Stability and Bonding Situation of Electron-Deficient Transition-Metal Complexes. Theoretical Study of the CO-Labilizing Effect of Ligands L in $[W(CO)_5L]$ (L = C_2H_2, NCH, N_2, C_2H_4, OH_2, SH_2, NH_3, F^-, Cl^-, OH^-, SH^-) and $[W(CO)_4L]^{2-}$ ($L^{2-} = O_2C_2H_2{}^{2-}$, $S_2C_2H_2{}^{2-}$) and the Structure of the 16-Valence-Electron Complexes $[W(CO)_4L]$ and $[W(CO)_3L]^{2-}$ [†]

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The geometries of the formal 18-valence-electron (VE) complexes $[W(CO)_5L]$ with the π- and σ-bonded monodentate ligands L = N_2, NCH, C_2H_2, C_2H_4, OH_2, SH_2, NH_3, F^-, Cl^-, OH^-, SH^- and those of $[W(CO)_4L]^{2-}$ with the bidentate ligands $L^{2-} = O_2C_2H_2{}^{2-}$, $S_2C_2H_2{}^{2-}$ have been calculated at the B3LYP level of theory. The structures of the 16-VE complexes $[W(CO)_4L]$ and $[W(CO)_3L]^{2-}$ have also been optimized. The bonding situation of the 16- and 18-VE complexes was analyzed with the help of the CDA and NBO partitioning schemes. The goal of the study was to investigate the labilizing influence of the ligand L on the W−CO bonds in the 18-VE complexes and the stabilizing effect on the 16-VE species. Three different structural isomers of the 16-VE species with monodentate ligands have been found as energy minima. All complexes $[W(CO)_4L]$ have either distorted-trigonal-bipyramidal structures with L in the equatorial position (cis1) or square-based-pyramidal forms with L in the basal position (cis2) as the global energy minimum. Square-based-pyramidal structures with L in the apical position (trans) are energetically high-lying minima which have a different electronic state than the cis1 form. The ligand HCCH becomes a 4-electron donor in $[W(CO)_4(HCCH)]$(cis1) via donation from the out-of-plane π-orbital of acetylene, which significantly stabilizes the 16-VE complex. This mechanism is clearly weaker in the π-NCH complex, and it is very weak in the π-bonded dinitrogen and ethylene complexes. The negatively charged ligands F^-, Cl^-, OH^-, and SH^- have also a strong CO-labilizing effect in $[W(CO)_5L]^-$ because the ligands stabilize the formal 16-VE species $[W(CO)_4L]^-$ by electron donation from the p(π) lone-pair donor orbital. The stabilization by the negatively charged ligands is slightly weaker than that of HCCH. The σ-bonded ligands SH_2, NH_3, and N_2 stabilize $[W(CO)_4L]$ very poorly, and the ligands OH_2 and σ-NCH are only weakly stabilizing. The high stability of the 16-VE complexes with bidentate ligands $[W(CO)_3(X_2C_2H_2)]^{2-}$ (X = O, S) cannot solely be explained with strong $W \leftarrow X_2C_2H_2{}^{2-}$ π-donation, which is already operative and even stronger in the 18-VE parent complexes $[W(CO)_4(X_2C_2H_2)]^{2-}$. An important additional reason for the stability of the complexes $[W(CO)_3(X_2C_2H_2)]^{2-}$ lies in the ability of the ligands $X_2C_2H_2{}^{2-}$ to enhance the bond strength of the three W−CO bonds.

1. Introduction

One of the most fundamental concepts in chemistry concerns the explanation of the stability of a molecule in terms of the number of valence electrons of the atoms. Two important rules are frequently used in textbooks to rationalize the electronic structures of compounds of the main-group elements and those of transition metals, respectively. One is the octet rule, which has proven to be a very helpful guide to explain and to predict the stability of most compounds not only of the first octal row of the periodic system but also for molecules of the heavier main-group elements. This is because the main-group elements use the valence s and p orbitals for chemical binding while the d orbitals of the heavier elements are not true valence orbitals.[1] A related role is played for the transition metals by the 18-valence-electron (VE) rule (16-VE rule in the case of planar tetracoordinated compounds), although it is less strictly obeyed than the octet rule for main-group elements. The

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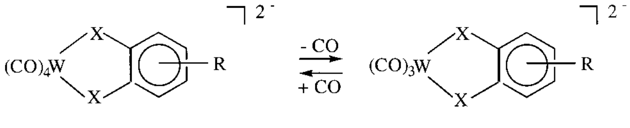
18-VE rule is usually explained with the use of the d, s, and p valence orbitals of the transition metals, which can accommodate 18 electrons. It has recently been suggested that transition metals actually use only the d and s functions as valence orbitals, which means that 18-electron compounds would be hypervalent.[2] This view has been challenged, however, by theoretical studies which support the 18-VE rule.[3]

Numerous experimental and theoretical studies have aimed at investigating the validity of the above electron-counting rules. Many efforts have been directed toward the synthesis and isolation of stable compounds in which atoms do not have a filled valence shell. This is usually achieved by either steric or electronic protection of the electron-deficient atoms in the molecule. In main-group chemistry for example, the synthesis of stable carbenes by Arduengo[4] and others[5] was achieved by placing the electron-deficient carbene carbon atom between two amino groups where the electron pairs of the nitrogen atoms donate electronic charge into the formally empty carbon p(π) AO, which makes the carbene resistant enough against nucleophilic attack that it can become isolated.[6] A purely steric protection by bulky aryl groups is the reason that the recently synthesized diplumbyne compound ArPbPbAr, which has lead atoms with only 6 valence electrons, could be isolated and characterized by X-ray structure analysis.[7,8]

It is not difficult to find examples for early- and late-transition-metal (TM) compounds which violate the 18-VE rule, but generally it holds rather strictly for donor−acceptor complexes of the middle transition metals. Carbonyl complexes of group 6−10 elements are classical examples of 18-electron complexes. Substitution of CO in $[TM(CO)_n]$ by other monodentate ligands L usually leads to stable complexes $[TM(CO)_{n-x}L_x]$ which also obey the 18-VE rule. Examples are $[W(CO)_6]$ and $[W(CO)_{6-x}L_x]$, which are the focus of this work. Very few stable tungsten carbonyl complexes with other ligands are known where tungsten does not have 18 valence electrons. One example apparently is $[W(CO)_3(PCy_3)_2]$, which is formally a 16-VE complex. However, there is evidence for agostic interactions between the C−H bonds of the cyclohexyl groups and the vacant sixth coordination site at W which effectively causes the compound to become a 18-VE complex.[9] The only 16-VE tungsten complex which has been isolated and characterized by X-ray structure analysis is the catecholate complex $[W(CO)_3(O_2C_6H_2R_2)]$ (R_2 = 3,5-di-*tert*-butyl; **O16** in Scheme 1).[10] The related dithiolate complex $[W(CO)_3(S_2C_6H_4)]^{2-}$ (**S16**) had been synthesized earlier.[11a] The compound **S16** is a very stable species[11a,b] but could not by characterized by X-ray structure analysis, unlike the analogous chromium complex $[Cr(CO)_3(S_2C_6H_4)]^{2-}$.[11c]

