O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, 87, 307) the authors compiled 10 different Cp binding modes. Early theoretical studies of olefin distortion upon binding to metals include: Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591. Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

[2] Hansen, L. M.; Marynick, D. S. *Organometallics* **1989**, *8*, 2173.

[3] Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329.

[4] van Raaij, E. U.; Brintzinger, H. H. *J. Organomet. Chem.* **1988**, *356*, 315.

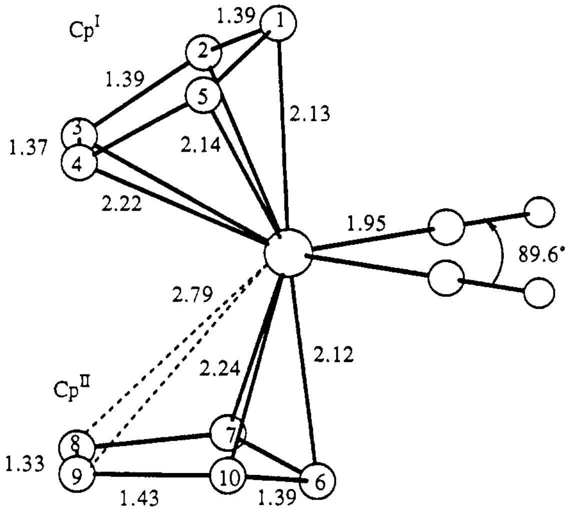
[5] Millar, J. M.; Kastrup, R. V.; Harris, S.; Horvath, I. T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 194.

0276-7333/91/2310-0543$02.50/0

η^3 coordination geometry. Finally, the entire potential energy surface for the $\eta^5 \leftrightarrow \eta^3$ interconversion is calculated.

All calculations were performed with the PRDDO approximations[6] on a Solbourne Series 5/602 computer. With the exception of C–H distances and Cr–C–O angles (fixed at 1.07 Å and 180°, respectively), the geometries were fully optimized for $(\eta^5\text{-Cp})(\eta^1\text{-Cp})Cr(CO)_2$, $(\eta^5\text{-Cp})(\eta^2\text{-Cp})Cr(CO)_2$, $(\eta^5\text{-Cp})(\eta^3\text{-Cp})Cr(CO)_2$, and $(\eta^5\text{-Cp})_2Cr(CO)_2$ under the constraint of C_s symmetry. For $(\eta^5\text{-Cp})_2Cr(CO)_2$ an additional geometrical constraint (see below) was required to prevent the structure from collapsing to a lower energy conformation.

Starting from an assumed endo–endo orientation for Cp^{I} (top) and Cp^{II} (bottom), as found experimentally for $(Cp)_2W(CO)_2$,[3] we obtained the optimized geometry of $(\eta^3\text{-Cp})(\eta^5\text{-Cp})Cr(CO)_2$ as shown in structure I. The η^5-Cp ring (Cp^{I}) has C–C distances of ~1.4 Å, which are typical for aromatic rings. The Cr–C distances vary from 2.13 to 2.22 Å, well in the range of Cr–olefin bond lengths. The η^3 ring has Cr–C bond lengths that vary from 2.12 to 2.79 Å. The longest distances (R(Cr–C^8) and R(Cr–C^9)) are certainly too long to be interpreted as Cr–C bonds. The most remarkable finding is that the η^3-Cp ring is nonplanar. The angle defined by the intersection of the two planes that contain C^6, C^7, C^{10} and C^7, C^8, C^9, C^{10} is 160°. This is the same angle found in $(Cp)_2W(CO)_2$.[3] Notice that the C–C atom pair in Cp^{II} which is not bound to Cr has a bond length of 1.33 Å. This should be considered a double bond. Thus, two of the π electrons in Cp^{II} are not donated to Cr, resulting in an 18-electron complex.



I

After the geometry was optimized with the above constraint, we optimized two other possible Cp ring orientations and found energies relative to structure I as follows: endo–exo (0.9 kcal/mol), and exo–endo (2.5 kcal/mol). Although the three structures are very close in energy, the low-energy structure has the same conformation of the Cp rings as the X-ray crystal structure of the analogous tungsten system $(\eta^3\text{-Cp})(\eta^5\text{-Cp})W(CO)_2$.

