 

# Interaction of a Coordinatively Unsaturated Transition-Metal Center with Small Molecules: DFT Studies on $W(CO)_5L$ (L = None, $C_2H_4$, and $NH_3$)

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DFT calculations were performed in order to investigate the interactions between coordinatively unsaturated sites on $W(CO)_5$ and $C_2H_4$ as a typical $\pi$-acceptor and $NH_3$ as a typical $\sigma$-donor. B3LYP-based DFT calculations with ECPs (LANL2DZ) on W and 6-311G(d,p) all-electron basis sets on H, C, N, and O reproduced the characteristic shifts in vibrational frequency of carbonyls that have been experimentally observed for the successive processes $W(CO)_6$ $(-\ CO) \rightarrow W(CO)_5$ $(+\ L) \rightarrow W(CO)_5L$ ($L = C_2H_4$ and $NH_3$). Based on the calculations, $C_2H_4$ coordinates to the coordinatively unsaturated site of W atom in a side-on fashion with a 23.1 kcal mol$^{-1}$ bond dissociation enthalpy (BDE), where the center of the C=C double bond was 2.39 Å from W atom, and $NH_3$ coordinates with a BDE of 31.9 kcal mol$^{-1}$ and a distance of 2.37 Å. As well, the C=C bond length (1.38 Å) in $C_2H_4$ was found to be slightly longer than that of free $C_2H_4$ (1.33 Å).

The interaction between $d^6$ $ML_5$ and a small molecule gives a useful model for the elucidation of the intricate interactions between active sites of transition metals and small molecules in conjunction with theoretical calculations.[1–3] This interaction is considered to be associated not only to homogeneous chemical processes, such as hydroformylation and alcohol synthesis, but also to model surface chemistry for catalysis and synthesis. One of the most studied coordinatively unsaturated organometallic species is the transition-metal carbonyl, because the carbonyls coordinated to transition-metal atom have characteristic vibrational frequencies that are extremely sensitive to the number of unsaturated sites or to the coordinated small molecule.[4–7] These vibrational frequency shifts are thought to be a good measure of the interaction between metal center and coordinating molecule (ligand).[8]

Previous transient infrared spectroscopic studies have provided valuable information about the reactivity and the qualitative structure of coordinatively unsaturated transition-metal carbonyls.[4,5] However, the quantitative structure, the metal–ligand bond dissociation enthalpy (BDE), and the nature of the metal–ligand bond are still interesting subjects. For example, the BDEs of $M(CO)_5$–L have been experimentally estimated only for a limited number of complexes with weakly bound ligands (BDE $\approx$ 10 kcal mol$^{-1}$), meaning that the equilibrium in the bond formation can be observed even at room temperature.[5,9–15] Density functional theory (DFT), using an appropriate basis set, has been recently reported to give a better description of not only the geometry but also the vibrational frequencies of transition-metal compounds.[7,16,17] These theoretical calculations should give useful information on the interaction between transition-metal center and ligand.[18,19]

In this paper, the geometries of $W(CO)_5$, $W(CO)_5$–$C_2H_4$, $W(CO)_5$–$NH_3$, and $W(CO)_5$–CO were optimized using DFT calculations and the characteristic shifts in the C–O vibrational frequency observed by using transient infrared spectroscopy could be reproduced.[13] The geometries, BDEs of metal–ligand, and interaction of these complexes are discussed based on the calculation results.

## Computational Methods

**Computational Details.** DFT calculations were performed on all related chemical species using Gaussian 03W program.[20] Becke's three-parameter hybrid functional including a mixture of Hartree–Fock exchange with DFT exchange-correlation combined with Lee–Yang–Parr correlation functional (B3LYP) and with Perdew-Wang's 1991 gradient-corrected correlation functional (B3PW91) were used in all calculations as well as Becke's 1988 exchange-correlation functional (BLYP and BPW91). Hartree–Fock (HF) calculations were also carried out for all species for a reference. Basis set A (BS-A) consisted of 6-311G(d,p) functions on hydrogen, carbon, nitrogen, and oxygen atoms and LANL2DZ basis functions with ECP on a tungsten atom. Basis set B (BS-B) had larger basis functions of 6-311+G(3df,2p) on H, C, N, and O atoms, which was used only in combination with B3LYP calculation. Vibrational frequencies of the optimized structures were used to interpret the previously reported time-resolved infrared absorption spectra.