Scheme 1. Experimentally Known 16-VE Complexes O16 and S16 and Parent 18-VE Complexes O18 and S18



O 18
S 18

X = O, R = 3,5-*t*-butyl
X = S, R = H

O 16
S 16

We want to point out that the 16-VE complexes **S16** and **O16,** under the reaction conditions, are in equilibrium with the 18-VE complexes **S18** and **O18**.[10] This shows that the additional electronic stabilization of the metal by the bidentate ligands in **S16** and **O16** is comparable to the W−CO first bond dissociation energy of the respective 18-VE complexes. It is interesting to note that the 16-VE tungsten complex with the unsubstituted catecholate ligand $[W(CO)_3(O_2C_6H_4)]^{2-}$ could not be isolated, although the CO ligands in $[W(CO)_4(O_2C_6H_4)]^{2-}$ were found to be labile.[10]

The CO-labilizing effect of ligands L in $[TM(CO)_nL]$ has been explained by the presence of π-donor orbitals of L, which stabilize the electron-deficient species $[TM(CO)_{n-1}L]$ via electron donation to the metal.[12,13] This is a very important effect, because substitution of CO by other ligands may become greatly facilitated by ancillary ligands L which have energetically high-lying π-donor ligands. Negatively charged ligands are particularly helpful for this purpose, because they have very high-lying occupied orbitals. Experimental studies have shown that the negatively charged complexes $[W(CO)_5L]^-$ with $L^- = F^-, Cl^-, OR^-$ easily lose CO and that the 16-VE species $[W(CO)_4L]^-$ either form oligomers or bind other ligands.[10,14] However, also neutral ligands L may have significant π-donor strength which labilizes CO ligands in mixed complexes. Experimental[15] and theoretical[16] studies have shown that alkyne ligands facili-

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tate CO substitution reactions in the carbonyl alkyne complexes [TM(CO)$_4$(RCCR)] (TM = Fe, Ru, Os) because the alkyne ligand becomes effectively a 4-electron donor in the formal 16-VE complex [TM(CO)$_3$(RCCR)]. The alkyne ligand plays also a pivotal role in the initial CO substition of the Dötz reaction.[17]

Donor−acceptor interactions between metals TM and ligands L are usually discussed in terms of TM←L σ-donation and TM→L π-back-donation.[18] The above reasoning indicates that the TM←L π-donation may become important for substitution reactions where L is formally a spectator ligand, although the π-donation attributes a more important role to the ligand than just being a spectator. Many theoretical studies have been devoted to understanding the nature of the TM−L interactions.[18] There is no systematic study known to us where the influence of a wide range of neutral and negatively charged ligands on the TM−CO bond dissociation energy in [TM(CO)$_n$L] has been studied. A work by Decker and Klobukowski[17] focused on the effect of acetylene as a ligand. Another theoretical study by van Wüllen investigated the effect of various ligands L on the TM−CO$_{trans}$ bond in [TM(CO)$_5$L] with TM = Cr, Mo, W.[19] It will be shown below that the ligand L weakens the cis carbonyl bond more than the trans W−CO bond.

A theoretical study at the EHT level of the possible structures of d^6 complexes [TML$_5$] using iridium model compounds has been reported by Eisenstein and coworkers.[20a] The same group later reported an ab initio study of the structures of negatively charged 16-VE iridium complexes.[20b] The most relevant previous work which is related to our investigation is a paper by Macgregor and MacQueen.[12a] These workers calculated with DFT methods the structures of the complexes [TM(CO)$_5$L]$^-$ with TM = Cr, Mo, W and L = NH$_2$, OH, halide, H, methyl. They found that the π-destabilization of the 18-VE parent complexes by the ligands L is equally significant for CO(cis) labilization as the stabilization of the 16-VE species [TM(CO)$_4$L]$^-$.[12a] The work was restricted, however, to complexes with negatively charged ligands L.

In this work we have theoretically investigated the electronic stabilization of electron-deficient 16-VE complexes by neutral and charged σ- and π-bonded ligands. We report quantum-chemical calculations using gradient-corrected density functional theory (DFT) of the structures and bonding situation of the 18-VE complexes [W(CO)$_5$L] and the 16-VE species [W(CO)$_4$L] with the monodentate ligands L = N$_2$, NCH, C$_2$H$_2$, C$_2$H$_4$, OH$_2$, SH$_2$, NH$_3$, F$^-$, Cl$^-$, OH$^-$, SH$^-$. We have also investigated the 18- and 16-VE complexes with bidentate ligands [W(CO)$_4$L]$^{2-}$ and [W(CO)$_3$L]$^{2-}$ (L^{2-} = O$_2$C$_2$H$_2$$^{2-}$, S$_2C_2H_2$$^{2-}$). We have analyzed the tungsten−ligand interactions with the help of charge decomposition analysis (CDA)[21a] and the NBO method[21b] in order to understand more deeply the electronic factors which influence the W−CO bond strength of cis and trans carbonyls by adjacent ligands.

