Agostic Interaction between Tungsten Center and Cycloalkane: DFT Studies on $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$

Yo-ichi Ishikawa* and Ye Xie
Department of Chemistry and Materials Technology, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606-8585

(Received March 19, 2007; CL-070291; E-mail: ishikawa@kit.ac.jp)

An agostic interaction in $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ is investigated using a hybrid density functional theory (B3LYP) with ECPs (LanL2DZ) on W and 6-311+G(2d,p) on C, O, and H atoms. The structure with the minimum energy is confirmed on the basis of the reproducibility of the characteristic frequency shifts in the C–O stretching region observed by a time-resolved infrared absorption spectroscopy on the coordination of *cyclo*-C_3H_6 to "naked" $W(CO)_5$. The C–H bond is found to coordinate to the W atom in η^2-form with the bond enthalpy of $5.5\,\mathrm{kcal\,mol^{-1}}$.

Transition-metal center plays an important role in C–H bond activation under the mild conditions[1] and has been extensively studied experimentally[2,3] and theoretically.[4–6] An agostic complex is thought to be the precursor in the oxidative addition of saturated hydrocarbon by coordinatively unsaturated transition-metal complex. Theoretical approaches would be useful for understanding of the agostic interaction because of the lability of such an alkane complex.[7]

As the carbonyls of "naked" $M(CO)_5$ (M = Cr, Mo, or W) show the characteristic vibrational frequency shifts on the coordination process of $M(CO)_5 + L$, which are extremely sensitive to the ligand L, the shifts are thought to be a good measure of the interaction between transition-metal center and the ligand.[8,9] Even when L was a noble gas, meaningful vibrational shifts were observed[10] and theoretically analyzed.[11] Two theoretical improvements of density functional theory (DFT) and effective core potentials (ECP) have allowed to calculate not only the structure but also the frequency and the bond enthalpy of transition-metal carbonyls[12–16] comparable with experimental values.

In this paper, the geometries of $W(CO)_5$, *cyclo*-C_3H_6, and $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ optimized using DFT are reported and the bond enthalpy of W–(*cyclo*-C_3H_6) is estimated. The rationality of the structure with the lowest energy is confirmed on the basis of the C–O vibrational analysis other than the energy. The agostic interaction in $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ is discussed on the calculation results.

Hybrid DFT (B3LYP) calculations were carried out on $W(CO)_5$, *cyclo*-C_3H_6, and $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ using Gaussian 03W program.[17] Basis set composed of 6-311+G(2d,p) functions on C, O, and H atoms and LANL2DZ function with ECP on W atom (abbreviated to "BS-A" hereafter) was used in combination with B3LYP calculation. The basis set was chosen because it gave a reasonable structure and vibrational frequency results for C–O stretching mode of coordinatively unsaturated transition-metal carbonyl ($M(CO)_n$; M = Cr, Mo, and W, $n = 3$–5)[18] and $W(CO)_5L$ (L = NH_3 and C_2H_4).[19] An appropriate, generally accepted correction was made for the calculated harmonic frequency (ω_{cal}) to estimate the theoretical fundamental frequency (ν_{corr}) by multiplying ω_{cal} with a scaling factor ($\lambda = 0.9679$).[20]

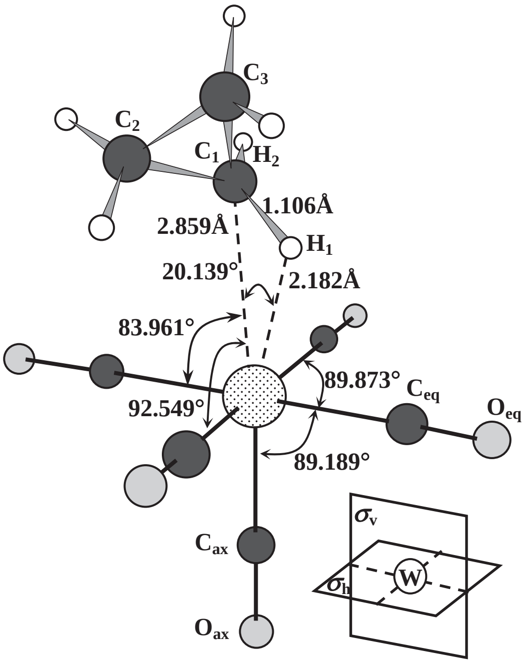

Figure 1. $W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ complex structure with the global minimum energy determined in this DFT calculation.