**Estimation of BDE ($-\Delta H_{298}$).** Thermochemical data of the related compounds with optimized geometries were used in the estimation of the BDE between a typical ligand ($C_2H_4$, $NH_3$, or CO) and metal center. The BDE at 298 K (BDE = $-\Delta H_{298}$) was calculated using the expression:

$$\Delta H_{298} = \Delta E_c + \Delta ZPE + \Delta E_{th} + \Delta(PV), \quad (1)$$

where $\Delta E_c$ was the difference in the optimized energies be-

Published on the web January 12, 2007; doi:10.1246/bcsj.80.166

Table 1. Comparison between the Experimental Values[a] and the Calculated Values Using BS-A of the Geometries and Vibrational Frequencies

| | | Exp. | HF | BLYP | BPW91 | B3LYP | B3PW91 |
|---|---|---|---|---|---|---|---|
| CO | $\omega_e$/cm$^{-1}$ | 2170[b] | 2441 | 2120 | 2133 | 2220 | 2228 |
| | $r_e$/Å | 1.128[b] | 1.105 | 1.139 | 1.168 | 1.127 | 1.127 |
| $NH_3$ | $\omega_0$(N–H)/cm$^{-1}$ | 1626.1[c] | 1802 | 1648 | 1645 | 1682 | 1678 |
| | $r_e$(N–H)/Å | 1.0124[c),d] | 1.001 | 1.025 | 1.023 | 1.016 | 1.015 |
| | $\theta_e$(H–N–H)/° | 106.7[c),d] | 107.4 | 105.7 | 106.7 | 106.5 | 106.4 |
| $C_2H_4$ | $\omega_0$(C=C)/cm$^{-1}$ | 1622.6[c] | 1822 | 1637 | 1645 | 1691 | 1696 |
| | $r_0$(C=C)/Å | 1.337[c] | 1.317 | 1.336 | 1.335 | 1.327 | 1.326 |
| | $r_0$(C–H)/Å | 1.0836[c] | 1.077 | 1.091 | 1.092 | 1.085 | 1.086 |
| | $\theta_0$(H–C–H)/° | 117.5[c] | 116.6 | 116.4 | 116.5 | 116.5 | 116.6 |
| $W(CO)_6$ | $\omega_e$(C–O) ($T_{1u}$)/cm$^{-1}$ | 2037.6[e] | 2287 | 1974 | 1996 | 2069 | 2084 |
| | $r_0$(W–C)/Å | 2.06 ± 0.04[f] | 2.101 | 2.078 | 2.061 | 2.069 | 2.057 |
| | $r_0$(C–O)/Å | 1.13 ± 0.05[f] | 1.114 | 1.156 | 1.155 | 1.142 | 1.141 |

a) The subscript e is used for the molecular constant of the equilibrium structure and the subscript 0 is used for that of the vibrationally ground state ($v = 0$). The calculated value might be compared directly to the experimental values with the subscripte. b) Ref. 21. c) Ref. 22. d) $r_0$(N–H) = 1.0173 Å and $\theta_0$(H–N–H) = 107.8°. e) Ref. 23. f) Ref. 24.

tween the reactant ($W(CO)_5$ + L) and the product ($W(CO)_5L$) (L = $C_2H_4$, $NH_3$, and CO), ΔZPE was the zero point energy correction obtained from calculation of the vibrational frequencies, $\Delta E_{th}$ 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 $\Delta nRT$.[15]

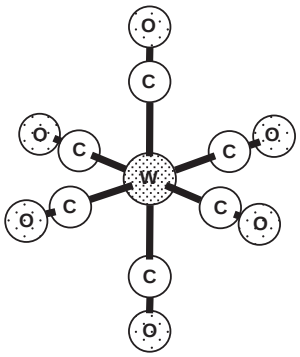
## Results and Discussion

Table 1 shows a comparison of some of the results from the DFT calculations using BS-A with Hartree–Fock calculation results. Generally, the DFT system involving Becke's three-parameter hybrid functional (B3LYP, B3PW91) is more trustworthy than the HF-based ab initio calculation and other DFT systems (BLYP, BPW91) in regards to the geometry of the relevant compounds. However, the calculations using B3LYP and B3PW91 give slightly higher (2–3%) absolute values of vibrational frequencies.

Figure 1 shows the optimized geometries of $W(CO)_6$, $W(CO)_5$, $W(CO)_5(C_2H_4)$, and $W(CO)_5(NH_3)$ by B3LYP with BS-B. The optimized structure of $W(CO)_6$ is in good agreement with the experimental data (Table 1),[24] as well as using the smaller basis set BS-A ($r_1$(W–C) = 2.069 Å, $r_2$(C–O) = 1.142 Å). $W(CO)_5(C_2H_4)$ has $C_{2v}$ symmetry, where the center of C=C double bond of $C_2H_4$ was 2.39 Å from the W atom. $C_2H_4$ coordinates on W atom in a side-on fashion where the C=C double bond is parallel to the $C_{eq//}$–W–$C_{eq//}$ direction. $W(CO)_5(NH_3)$ has pseudo-$C_{4v}$ symmetry, where $NH_3$ coordinates on the W center 2.37 Å apart. In the optimized geometry, one N–H bond is strictly parallel to one W–$C_{eq}$–$O_{eq}$. However, the four equatorial COs can be considered to be almost equivalent because the four W–$C_{eq}$ lengths are within a narrow range (2.056–2.058 Å) and the four $C_{eq}$–$O_{eq}$ lengths are similar (≈1.145 Å), while the W–$C_{ax}$ and $C_{ax}$–$O_{ax}$ bond lengths are 1.993 and 1.151 Å, respectively.