2. Methods

The calculations have been performed at the gradient-corected DFT level using the Becke−Lee−Yang−Parr three-parameter fit (B3LYP) of the exchange and correlation functionals.[22] The atomic basis sets which were used in the calculations comprise a quasi-relativistic small-core ECP[23] for tungsten with a (441/2111/21) valence basis set and 6-31G(d) all-electron basis sets for the other atoms.[24] This combination is our standard basis set II,[25] which was augmented by a set of diffuse functions at F, O, S, and Cl for the calculations of the negatively charged species. The character of the stationary points on the potential energy surface was examined by vibrational frequency analysis. The calculated zero-point vibrational energies (ZPEs) are unscaled. The calculations have been carried out with the program packages Gaussian 94 and Gaussian98.[26] The CDA analysis was performed with the program CDA 2.1.[27]

3. Results and Discussion

The presentation of the results is organized as follows. Figure 1 gives an overview of the structures which have been found as minima on the potential energy surface. The calculated W−CO bond dissociation energies (BDEs) with respect to [W(CO)$_5$L] are also given. Figure 1a displays the molecules [W(CO)$_5$L] and [W(CO)$_4$L], where L is bonded through a π-orbital of the free ligands C$_2$H$_2$, C$_2$H$_4$, N$_2$, and HCN. Please note that this orbital has σ-symmetry in the complex. Three different isomers have been found for the 16-VE species [W(CO)$_4$L]. The notation for the three isomeric forms refers to the CO ligand which has been removed from [W(CO)$_5$L] in order to yield a starting structure for the geometry optimization. [W(CO)$_4$L](trans) means that the CO(trans) ligand of the pentacarbonyl has dissociated. Two different cis forms of [W(CO)$_4$L] which have a distorted-trigonal-bipyramidal geometry (cis1) or square-pyramidal geometry (cis2) were found as energy minima when L = C$_2$H$_2$, C$_2$H$_4$, π-NCH, while only the cis1 form was found when L = π-N$_2$. The energy values below the

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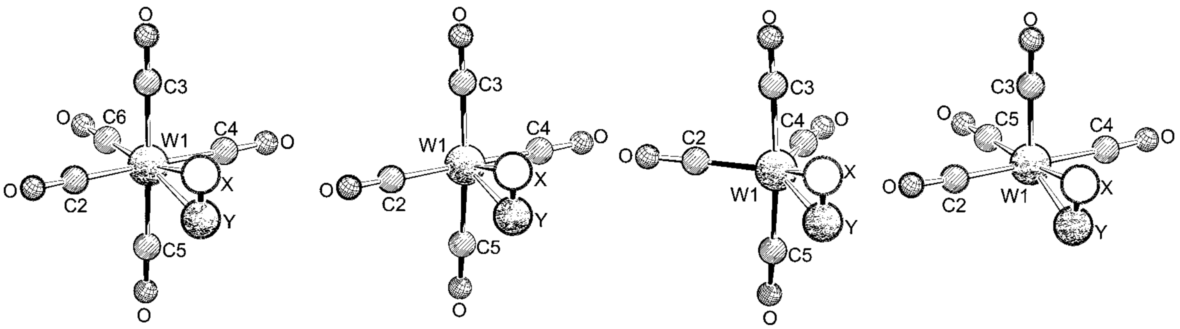
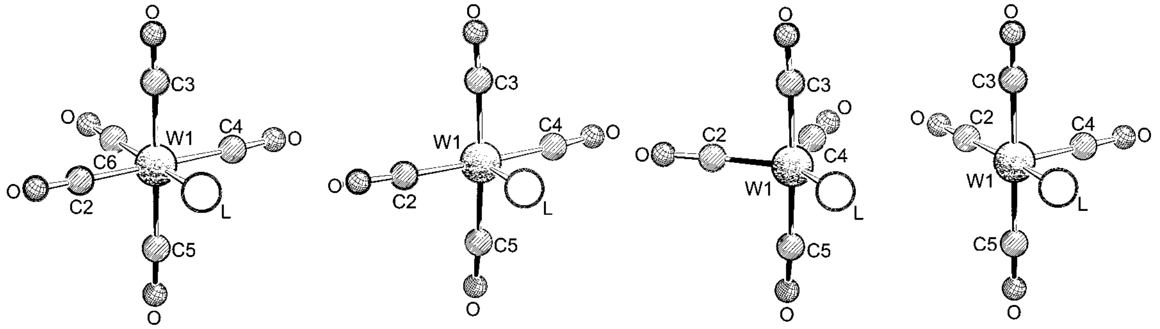


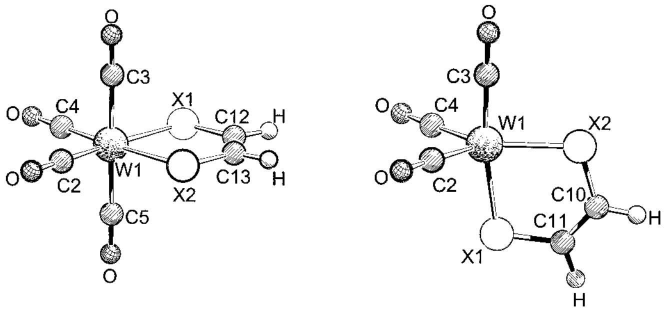
(a)

	W(CO)$_5$L	W(CO)$_4$L trans $D_e(D_0)$	W(CO)$_4$L cis1 $D_e(D_0)$	W(CO)$_4$L cis2 $D_e(D_0)$
XY:	C_2H_2	56.9 (54.6)	19.2 (18.1)	44.5 (42.1)
	NCH	58.5 (56.4)	30.1 (28.7)	46.9 (44.7) X=N 38.3 (36.3) X=C
	N_2	64.5 (62.2)	41.9 (40.1)	
	C_2H_4	55.3 (53.2)	39.8 (37.3)	44.9 (42.5)



(b)

	W(CO)$_5$L	W(CO)$_4$L trans $D_e(D_0)$	W(CO)$_4$L cis1 $D_e(D_0)$	W(CO)$_4$L cis2 $D_e(D_0)$
L:	CO	45.9 (43.8)		
	N_2	55.9 (53.7)		44.9 (42.8)
	NCH	51.9 (49.2)		37.4 (35.0)
	OH_2	66.7 (64.5)	40.2 (38.2)	
	SH_2	60.9 (58.8)		44.1 (42.2)
	NH_3			43.7 (41.5)[a]
	F^-		25.4 (23.7)	
	Cl^-	72.6 (70.2)	31.5 (29.6)	
	OH^-		20.2 (19.2)	
	SH^-		26.9 (25.6)	



(c)

	W(CO)$_4$L	W(CO)$_3$L $D_e(D_0)$
L:	$O_2C_2H_2^{2-}$	22.3 (20.6)
	$S_2C_2H_2^{2-}$	24.8 (23.2)

Figure 1. Overview of structural isomers which have been found as energy minima for the 18- and 16-VE complexes. Calculated W−CO bond dissociation energies D_e and D_0 (kcal/mol) of the 18-VE complexes yielding the respective 16-VE species: (a) π-bonded ligands L; (b) σ-bonded monodentate ligands L; (c) σ-bonded bidentate ligands L. For W(CO)$_4$L cis 2: [a] The structure is intermediate between cis1 and cis2 (see text).

structures give the W−CO BDE with respect to $[W(CO)_5L]$.