Figure 1 shows the η^2-$W(CO)_5(\textit{cyclo}\text{-}C_3H_6)$ complex structure, which has the lowest energy in the geometries optimized at the B3LYP/BS-A level. Of course, the optical isomer of this structure has the same energy and the C–O stretching frequencies. The important geometrical parameters are shown in the figure. On the *cyclo*-C_3H_6 coordination, $W(CO)_5$ part alters little its structure: $r(\mathrm{W–C_{eq}}) = 2.060$–$2.065$ Å (2.063 Å in "naked" $W(CO)_5$), $r(\mathrm{W–C_{ax}}) = 1.973$ Å (1.955 Å), $r(\mathrm{C_{eq}–O_{eq}}) = 1.143$–$1.144$ Å (1.143 Å), $r(\mathrm{C_{ax}–O_{ax}}) = 1.152$ Å (1.151 Å), $\angle(\mathrm{C_{eq}–W–C_{ax}}) = 89.19$–$90.24°$ (90.39°), and $\angle(\mathrm{C_{eq}–W–C_{eq}}) = 89.87$–$90.13°$ (90.00°). The plane of C3-ring of *cyclo*-C_3H_6 slants to σ_h with about 65°, in which $r(\mathrm{W–C_1}) = 2.859$ Å, $r(\mathrm{W–C_2}) = 3.664$ Å, and $r(\mathrm{W–C_3}) = 4.209$ Å. The C_1–H_1 bond is slightly lengthened to 1.106 Å from 1.082 Å in *cyclo*-C_3H_6 molecule while that of C_1–H_2 is shortened to 1.079 Å. The other C–H bonds in the complex are identical to the C–H bonds in *cyclo*-C_3H_6 molecule. The geometrical symbols used here are shown in Figure 1.

As the some local minimum structures are expected, some initial structures are systematically selected for the optimization. By the geometrical optimization, two local minimum and two transition structures were also obtained. Both structures with local minimum energy have one C–C bond parallel to σ_h, in

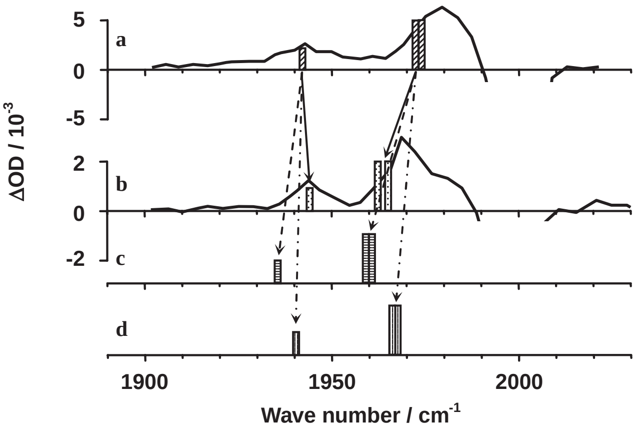

Figure 2. Comparison of the infrared difference absorption spectra (solid lines) of $W(CO)_5$ (a) and $W(CO)_5$(*cyclo*-C_3H_6) (b) observed in the gas phase and the vibrational frequencies (ν_{cal}) calculated for $W(CO)_5$ (slant-line hatched rectangles in (a)) and $W(CO)_5$(*cyclo*-C_3H_6) (dot-hatched rectangles in (b)). Horizontal-line hatched rectangles represent IR absorption frequencies of a local minimum state in C–C η^2-form (c) and vertical-line hatched rectangles does those of a transition state in H–C–H bifurcate-form (d). The height of each rectangle reflects a relative absorption intensity ratio for each compound. The ordinate scale ΔOD indicates the difference optical density between before and at ≈3-μs after XeCl laser photolysis ($\lambda = 308$ nm) of $W(CO)_6$ (≈10 mTorr) in the absence (a) and in the presence of 0.69-Torr *cyclo*-C_3H_6 at a total pressure of ca. 6.0 Torr with balance Ar.

which r(W–C) is ca. 3.1 Å and r(W-center of C–C bond) is ca. 3.0 Å. One has the σ(C_3-ring plane) parallel to the σ_v plane (P1) and the other at 45° (P2). These locate at 0.66 kcal mol^{-1} and at 0.85 kcal mol^{-1} higher than the global minimum state in the electronic energy, respectively.