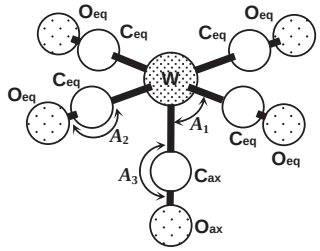
Table 2 shows the harmonic frequencies ($\omega_e$) of $W(CO)_5L$ (L = none, $C_2H_4$, $NH_3$, and CO) with an optimized geometry, which was determined by DFT calculations with BS-A, together with the experimental absorption frequencies ($\nu_e$). Though the DFT calculation using BLYP and BPW91, especially using BPW91, gives harmonic frequencies that correspond to the absorption frequencies at first sight, these values are not comparable directly as mentioned below. The vibrational energy term in wavenumber can be approximately written as $E(v) = \omega_e(v + 1/2) - \omega_e\chi_e(v + 1/2)^2$. Here, $v$ is the vibrational quantum number, $\omega_e$ is a harmonic frequency in cm$^{-1}$, and $\omega_e\chi_e$ is an anharmonicity constant in cm$^{-1}$.[25] Then, the observed absorption frequency $\nu_e$ corresponds to $\omega_e - 2\omega_e\chi_e$ ($=E(1) - E(0)$). The anharmonicity constant of coordinated CO stretching mode in $W(CO)_6$ is estimated to be about 23 cm$^{-1}$, which was reported for a $CCl_4$ solution of $W(CO)_6$,[26] in which $\nu_e$ is 1980 cm$^{-1}$ and then $\omega_e$ is 2026 ± 10 cm$^{-1}$. This anharmonicity term is larger than that of free CO ($X^1\Sigma^+$) (13.461 cm$^{-1}$).[21] Because the absorption peak value ($\nu_e$) is usually lower than the harmonic frequency ($\omega_e$) by about $2\omega_e x_e$ as mentioned above, the observed fundamental frequency and the theoretical harmonic frequency by DFT are not comparable without accurate knowledge of the anharmonicity. In the four DFT calculations (BLYP, BPW91, B3LYP, and B3PW91) studied here, B3LYP appeared to give a set of reasonable CO frequencies taking account the anharmonic correction terms, though the corrected absolute values seem still to be larger than the true values.

We also checked the characteristic shifts in the vibrational frequency of carbonyls in the coordination processes of $W(CO)_5$ (+ L) → $W(CO)_5L$ (L = $C_2H_4$ and $NH_3$). Figure 2 shows a comparison between experiment ($\nu_{exp}$, lower abscissa scale) and theory (B3LYP with BS-A) ($\omega_{cal}$, upper abscissa scale) for the CO vibrational frequency shifts. Note that a different scale for each frequency is used ($\omega_{cal} - \nu_{exp} = 70$ cm$^{-1}$). Using B3LYP, the following three experimental characteristic properties observed for the C–O stretching frequency during the coordination of $C_2H_4$ and $NH_3$, excluding the absolute value[13] could be reproduced: 1) $W(CO)_5$ has two absorption bands about 40 cm$^{-1}$ apart, where the larger absorption band has been assigned to the E vibration (equatorial CO antisymmetric stretching, $\nu_{exp}$ = 1980 cm$^{-1}$) and the smaller band to the $A_1$ vibration (axial CO stretching, $\nu_{exp}$ = 1942 cm$^{-1}$) mainly because the absorption intensity ratio of these two bands is roughly 4:1.[27] The calculation results, in which the intensity ratio of two absorption bands at 2050 cm$^{-1}$ (E) and