Figure 1b shows the energy minima of the molecules $[W(CO)_5L]$ and $[W(CO)_4L]$, where L is bonded through a σ-lone-pair orbital of the free ligands CO, N_2, NCH, OH_2, SH_2, NH_3, F^-, Cl^-, OH^-, and SH^-. Energy minima with a $[W(CO)_4L]$(trans) geometry were found for L = CO, σ-N_2, σ-NCH, OH_2, SH_2, Cl^-. Energetically lower lying isomers with dist-TBP geometries $[W(CO)_4L]$(cis1) are predicted for L = OH_2, Cl^-. The latter form is the only energy minimum structure for L = F^-, OH^-, SH^-. Isomers with square-pyramidal geometry $[W(CO)_4L]$(cis2) which have the ligand L in the basal position have been found as energetically lower lying forms than $[W(CO)_4L]$(trans) when L = σ-N_2, σ-NCH, SH_2. The only energy minimum structure of $[W(CO)_4(NH_3)]$ which was found on the potential energy surface is intermediate between a trigonal-bipyramidal (cis1) form and the cis2 square-planar form. This will be discussed below. Figure 1c shows the energy minima of $[W(CO)_4L]$ and $[W(CO)_3L]$ and the W−CO BDEs for L = $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$.

Table 1 gives calculated energies which are important for the discussion and which may be helpful for other studies. Note that the calculated dissociation energies D_e give directly the relative energies of the σ- and π-bonded isomers of $[W(CO)_5(NCH)]$ and $[W(CO)_5(N_2)]$.

Table 1. Calculated Reaction Energies of the $W(CO)_5L$ and $W(CO)_4L$ Complexes According to the Isostructural Reactions $W(CO)_6 + L = W(CO)_5L + CO$ (ΔE_1) and $W(CO)_5 + L = W(CO)_4L + CO$ (ΔE_2)[a]

L	bond type	ΔE_1	ΔE_2	$\Delta E_2 - \Delta E_1$	D_e(W−CO)	ΔH_f(W-(CO)$_5$L)	D_e(W−L)
C_2H_2	π	13.0	−13.7	−26.7	19.2	−118.1	33.0
NCH	π	28.8	13.0	−15.8	30.1	−126.3	17.1
N_2	π	38.3	34.3	−4.0	41.9	−147.3	7.6
C_2H_4	π	18.3	12.2	−6.1	39.8	−154.9	27.7
CO	σ				45.9	−212.0[b]	45.9
NCH	σ	21.2	12.7	−8.5	37.4	−133.9	24.7
N_2	σ	21.5	20.5	−1.0	44.9	−164.1	24.5
OH_2	σ	20.4	14.7	−5.7	40.2	−223.0	25.6
NH_3	σ	10.5	8.3	−2.2	43.7	−186.1	35.5
SH_2	σ	23.4	21.6	−1.8	44.1	−167.1	22.6
F^-	σ	−30.6	−51.2	−20.6	25.4	−465.2	76.6
Cl^-	σ	−9.1	−23.6	−14.5	31.5	−421.7	55.1
OH^-	σ	−36.1	−61.8	−25.7	20.2	−358.7	82.1
SH^-	σ	−17.5	−36.6	−19.1	26.9	−284.1	63.5
$O_2C_2H_2^{2-}$	σ	−65.0	−88.6	−23.6	22.3	*c*	157.1
$S_2C_2H_2^{2-}$	σ	−31.7	−52.1	−20.4	24.8	*c*	123.8

[a] The isostructural reactions for the bidentate ligands $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$ are $W(CO)_6 + L = W(CO)_4L + 2CO$ (ΔE_1; L = $X_2C_2H_2^{2-}$) and $W(CO)_5 + L = W(CO)_3L + 2CO$ (ΔE_2; L = $X_2C_2H_2^{2-}$). Theoretically predicted W−CO and W−L bond dissociation energies D_e and heats of formation ΔH_f of the $W(CO)_5L$ complexes are given. All values are in kcal/mol. [b] Experimental value.[29] [c] Not calculated because the heat of formation of L is not known.

Very important information concerning the stabilization of the 16-VE compounds is given by the calculated energies of the isostructural[28] reactions

$$W(CO)_6 + L \rightarrow W(CO)_5L + CO \quad \Delta E_1$$

$$W(CO)_5 + L \rightarrow W(CO)_4L + CO \quad \Delta E_2$$

The reactions for the bidentate ligands L = $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$ are

$$W(CO)_6 + L \rightarrow W(CO)_4L + 2CO \qquad \Delta E_1\ (L = X_2C_2H_2^{2-})$$

$$W(CO)_5 + L \rightarrow W(CO)_3L + 2CO \qquad \Delta E_2\ (L = X_2C_2H_2^{2-})$$

The reaction energies give the differences between the W−L and W−CO BDEs in the 18-VE complexes (ΔE_1) and in the 16-VE complexes (ΔE_2). The calculated energy difference $\Delta E_2 - \Delta E_1$ indicates the extra stabilization of the 16-VE complexes which is provided by the ligand L with respect to CO. Table 1 gives also the calculated $(CO)_5W$−L BDEs and the theoretically predicted heats of formation $\Delta H_f°$ of the 18-VE complexes $[W(CO)_5L]$.[29]

3.1. Complexes with π-Bonded Ligands C_2H_2, NCH, N_2, C_2H_4. Figure 2 shows the theoretically predicted geometries of the complexes with π-bonded ligands and the most important geometrical variables. The relative energies of the $[W(CO)_4L]$ isomers are also given.

We begin the discussion of the results with the acetylene complexes $[W(CO)_5(HCCH)]$ and $[W(CO)_4(HCCH)]$, because the latter 16-VE compound has all three isomeric forms, trans, cis1, and cis2, as energy minima. The complexes with L = HCCH are therefore good examples to discuss the most relevant bonding properties of the molecules.