What makes the η^3-Cp distort? First, we note that the energy required to distort the PRDDO-optimized geometry of $C_5H_5^-$ into the same geometry as the η^3-Cp ring in $(\eta^3\text{-Cp})(\eta^5\text{-Cp})Cr(CO)_2$ is only 17.5 kcal/mol. This is significantly less than typical metal–carbon bond dissociation energies. Earlier Fenske–Hall calculations on $(\eta^3\text{-Cp})(\eta^5\text{-Cp})W(CO)_2$[5] indicated that the bending of the Cp results in a decrease of M–Cp antibonding character in the HOMO and subsequent increased back-bonding to the carbonyls. This was based, in part, on a previous DV-Xα calculation on the related $(Cp)_2Ti(CO)_2$ complex.[7] Our PRDDO calculations indicate minimal carbonyl participation in the first four HOMO's of $(\eta^3\text{-Cp})(\eta^5\text{-Cp})Cr(CO)_2$ but do suggest that a significant repulsive four-electron interaction exists in $(\eta^5\text{-Cp})_2Cr(CO)_2$. In Figure 1, we present a correlation diagram between the top four orbitals in the ground state and an identical molecule with the η^3-Cp planar and the H–C–C angles reoptimized. In Figure 2, we illustrate the shapes of the 1a′ and 2a′ orbitals of the ground-state structure. The HOMO (2a′), with a 50% electron population on the C^8–C^9 atom pair, is highly destabilized in going from a nonplanar Cp ring to a planar Cp ring. The second highest molecular orbital (2a″ and dominantly Cp^{I}–Cr character) remains virtually un-

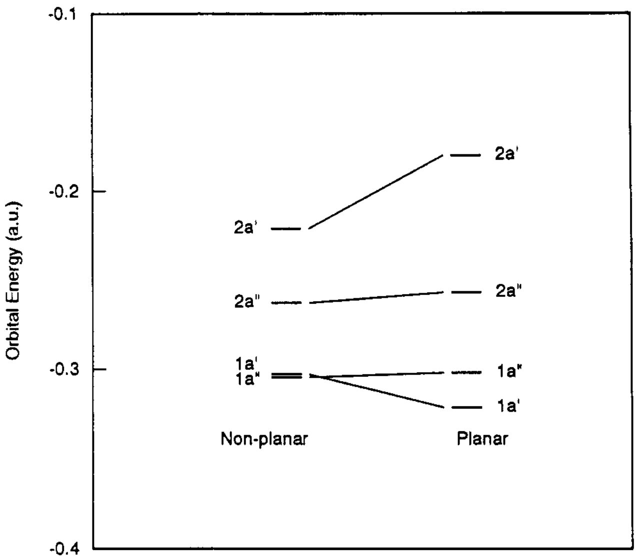


Figure 1. Orbital correlation diagram for structure I with planar and nonplanar η^3-Cp rings. The eigenvalues are from the PRDDO wave functions. The orbital populations for the 2a′ orbital are 0.10e (C^1), 0.11e (C^3), 0.11e (C^4), 0.31e (C^6), 0.50e (C^8), 0.50e (C^9), and 0.25e (Cr) in the nonplanar Cp structure and 0.18e (C^1), 0.24e (C^3), 0.24e (C^4), 0.25e (C^6), 0.38e (C^8), 0.38e (C^9) and 0.27e (Cr) for planar Cp complex. The 1a′ orbital is made up of 0.51e (C^1), 0.33e (C^3), 0.33e (C^4), 0.20e (C^6), 0.08e (C^8), 0.08e (C^9), and 0.33e (Cr) for the nonplanar complex and 0.45e (C^1), 0.20e (C^3), 0.20e (C^4), 0.24e (C^6), 0.11e (C^8), 0.11e (C^9), and 0.53e (Cr) for the planar complex.

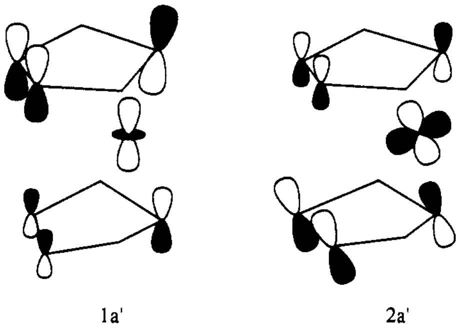


Figure 2. Shapes of the 1a′ and 2a′ molecular orbitals in $(\eta^3\text{-Cp})(\eta^5\text{-Cp})Cr(CO)_2$.

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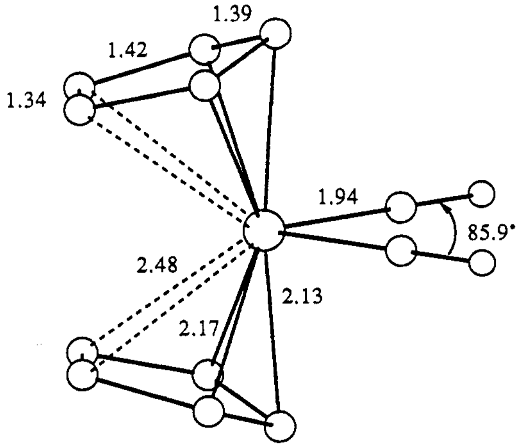
[6] (a) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. (b) Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.

[7] Casarin, M.; Cilberto, E.; Gulino, A.; Fragala, I. *Organometallics* **1989**, *8*, 900.

changed, as does the 1a″ orbital (dominantly Cp^{II}–Cr character). However, the 1a′ orbital, which is an admixture of Cp^{II}–Cr and Cp^{I}–Cr bonding interactions, decreases in energy. The detailed population analysis clearly shows that flattening of the ring results in mixing of the HOMO and the 1a′ molecular orbital and no significant changes in any other orbitals. This is a repulsive four-electron interaction that should be destabilizing.