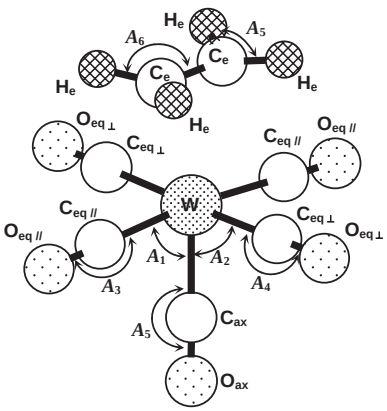

**a. $W(CO)_6$ ($O_h$)**

$r_1$ (W - C) = 2.070 Å
$r_2$ (C - O) = 1.140 Å
$A_1$ (C – W - C) = 90.00 °
$A_2$ (W – C - O) = 180.0 °



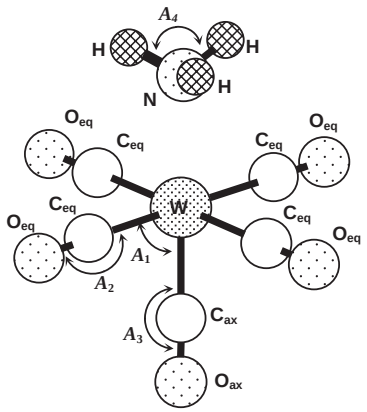

**b. $W(CO)_5$ ($C_{4v}$)**

$r_1$ (W - $C_{eq}$) = 2.062 Å
$r_2$ ($C_{eq}$ - $O_{eq}$) = 1.141 Å
$r_3$ (W - $C_{ax}$) = 1.951 Å
$r_4$ ($C_{ax}$ – $O_{ax}$) = 1.151 Å
$A_1$ ($C_{eq}$ – W – $C_{ax}$) = 90.48 °
$A_2$ (W - $C_{eq}$ - $O_{eq}$) = 178.7 °
$A_3$ (W – $C_{ax}$ – $O_{ax}$) = 180.0 °




**c. $W(CO)_5(C_2H_4)$ ($C_{2v}$)**

$r_1$ (W - $C_{eq//}$) = 2.064 Å
$r_2$ ($C_{eq//}$ - $O_{eq//}$) = 1.142 Å
$r_3$ (W - $C_{eq\perp}$) = 2.059 Å
$r_4$ ($C_{eq\perp}$ - $O_{eq\perp}$) = 1.143 Å
$r_5$ (W - $C_{ax}$) = 2.013 Å
$r_6$ ($C_{ax}$ - $O_{ax}$) = 1.146 Å
$r_7$ (W - $C_e$•$C_e$) = 2.387 Å
$r_8$ ($C_e$ - $C_e$) = 1.374 Å
$r_9$ ($C_e$ - $H_e$) = 1.080 Å
$A_1$ ($C_{eq//}$ - W - $C_{ax}$) = 87.05 °
$A_2$ ($C_{eq\perp}$ - W - $C_{ax}$) = 91.03 °
$A_3$ (W - $C_{eq//}$ - $O_{eq//}$) = 178.5 °
$A_4$ (W - $C_{eq\perp}$ - $O_{eq\perp}$) = 179.5 °
$A_5$ (W – $C_{ax}$ - $O_{ax}$) = 180.0 °
$A_6$ ($H_e$ - $C_e$ - $H_e$) = 116.0 °
$A_6$ ($H_e$ - $C_e$ - $C_e$) = 120.7 °
$D$ ($H_e$ - $C_e$ - $C_e$ - $H_e$) = 160.6 °
$C_e$•$C_e$ : center of $C_e$ - $C_e$ bond




**d. $W(CO)_5(NH_3)$ ($C_s$ ~ $C_{4v}$)**

$r_1$ (W - $C_{eq}$) ~ 2.057 Å
$r_2$ ($C_{eq}$ - $O_{eq}$) ~ 1.145 Å
$r_3$ (W-$C_{ax}$) = 1.993 Å
$r_4$ ($C_{ax}$-$O_{ax}$) = 1.151 Å
$r_5$ (W-N) = 2.374 Å
$r_6$ (N-H) ~ 1.014 Å
$A_1$ ($C_{eq}$ -W-$C_{ax}$) ~ 89.58 °
$A_2$ (W-$C_{eq}$ - $O_{eq}$) ~ 178.6 °
$A_3$ (W-$C_{ax}$ - $O_{ax}$) ~ 180.0 °
$A_4$ (H – N - H) ~ 106.9 °
$D$ (H - N – W – H) ~ 120.0 °

Fig. 1. Optimized geometries of (a) $W(CO)_6$, (b) $W(CO)_5$, (c) $W(CO)_5(C_2H_4)$, and (d) $W(CO)_5(NH_3)$ by B3LYP calculation with BS-B.