The dissociation of the trans-CO ligand of $[W(CO)_5(HCCH)]$ yields the energetically highest lying tetracarbonyl acetylene species, $[W(CO)_4(HCCH)]$(trans). Figure 1a shows that the dissociation of CO_{trans} from $[W(CO)_5(HCCH)]$ costs D_e = 56.9 kcal/mol. The large BDE is in agreement with the short W−CO_{trans} bond length of $[W(CO)_5(HCCH)]$ (2.028 Å). Breaking one of the W−CO_{cis1} bonds of $[W(CO)_5(HCCH)]$ which are orthogonal to the W−HCCH plane is energetically much easier. Figure 1a shows that the BDE of $[W(CO)_5(HCCH)]$, yielding $[W(CO)_4(HCCH)]$(cis1), is only D_e = 19.2 kcal/mol. The dissociation of CO_{cis} leads to a change in the structure of the remaining $[W(CO)_4(HCCH)]$ fragment toward the distorted-trigonal-bipyramidal geometry of $[W(CO)_4(HCCH)]$(cis1), which conceals where the missing CO ligands came from. It is surprising at first sight that $[W(CO)_4(HCCH)]$(cis1) is 37.7 kcal/mol lower in energy than $[W(CO)_4(HCCH)]$(trans) and that both structures are minima on the potential energy surface. Figure 2 shows that $[W(CO)_4(HCCH)]$(cis1) has significantly shorter W−C(acetylene) and W−CO_{cis1} bond distances than $[W(CO)_4(HCCH)]$(trans) and that the C2−W−C4 bond angle of the former isomer is more acute.

We searched for a transition state between the two isomers $[W(CO)_4(HCCH)]$(cis1) and $[W(CO)_4(HCCH)]$(trans). To this end we calculated the energy of the two

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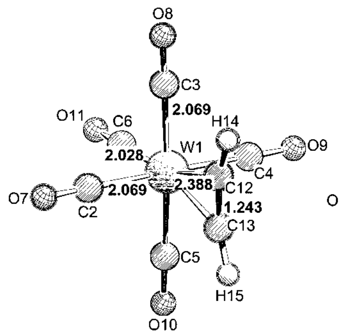
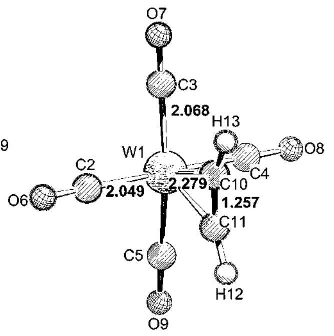
[28] Dapprich, S.; Pidun, U.; Ehlers, A. W.; Frenking, G. *Chem. Phys. Lett.* **1995**, *242*, 521.

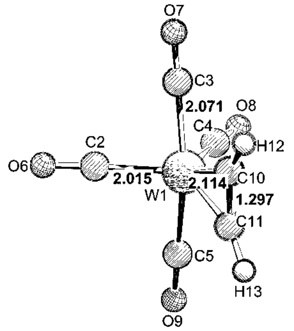
[29] The heats of formation of the tungsten complexes have been calculated via eq 1 using the experimental $\Delta H_f°$ values of $W(CO)_6$ (−212.0 kcal/mol), CO (−26.4 kcal/mol), HCN (32.3 kcal/mol), C_2H_2 (54.5 kcal/mol), C_2H_4 (12.5 kcal/mol), H_2O (−57.8 kcal/mol), H_2S (−4.9 kcal/mol), NH_3 (−11.0 kcal/mol), F^- (−249.0 kcal/mol), Cl^- (−227.0 kcal/mol), OH^- (−137.0 kcal/mol), and SH^- (−81.0 kcal/mol). The values were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*.



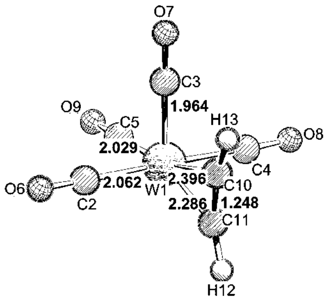
(a) [W(CO)$_5$(HCCH)]
∠C2–W–C4: 183.2
∠C3–W–C5: 173.7
∠C–C–H: 157.3



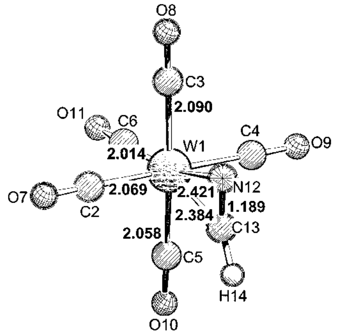
(b) [W(CO)$_4$(HCCH)](trans)
∠C2–W–C4: 182.7
∠C3–W–C5: 169.8
∠C–C–H: 152.0
E_{rel} = 0.0 kcal/mol



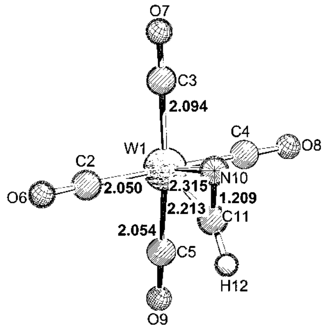
(c) [W(CO)$_4$(HCCH)](cis1)
∠C2–W–C4: 99.8
∠C3–W–C5: 163.7
∠C–C–H: 143.1
E_{rel} = -37.7 kcal/mol



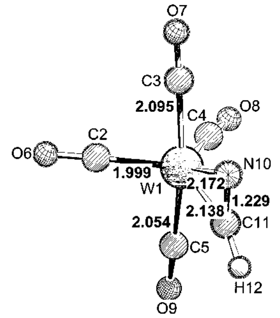
(d) [W(CO)$_4$(HCCH)](cis2)
∠C2–W–C4: 181.8
∠C3–W–C5: 90.8
∠C–C–H12: 151.2 (below)
∠C–C–H13: 161.8 (top)
E_{rel} = -12.4 kcal/mol



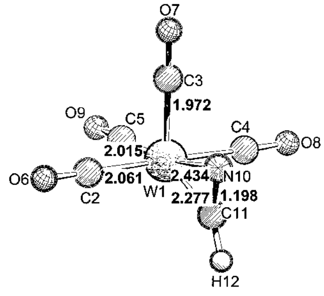
(e) [W(CO)$_5$(π-NCH)]
∠C2–W–C4: 182.5
∠C3–W–C5: 174.9
∠N–C–H: 150.7



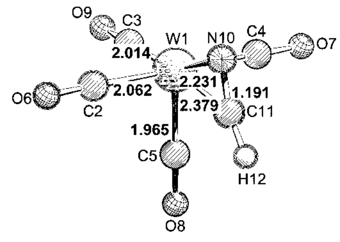
(f) [W(CO)$_4$(π-NCH)](trans)
∠C2–W–C4: 181.4
∠C3–W–C5: 170.7
∠N–C–H: 141.1
E_{rel} = 0.0 kcal/mol