The $W(CO)_5$(*cyclo*-C_3H_6) complex has been observed in reaction of *cyclo*-C_3H_6 with $W(CO)_5$ by the time-resolved infrared absorption spectroscopy in the gas phase (Figures 2a and 2b).[21] On *cyclo*-C_3H_6 coordination, it was observed that the equatorial CO absorption band (1980 cm^{-1} in $W(CO)_5$) shifted to a low frequency side by ca. 10 cm^{-1} (1969 cm^{-1} in the complex) while the axial CO absorption band (1942 cm^{-1} in $W(CO)_5$) did to a high frequency side only by a few cm^{-1} (1944 cm^{-1} in the complex). The calculation results suggest that, on *cyclo*-C_3H_6 coordination, the band of the equatorial carbonyls in $W(CO)_5$ ($\nu_{corr} = 1973$ cm^{-1}) separates into two bands at 1965 and 1962 cm^{-1}) with a similar intensity while the axial CO absorption band shifts to a high frequency side only by 2 cm^{-1}. The low resolution of ca. 4 cm^{-1} of the CO laser used for IR absorption spectroscopy is thought not to allow the observation of the expected small splitting of 3 cm^{-1} in the equatorial CO modes. The similarities in the characteristic shifts in C–O stretching frequency on the *cyclo*-C_3H_6 coordination between the observed spectra and the theoretical C–O frequencies confirm that the global minimum state has the optimized structure in C–H η^2-form, though the absolute frequency value did not completely coincide with each other. Both local minimum complexes with a C–C bond parallel to σ_h (P1 and P2) are calculated to have a equatorial C–O frequency of ca. 1960 cm^{-1} (ν_{corr}) and a axial C–O frequency of ca. 1936 cm^{-1} (ν_{corr}) as shown in Figure 2c, which does not reproduce the characteristic frequency shifts on the coordination, especially in C–O_{ax} frequency. Figure 2d shows the calculated C–O stretching frequencies for one transition state in H–C–H bifurcate form with an electronic energy higher than the ground state by ca. 2 kcal mol^{-1}. Any bifurcate structure could not be optimized in this tungsten complex at B3LYP/BS-A level calculation.

The bond dissociation enthalpy (BDE) at 298 K is calculated using the equation:

$$BDE = \Delta E_c + \Delta ZPE + \Delta E_{th} + \Delta(PV) \tag{1}$$

where ΔE_c was the difference in the optimized energies between the reactant and the product, ΔZPE was the zero point energy correction obtained from calculation of the vibrational frequencies, ΔE_{th} was the difference associated with the translational, rotational, and vibrational energies at 0 and 298 K, and $\Delta(PV)$ was the molar work equal to ΔnRT. The BDE is calculated to be 5.5 kcal mol^{-1}, which is almost comparable to the experimental one (8.8 ± 2 kcal mol^{-1}).[21]

The characteristic C–O stretching frequency shifts observed on the *cyclo*-C_3H_6 is well similar to the shift on the coordination of Xe.[22,23] $W(CO)_5$(Xe) has two C–O stretching frequencies of 1973 cm^{-1} (← 1980 cm^{-1} in "naked" $W(CO)_5$) and 1952 cm^{-1} (← 1942 cm^{-1} in "naked" $W(CO)_5$) in the gas phase,[23] suggesting that an alkane coordinates to W center as a simple σ donor of C–H bond in η^2-form.

References and Notes

1 R. A. Periana, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 7332.
2 E. P. Wasserman, C. B. Moore, R. G. Bergman, *Science* **1992**, *255*, 315.
3 S. E. Bromberg, H. Yang, M. C. Asplund, T. Lian, B. K. McNamara, K. T. Kotz, J. S. Yeston, M. Wilkens, H. Frei, R. G. Bergman, C. B. Harris, *Science* **1997**, *278*, 260.
4 N. Koga, K. Morokuma, *J. Phys. Chem.* **1990**, *94*, 5454.
5 N. Koga, K. Morokuma, *Chem. Rev.* **1991**, *91*, 823.
6 I. H. Hristov, T. Ziegler, *Organometallics* **2003**, *22*, 3513.
7 S. Zaric, M. B. Hall, *J. Phys. Chem. A* **1997**, *101*, 4646.
8 E. Weitz, *J. Phys. Chem.* **1994**, *98*, 11256.
9 F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, **1980**, p. 82.
10 J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **1992**, *114*, 2783.
11 A. W. Ehlers, G. Frenking, E. J. Baerends, *Organomettallics* **1997**, *16*, 4896.
12 A. W. Ehlers, G. Frenking, *J. Am. Chem. Soc.* **1994**, *116*, 1514.
13 G. Frenking, U. Pidum, *J. Chem. Soc., Dalton Trans.* **1997**, 1653.
14 M. Zhou, L. Andrews, C. W. Bauschlicher, Jr., *Chem. Rev.* **2001**, *101*, 1931.
15 V. Jonas, W. Thiel, *J. Chem. Phys.* **1995**, *102*, 8474.
16 A. Kovacs, G. Frenking, *Organometallics* **2001**, *20*, 2510.
17 M. J. Frisch, et al., *Gaussian 03 (Revision B.05)*, Gaussian, Inc., Pittsburgh PA, **2003**.
18 Y. Ishikawa, K. Kawakami, *J. Phys. Chem. A*, in press.
19 K. Kawakami, H. Nakazawa, T. Kinoshita, Y. Ishikawa, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 166.
20 M. P. Andersson, P. Uvdal, *J. Phys. Chem. A* **2005**, *109*, 2937.
21 C. E. Brown, Y. Ishikawa, P. A. Hackett, D. M. Rayner, *J. Am. Chem. Soc.* **1990**, *112*, 2530.
22 J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **1992**, *114*, 2783.
23 M. Jyo-o, H. Takeda, K. Omiya, Y. Ishikawa, S. Arai, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3618.