2023 $cm^{-1}$ ($A_1$) is about 4:1, also support these assignments. 2) During the $NH_3$ coordination, the equatorial CO absorption band shifts to a lower frequency by ca. 30 $cm^{-1}$ while the axial CO absorption band does not move. 3) During the $C_2H_4$ coordination, the axial CO absorption band shifts to a higher frequency by ca. 30 $cm^{-1}$ while the equatorial CO absorption band is interpreted to shift to a slightly lower frequency. The calculation results suggest that, on $C_2H_4$ coordination, the band of the equatorial carbonyls in $W(CO)_5$ separates into two bands at 2053 $cm^{-1}$ ($CO_{eq//}$) and 2038 $cm^{-1}$ ($CO_{eq\perp}$) with a similar intensity while the axial CO absorption band shifts to a higher frequency by ca. 24 $cm^{-1}$. These characteristic shifts in C–O stretching frequency during the coordination reflect the interaction between the tungsten atom and the coordinating ligand, meaning that B3LYP calculations with BS-A works well for investigating the interaction between a transition-metal atom and a typical small molecule based on the vibrational frequency analysis.[28,29]

The absolute vibrational frequencies could be slightly improved by using the larger basis function set BS-B in the B3LYP calculations: for $W(CO)_6$, $\omega(CO) = 2060\,cm^{-1}$; for $W(CO)_5$, $\omega(CO_{eq}) = 2041\,cm^{-1}$, $\omega(CO_{ax}) = 2009\,cm^{-1}$; for $W(CO)_5(C_2H_4)$, $\omega(CO_{eq//}) = 2044\,cm^{-1}$, $\omega(CO_{eq\perp}) = 2029\,cm^{-1}$, $\omega(CO_{ax}) = 2036\,cm^{-1}$; for $W(CO)_5(NH_3)$, $\omega(CO_{eq}) = 2013\,cm^{-1}$, $\omega(CO_{ax}) = 2006\,cm^{-1}$ (refer to the results using the smaller basis function set BS-A in Table 2). The larger ba-

Table 2. Comparison between the Experimental Vibrational Frequencies ($cm^{-1}$) and the Calculated Ones Using DFT Methods with BS-A for $W(CO)_5L$ (L = None, $C_2H_4$, $NH_3$, and CO)[a)]

| | $W(CO)_5$ | | $W(CO)_5(C_2H_4)$[b)] | | $W(CO)_5(NH_3)$[b)] | | $W(CO)_6$ |
|---|---|---|---|---|---|---|---|
| | $CO_{eq}$ (E) | $CO_{ax}$ ($A_1$) | $CO_{eq}$ ($\approx$E) | $CO_{ax}$ ($\approx A_1$) | $CO_{eq}$ ($\approx$E) | $CO_{ax}$ ($\approx A_1$) | CO ($T_{1u}$) |
| Exp. | 1980[c)] | 1942[c)] | 1968[c)] | 1985[c)] | 1950[c)] | (1942)[c)] | 1997.6[d)] |
| BLYP | 1951 | 1934 | $1942_v$<br>$1958_p$ | 1954 | 1928 | 1932 | 1974 |
| BPW91 | 1976 | 1961 | $1967_v$<br>$1985_p$ | 1982 | 1953 | 1960 | 1996 |
| B3LYP | 2050 | 2023 | $2038_v$<br>$2053_p$ | 2047 | 2023 | 2020 | 2069 |
| B3PW91 | 2067 | 2039 | $2055_v$<br>$2071_p$ | 2066 | 2039 | 2038 | 2084 |

a) The caluculated values are the harmonic frequencies ($\omega_e$) and the experimental ones are the infrared absorption peak positions ($\nu_e$) in the gas phase. $CO_{eq}$ and $CO_{ax}$ mean COs at equatorial and axial sites, respectively (See Fig. 1). b) The symmetry is not $C_{4v}$ strictly. Subscripts v and p in $W(CO)_5(C_2H_4)$ mean the vibrational frequencies of coordinated CO vertical and parallel to the C=C axis of coordinated $C_2H_4$, respectively. c) Ref. 13. d) Ref. 23. A fundamental frequency of 2037.6 $cm^{-1}$ in vapor phase was estimated by applying anharmonic corrections to this observed value (1997.6 $cm^{-1}$).

sis function 6-311+G(3df,2p) is thought to approximate more accurately the molecular orbitals by imposing fewer restrictions on the location of the electrons in space compared to the smaller basis function 6-311G(d,p). The small improvement in the absolute vibrational frequency by introducing the larger basis function 6-311+G(3df,2p) suggests a gentle curvature of the quadratic potential surface in a longer region than the equilibrium nuclear distance, meaning that the coordinated CO has a relatively large anharmonicity constant. In other words, this is consistent with the relatively large anharmonicity constant of about 23 $cm^{-1}$ compared to that of the isolated CO (13.461 $cm^{-1}$).