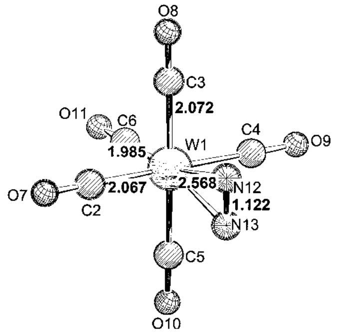
(g) [W(CO)$_4$(π-NCH)](cis1)
∠C2–W–C4: 95.3
∠C3–W–C5: 166.3
∠N–C–H: 138.4
E_{rel} = -28.4 kcal/mol



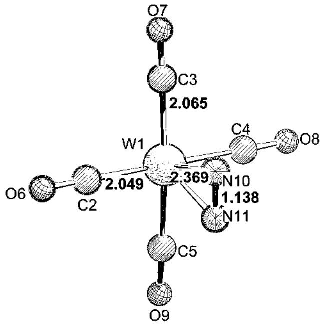
(h) [W(CO)$_4$(π-NCH)](cis2a)
∠C2–W–C4: 181.7
∠C3–W–C5: 92.3
∠N–C–H: 144.8
E_{rel} = -11.6 kcal/mol



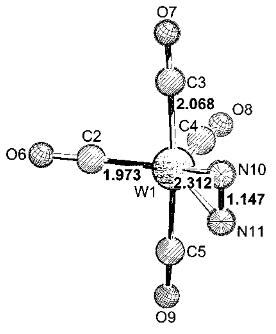
(i) [W(CO)$_4$(π-NCH)](cis2b)
∠C2–W–C4: 179.8
∠C3–W–C5: 89.4
∠N–C–H: 153.8
E_{rel} = -20.2 kcal/mol



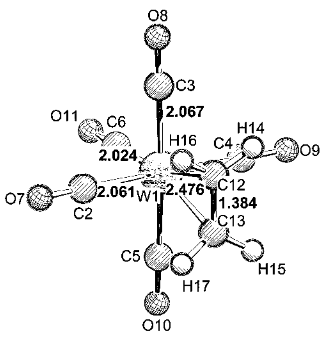
(j) [W(CO)$_5$(π-N$_2$)]
∠C2–W–C4: 181.6
∠C3–W–C5: 177.3



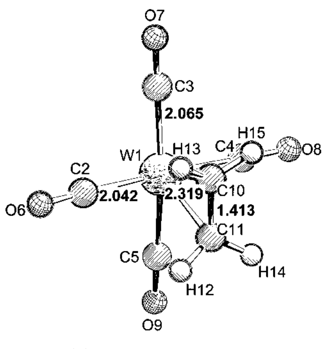
(k) [W(CO)$_4$(π-N$_2$)](trans)
∠C2–W–C4: 180.7
∠C3–W–C5: 172.9
E_{rel} = 0.0 kcal/mol



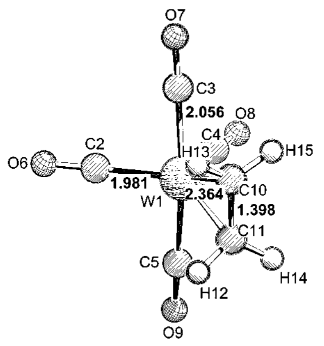
(l) [W(CO)$_4$(π-N$_2$)](cis1)
∠C2–W–C4: 90.9
∠C3–W–C5: 170.9
E_{rel} = -22.6 kcal/mol



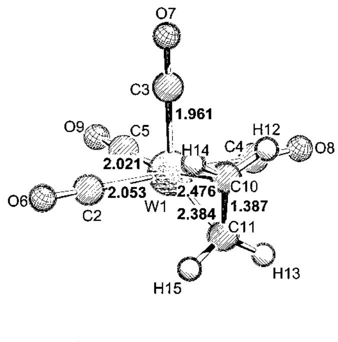
(m) [W(CO)$_5$(C$_2$H$_4$)]
∠C2–W–C4: 183.3
∠C3–W–C5: 174.6



(n) [W(CO)$_4$(C$_2$H$_4$)](trans)
∠C2–W–C4: 184.2
∠C3–W–C5: 170.1
E_{rel} = 0.0 kcal/mol

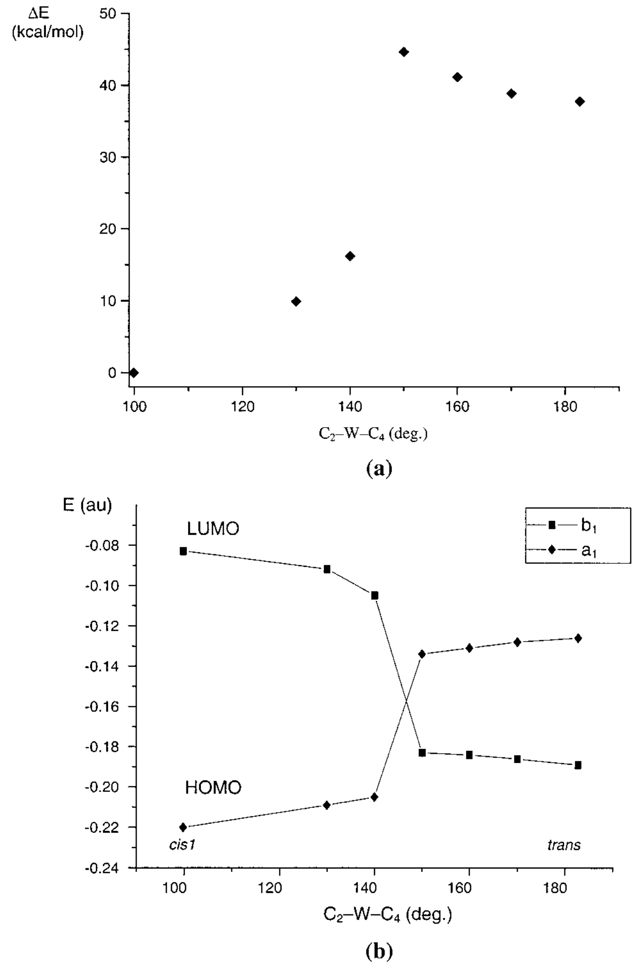


(o) [W(CO)$_4$(C$_2$H$_4$)](cis1)
∠C2–W–C4: 92.4
∠C3–W–C5: 168.8
E_{rel} = -15.5 kcal/mol



(p) [W(CO)$_4$(C$_2$H$_4$)](cis2)
∠C2–W–C4: 181.9
∠C3–W–C5: 90.0
E_{rel} = -10.4 kcal/mol

Figure 2. Optimized geometries (B3LYP/II) of the complexes [W(CO)$_5$L] and [W(CO)$_4$L] with π-bonded ligands L. Bond distances are given in Å, bond angles in deg, and relative energies of the [W(CO)$_4$L] isomers in kcal/mol.