In order to verify that our calculated structure represents a global minimum, it is obviously important to examine other chemically reasonable cyclopentadienyl coordination modes. The optimized structure for the 16-electron (η^5-Cp)(η^1-Cp)Cr(CO)$_2$ complex[8a] yielded an energy relative to structure I of +7.7 kcal/mol, while the relative energy of the 17-electron (η^5-Cp)(η^2-Cp)Cr(CO)$_2$ species[8b] was calculated to be only +5.5 kcal/mol. The (η^5-Cp)$_2$Cr(CO)$_2$ structure could not be optimized without additional constraints, since it collapsed to a structure that contains an η^2-Cp group. If an η^5 structure was forced by constraining Cr–C distances within a given Cp to be equal, a high-energy structure[8c] (relative energy of +21.5 kcal/mol) results. Thus, our calculations predict that the ground-state structure has precisely the same conformation as found in the corresponding tungsten system; however, the energy differences between the ground state and the structures with one Cp either η^1 or η^2 bound are small. This is necessarily the case, since ring *rotation*, making the carbons of each individual Cp ring equivalent on the NMR time scale, occurs even at −140 °C.[5]

Because the barrier for ring *interchange* has been measured experimentally, it is important to examine the potential energy surface for the $\eta^3 \leftrightarrow \eta^5$ conversion in order to test the reasonableness of our calculated structure. The pathway for the $\eta^3 \leftrightarrow \eta^5$ interconversion was calculated by using the linear synchronous transit (LST)/orthogonal optimization approach.[9] The potential energy surface is symmetric with a maximum at a path coordinate of 0.50. The structure of the estimated transition state is shown by II. At the estimated transition state, both Cp rings are planar and η^3-coordinated to the metal. The symmetry is C_{2v}, and the calculated energy is only 5 kcal/mol higher than the ground-state structure. Although the ring interchange is clearly facile, it would appear that PRDDO slightly underestimates the barrier, since the experimental barrier is ~13 kcal/mol. The Cr–C distances range from 2.13 to 2.48 Å. The C–C distance for the two carbon atoms in each Cp that are not bound to the metal is 1.34 Å, again indicative of a C–C double bond. The interconversion of binding modes can be thought of as proceeding via a dissociative step to the transition state, since two Cr–C bonds on the η^5-Cp ring are broken before the other two Cr–C bonds on the η^3-Cp ring are formed. The transition state is clearly a 16-electron complex.



II

In conclusion, our calculations predict the ground-state geometry of (Cp)$_2$Cr(CO)$_2$ to contain one η^5- and one η^3-Cp group, with the η^3-Cp bent. We show that all other chemically reasonable structures yield higher calculated total energies and/or fail to converge to a stable minimum. The electronic factors that result in the bending of the η^3-bound Cp have been clearly isolated. The calculated (η^3-Cp)(η^5-Cp)Cr(CO)$_2$ structure has also been shown to be consistent with the observed fluxional behavior of the molecule, since ring interchange through a (η^3-Cp)$_2$Cr(CO)$_2$ transition state with planar Cp rings is very facile.

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(8) (a) In this structure the average Cr–C bond length, for the η^5-Cp ring, is 2.15 Å. The C–C bond lengths are all ~1.39 Å in the η^5-Cp ring. The η^1-Cp ring has Cr–C distances of R(Cr–C^6) = 2.07 Å, R(Cr–C^7) = R(Cr–C^{10}) = 2.83 Å, and R(Cr–C^8) = R(Cr–C^9) = 3.64 Å. The C–C distances in Cp^{II} are R(C^6–C^7) = R(C^6–C^{10}) = 1.46 Å, R(C^7–C^8) = R(C^9–C^{10}) = 1.32 Å, and R(C^8–C^9) = 1.43 Å. (b) For the η^2-Cp complex, the rings are in an endo–exo conformation with C^6 and C^7 directly attached to chromium. The structure has an average Cr–C bond length of 2.16 Å and an average R(C–C) bond distance equal to 1.39 Å for the η^5-Cp ring. The η^2-Cp ligand has Cr–C distances of R(Cr–C^6) = R(Cr–C^7) = 2.18 Å, R(Cr–C^8) = R(Cr–C^{10}) = 2.80 Å, and R(Cr–C^9) = 3.14 Å. The C–C distances are R(C^6–C^7) = 1.42 Å, R(C^7–C^8) = R(C^6–C^{10}) = 1.39 Å, and R(C^8–C^9) = R(C^9–C^{10}) = 1.37 Å. (c) This structure is characterized by R(Cr–C) distances of 2.43 and 2.19 Å for Cp^{I} and Cp^{II}, respectively.

(9) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* 1977, *49*, 225. For a review of the application of this methodology to organometallic potential energy surfaces, see: Marynick, D. S.; Axe, F. U.; Hansen, L. M.; Jolly, C. A. In *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Freund: London, 1989; Vol. 3, pp 43–84.