Figures 3 and 4 show the molecular orbital interactions of a $\sigma$-bond of $NH_3$ and $\pi$- and $\pi^*$-bonds of $C_2H_4$ with $W(CO)_5$, constructed based on the B3LYP calculations with BS-A. Since the occupied $\sigma$-orbital (C5) of $NH_3$ interacts with the vacant $\sigma$-orbital (A43) of $W(CO)_5$, which mixes well with $\pi^*$-orbitals of the four $CO_{eq}$s, the electron population on the $\pi^*$-orbitals of $CO_{eq}$s increases and the equatorial C–O stretching frequency (almost E mode) decreases, while there is little effect on the $CO_{ax}$. The Mulliken atomic charges on $O_{eq}$($\delta_c(O_{eq})$) changes considerably from $-0.144$ in $W(CO)_5$ to $-0.165$ in $W(CO)_5(NH_3)$, while the $\delta_c(O_{ax})$ varies little from $-0.180$ in $W(CO)_5$ to $-0.191$ in $W(CO)_5(NH_3)$. Here, the $\delta_c$ on O atom of CO ligand was used as a measure of $\pi$-back donation because the electron population of $\pi^*$-orbital of CO is considered to be reflected in $\delta_c$ on the terminal O atom without interference from any other bondings. In the case of $W(CO)_5(C_2H_4)$, one component of the *e* set (A41 and A42) mixed with the $\pi^*$-orbitals of two $CO_{eq//}$s and $CO_{ax}$ of $W(CO)_5$ interacts with the $\pi^*$-orbital of $C_2H_4$ (C9), resulting in a decrease in the electron population on the $\pi^*$-orbitals of two $CO_{eq//}$s and $CO_{ax}$. This electron outflow from the $\pi^*$-orbitals of two $CO_{eq//}$ s cancels out the electron inflow from the $\pi$-orbital of $C_2H_4$ through the interaction between C8 and A43 keeping the electron population on the $\pi^*$-orbitals of two $CO_{eq//}$s almost constant. The $\delta_c(CO_{eq//})$ decreases only a little from $-0.144$ for $W(CO)_5$ to $-0.154$ for $W(CO)_5(C_2H_4)$ while that on $CO_{eq\perp}$ decreases from $-0.144$ in $W(CO)_5$ to $-0.157$ for $W(CO)_5(C_2H_4)$. Of course, the frequency of $CO_{ax}$ increases owing to the electron outflow from the $\pi^*$-orbital. The $\delta_c(CO_{ax})$ varies from $-0.180$ in $W(CO)_5$ to $-0.167$ in $W(CO)_5(C_2H_4)$, meaning that there is an increase in $C–O_{ax}$ bond strength. These interactions are the essence of the Dewar–Chatt–Duncanson model for metal–olefin bonding.[30]

The vibrational calculations suggest that the observed broad band in $W(CO)_5(C_2H_4)$ with two peaks at 1968 and 1985 $cm^{-1}$ consists of three C–O stretching modes (Fig. 2): $CO_{eq//}$ ($\omega_{cal}$ = 2053 $cm^{-1}$), $CO_{ax}$ ($\omega_{cal}$ = 2047 $cm^{-1}$), and $CO_{eq\perp}$ ($\omega_{cal}$ = 2038 $cm^{-1}$). The intensity ratio between the three peaks for $CO_{eq//}$:$CO_{ax}$:$CO_{eq\perp}$ was calculated to be 2160:920:1990 ($\approx$2:1:2), which is approximately proportional to the number of the related CO ligands. $C_2H_4$ coordination should weaken particularly the $\pi$-back donation from W atom to the axial CO. The observed fact that $W(CO)_5(NH_3)$ has only one peak with a small shoulder at 1950 $cm^{-1}$ can also be explained by using the calculation results, which predicted that both equatorial COs ($\omega_{cal}$ = 2023 $cm^{-1}$) and axial CO ($\omega_{cal}$ = 2020 $cm^{-1}$) have similar vibrational frequency.

The bond energy ($-\Delta E_c$) and BDE at 298 K calculated using DFT methods with BS-A are summarized in Table 3, together with the previous values. The BPW91 and B3PW91 calculations tend to estimate higher values than the values by BLYP and B3LYP in our system. The experimental BDE (46 kcal $mol^{-1}$) that was reported for $W(CO)_5$–CO[31] is similar to the calculated value of 40.7 kcal $mol^{-1}$ using B3LYP, which is also consistent with the experimental value for the $Cr(CO)_5$–CO bond (37 kcal $mol^{-1}$).[33,34] For the BDEs between W atom and $C_2H_4$ or $NH_3$, there is no reported experimental data. Weitz has summarized the bond enthalpies for a number of small molecules to $M(CO)_5$ (M = Cr, Mo, and W), in which the BDE ($24.7 \pm 2.4$ and $25.7 \pm 1.0$ kcal $mol^{-1}$) was reported for $Cr(CO)_5$–$(C_2H_4)$.[5] These values are also consistent with the DFT calculation results.