(a)

(b)

Figure 3. (a) Relative energies of the [W(CO)$_4$(HCCH)] isomers cis1 (left side) and trans (right side) as a function of the C2−W−C4 bond angle. (b) Relative energies of the HOMO and LUMO eigenvalues of [W(CO)$_4$(HCCH)] isomers cis1 (left side) and trans (right side) as a function of the C2−W−C4 bond angle.

molecules as a function of the C2−W−C4 angle. Figure 3a shows the results. The energy of [W(CO)$_4$(HCCH)](cis1) increases when the angle becomes larger, and the energy of [W(CO)$_4$(HCCH)](trans) increases when the angle becomes smaller, but a transition state for interconversion of the two structures could not be located. An explanation for the situation was found when we analyzed the electronic structure of the two isomeric forms. Figure 3b shows that the HOMO and LUMO of the two molecules have different symmetries. [W(CO)$_4$(HCCH)](cis1) has a HOMO with a$_1$ symmetry and a LUMO with b$_1$ symmetry. The opposite situation was found for [W(CO)$_4$(HCCH)](trans), where the occupation of the a$_1$ and b$_1$ frontier orbitals is switched. In the latter isomer the b$_1$ orbital is the HOMO and the a$_1$ orbital is the LUMO (Figure 3b). Before we give the explanation of the structures and energies of [W(CO)$_4$(HCCH)](trans) and [W(CO)$_4$(HCCH)](cis1) in terms of the electronic structure of the two isomers, we want to include the third isomer [W(CO)$_4$(HCCH)](cis2) in the discussion. Figure 2d shows that the latter form has a square-pyramidal form, like [W(CO)$_4$(HCCH)](trans), but the acetylene ligand is now in a basal position. The metal−ligand bond lengths of [W(CO)$_4$(HCCH)](cis2) are quite similar to those of [W(CO)$_5$(HCCH)], except that the W−CO distance of the apical ligand is significantly shorter (1.964 Å) than in the parent compound (2.069 Å). The structures and energies of the three [W(CO)$_4$(HCCH)] isomers are easily understood when the most important orbital interactions are considered.

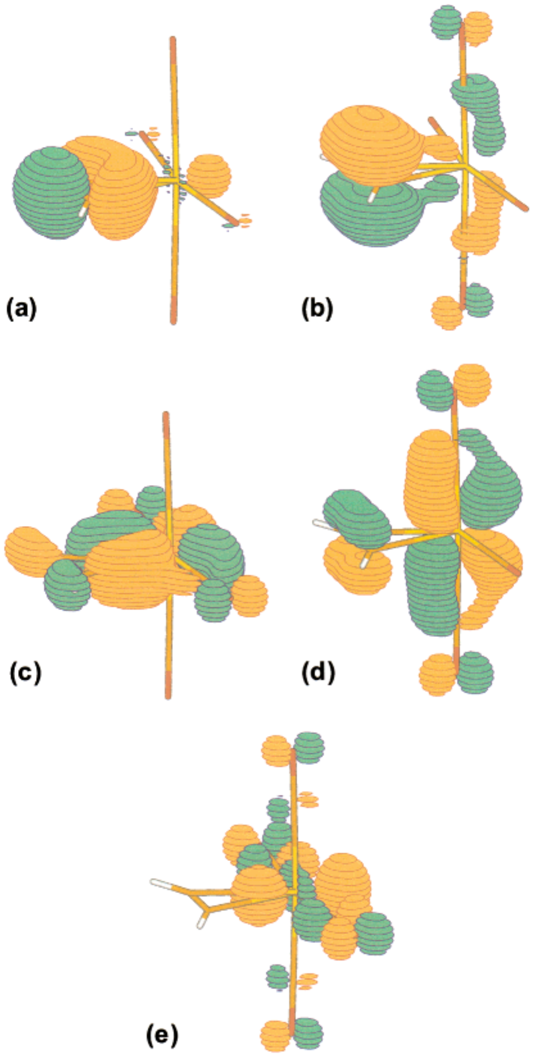


Figure 4. Contour line diagrams of important orbitals of [W(CO)$_4$(HCCH)](trans): (a) HOMO-4; (b) HOMO-3; (c) HOMO-2; (d) HOMO; (e) LUMO. See text for a discussion.

Parts a−d of Figure 4 show the contour line diagrams of those occupied orbitals of [W(CO)$_4$(HCCH)](trans) which contribute to the W−acetylene interactions. The shapes of the orbitals nicely illustrate the model of synergistic donor−acceptor interactions. The HOMO-4 orbital (Figure 4a) shows the W←HCCH donation of the in-plane π-MO of the acetylene ligand. The higher lying HOMO-3 (Figure 4b) shows the contribution of the out-of-plane π-MO of the acetylene ligand to the W←HCCH donation. HOMO-2 (Figure 4c) shows the W→HCCH back-donation into the in-plane π*MO of the ligand. HOMO-1 does not have coefficients at the acetylene ligand. Therefore, it is not shown here. The crucial information comes from the HOMO. Figure 4d shows that the HOMO is the *antibonding* combination of the out-of-plane π-MO of acetylene with the tungsten orbitals. This means that the bonding contribution of HOMO-3 is essentially compensated by the antibonding nature of the HOMO, which leaves acetylene as a two-electron donor via HOMO-4. The LUMO of [W(CO)$_4$-

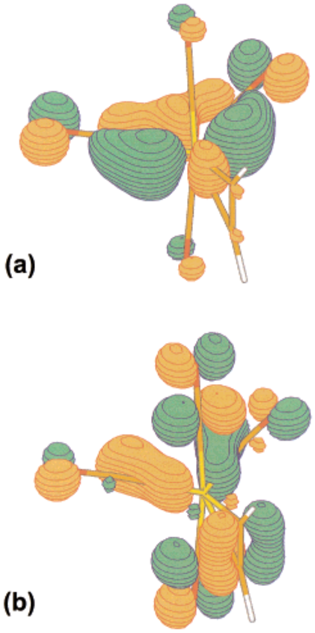


Figure 5. Contour line diagrams of the HOMO and LUMO of [W(CO)$_4$(HCCH)](cis1): (a) HOMO; (b) LUMO. See text for a discussion.