The double bond of $C_2H_4$ is lengthened on the coordination process from the calculated value of 1.33 Å for isolated $C_2H_4$

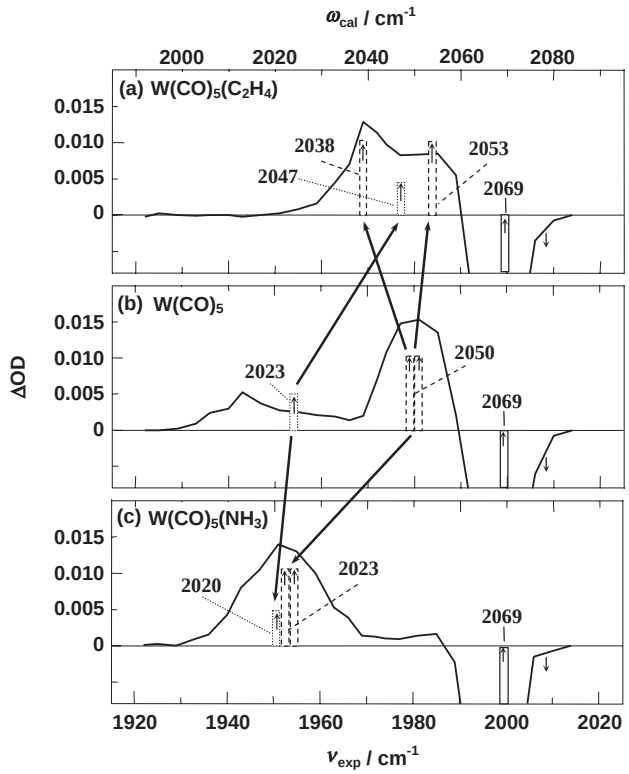



Fig. 2. A comparison of the experimental infrared absorption spectrum in the gas phase and the vibrational frequencies calculated using B3LYP with BS-A for (a) $W(CO)_5(C_2H_4)$, (b) $W(CO)_5$, and (c) $W(CO)_5(NH_3)$. The ordinate scale $\Delta$OD indicates the difference optical density between before and after a pulsed photolysis at 355 nm of a mixture of $W(CO)_6$ (ca. 10 mTorr) and L ($L = C_2H_4$ (0.2 Torr), none, and $NH_3$ (0.05 Torr)) at a total pressure of 6.0 Torr with balance Ar. The difference absorption spectra (solid lines) were recorded at (a) 1.5 μs, (b) 0.8 μs, and (c) 5.0 μs after photolysis. The calculated absorption frequency positions are shown by rectangular bars (dashed line bar, $CO_{eq}$; dotted line bar, $CO_{ax}$) with their relative intensities. The calculated CO stretching frequency of $W(CO)_6$ is indicated by the rectangular bar with solid line.

to 1.38 Å. However, taking into account the experimental C–C bond lengths of 1.337 Å for $C_2H_4$ and 1.536 Å for $C_2H_6$,[22] the tungsten center might be not efficient for activating an olefin's double bond.

## Conclusion

Using B3LYP level calculations with a basis set of LANL2DZ on W atom and 6-311G(d,p) on H, C, N, and O atoms, the characteristic shifts in the vibrational frequency of carbonyls that have been observed experimentally in the successive processes of $W(CO)_6$ ($-$ CO) $\rightarrow$ $W(CO)_5$ ($+$ L) $\rightarrow$ $W(CO)_5L$ ($L = C_2H_4$, $NH_3$, and CO) were reproduced.[13] The absolute frequency values of coordinated CO on tungsten center are consistent with the experimental values if anharmonicity is taken into account. BDEs at 298 K were calculated to be 40.7 kcal mol$^{-1}$ for $W(CO)_5$–CO, 23.1 kcal mol$^{-1}$ for $W(CO)_5$–($C_2H_4$), and 31.9 kcal mol$^{-1}$ for $W(CO)_5$–($NH_3$).

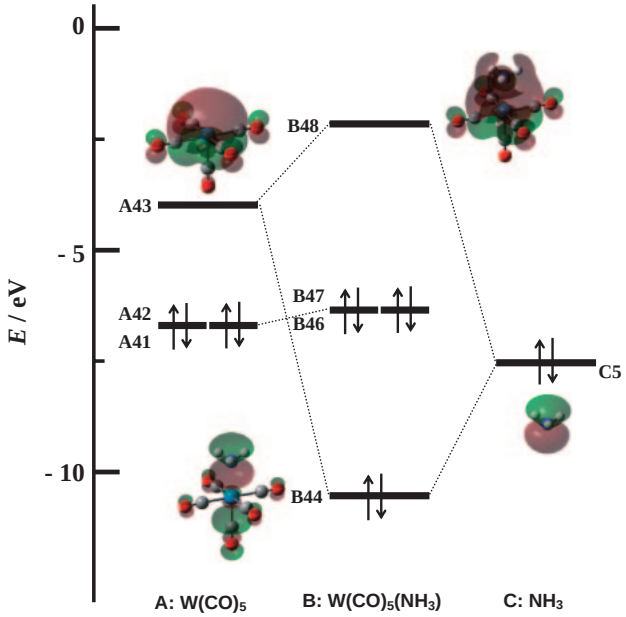



Fig. 3. Schematic representation of the important metal–ligand interactions in $W(CO)_5(NH_3)$ predicted from B3LYP calculations with BS-A.

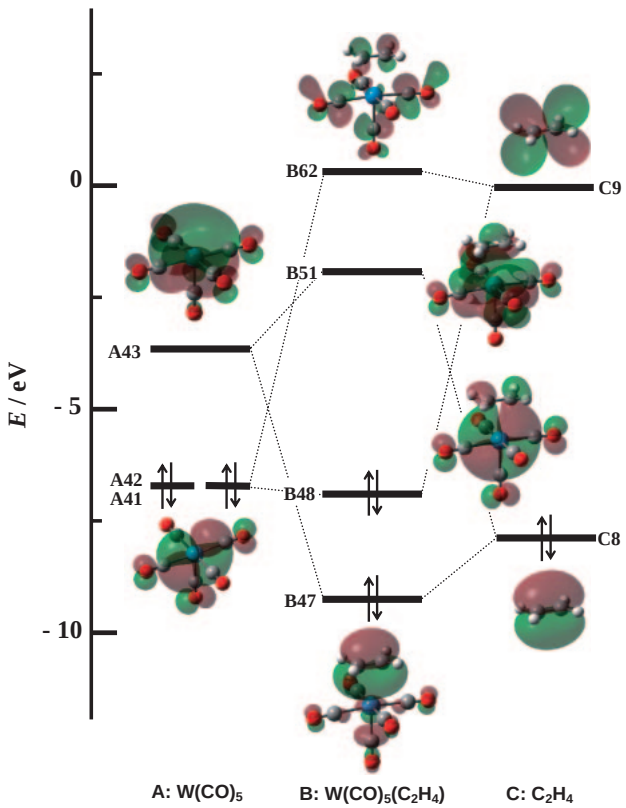



Fig. 4. Schematic representation of the important metal–ligand interactions in $W(CO)_5(C_2H_4)$ predicted from B3LYP calculations with BS-A.

The authors would like to thank Prof. Hisayoshi Kobayashi at Department of Chemistry and Materials Technology, Kyoto Institute of Technology for his fruitful discussion on quantum chemical calculation.

Table 3. Bond Energies ($-\Delta E_c$) and BDEs at 298 K between Tungsten Metal Center and Small Molecules Calculated Using DFT Methods with BS-A

| | $-\Delta E_c$/kcal mol$^{-1}$ | | | BDE/kcal mol$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | $W(CO)_5$–CO | $W(CO)_5$–($C_2H_4$) | $W(CO)_5$–($NH_3$) | $W(CO)_5$–CO | $W(CO)_5$–($C_2H_4$) | $W(CO)_5$–($NH_3$) |
| BLYP | 41.0 | 21.8 | 32.3 | 39.6 | 20.1 | 30.0 |
| BPW91 | 44.8 | 27.4 | 34.0 | 43.3 | 25.7 | 31.6 |
| B3LYP | 42.2 | 24.8 | 33.7 | 40.7 | 23.1 | 31.9 |
| | (42.3)[a] | (24.3)[a] | (29.2)[a] | (40.2)[a] | (22.0)[a] | (27.0)[a] |
| B3PW91 | 45.2 | 29.5 | 35.1 | 43.7 | 27.9 | 33.4 |
| Exp. | | | | 46[b] | | |
| Calcd | 45.9[c] | 27.7[c] | 35.5[c] | | | |
| | | 41.4[d] | | | | |

a) Calculated using B3LYP with BS-B. b) Ref. 31. c) Ref. 32; B3LYP/Quasi-relativistic small-core ECP for W with (441/2111/21) valence basis set and 6-31G(d) all-electron basis sets for the other atoms. d) Ref. 30; CCSD(T)/II//MP2/II(double-$\zeta$ basis plus polarization functions) level calculation.

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