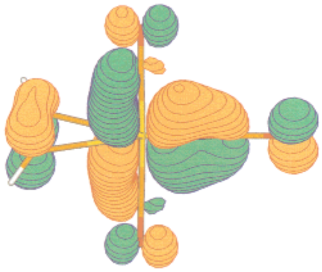


Figure 6. Contour line diagram of the HOMO of [W(CO)$_4$(HCCH)](cis2). See text for a discussion.

(HCCH)](trans) has no coefficients at the acetylene ligand atoms. It is shown in Figure 4e, because it will be relevant for the discussion of the bonding situation in [W(CO)$_4$(HCCH)](cis1).

Parts a and b of Figure 5 show the frontier orbitals of [W(CO)$_4$(HCCH)](cis1). A comparison with Figure 4d,e demonstrates that indeed the HOMO and LUMO of [W(CO)$_4$(HCCH)](cis1) and [W(CO)$_4$(HCCH)](trans) have switched. The W–HCCH antibonding combination of the out-of-plane π^* orbital of acetylene with the AOs of tungsten is unoccupied in [W(CO)$_4$(HCCH)](cis1), and the HOMO of the latter corresponds to the LUMO of [W(CO)$_4$(HCCH)](trans). This means that the acetylene ligand in [W(CO)$_4$(HCCH)](cis1) becomes a four-electron donor, and it explains why the W–C(acetylene) bond lengths in the latter compound are significantly shorter than in the [W(CO)$_4$(HCCH)](trans) isomer. The shorter W–C(acetylene) distances in [W(CO)$_4$(HCCH)](trans) with respect to [W(CO)$_5$(HCCH)] come from the fact that there is no CO ligand trans to acetylene which competes for the back-donation from the metal. The bonding situation in [W(CO)$_4$(HCCH)](cis2) is related to that in [W(CO)$_4$(HCCH)](trans). Figure 6 shows that the HOMO of [W(CO)$_4$(HCCH)](cis2) has a shape similar to that of the HOMO of [W(CO)$_4$(HCCH)](trans) (Figure 4d); i.e., it has W–acetylene antibonding character.

Table 2. CDA and NBO Results of the W(CO)$_5$L and W(CO)$_4$L Complexes with π-Bonded Ligands L: (CO)$_n$W←L Donation (*d*), (CO)$_n$W→L Back-Donation (*b*), NBO Partial Charges (*q*), and Wiberg Bond Indices (*P*(W–L))

L	complex	*d*	*b*	*q*(W)	*q*(L)	*P*(W–L)
C_2H_2	W(CO)$_5$L	0.544	0.223	−0.623	0.0	0.31
	W(CO)$_4$L(trans)	0.547	0.324	−0.142	−0.086	0.55
	W(CO)$_4$L(cis1)	0.704	0.491	−0.067	−0.212	0.64
	W(CO)$_4$L(cis2)	0.540	0.226	−0.186	−0.058	0.42/0.31[a]
NCH	W(CO)$_5$L	0.441	0.184	−0.601	−0.030	0.29/0.31[b]
	W(CO)$_4$L(trans)	0.425	0.282	−0.070	−0.159	0.55/0.53[b]
	W(CO)$_4$L(cis1)	0.495	0.364	−0.034	−0.255	0.54/0.57[b]
	W(CO)$_4$L(cis2a)	0.425	0.191	−0.193	−0.115	0.41/0.32[b]
	W(CO)$_4$L(cis2b)	0.450	0.183	−0.153	−0.065	0.30/0.44[b]
N_2	W(CO)$_5$L	0.283	0.105	−0.624	0.018	0.21
	W(CO)$_4$L(trans)	0.316	0.186	−0.085	−0.038	0.40
	W(CO)$_5$L(cis1)	0.334	0.218	−0.116	−0.064	0.38
C_2H_4	W(CO)$_5$L	0.500	0.175	−0.611	0.024	0.28
	W(CO)$_4$L(trans)	0.532	0.296	−0.112	−0.078	0.54
	W(CO)$_4$L(cis1)	0.539	0.278	−0.087	−0.126	0.35
	W(CO)$_4$L(cis2)	0.493	0.173	−0.192	−0.027	0.27/0.36[a]

[a] The higher value refers to the shorter W–C bond. [b] The first value refers to the W–C bond, and the second value refers to the W–N bond.

The interpretation of the W–HCCH interactions in the [W(CO)$_4$(HCCH)] isomers is quantitatively supported by the results of the CDA and NBO partitioning schemes which are given in Table 2. The CDA suggests that the W←HCCH donation in [W(CO)$_4$(HCCH)](trans) (0.547 e) is nearly the same as in the parent compound [W(CO)$_5$(HCCH)] (0.544 e), but the W→HCCH π-back-donation in the former complex (0.324 e) is stronger than in the latter (0.223 e), because the trans-CO ligand does not compete for π-back-donation. Significantly larger W←HCCH donation (0.704 e) and W→HCCH back-donation (0.491 e) in [W(CO)$_4$(HCCH)](cis1) are suggested by the CDA results. The stronger (formal) four-electron donation of acetylene also enhances the W→HCCH π-back-donation. Please note that the NBO partial charges suggest that there is an electronic charge flow from the metal fragment to the acetylene ligand in [W(CO)$_4$(HCCH)](cis1). The acetylene ligand carries a significant negative charge of −0.21 e in [W(CO)$_4$(HCCH)](cis1), while it is nearly neutral in the other acetylene complexes (Table 2). The W–C(acetylene) bond order in [W(CO)$_4$(HCCH)](cis1) is also the highest among the calculated species.

Table 1 shows that the acetylene ligand has the strongest labilization effect on the W–CO bonds. The calculated W–CO$_{\mathrm{cis1}}$ bond energy of [W(CO)$_5$(HCCH)], $D_e = 19.2$ kcal/mol, is the lowest value of all [W(CO)$_5$L] complexes, which is even lower than the W–CO bond energies of the negatively charged molecules. The strong labilization comes from the significantly different W–HCCH bond strengths in [W(CO)$_5$(HCCH)] and [W(CO)$_4$(HCCH)]. The calculated reaction energies ΔE_1 and ΔE_2 given in Table 1 predict that the acetylene ligand in the former compound is 13.0 kcal/mol *less* strongly bound than CO, while it is 13.7 kcal/mol *more* strongly bound than CO in the latter compound. This comes from the fact that acetylene becomes a four-electron donor in [W(CO)$_4$(HCCH)]. Acetylene is the only ligand investigated by us for which the relative W–L bond energy with respect to CO changes its sign from ΔE_1 to ΔE_2 (Table 1). We want to point out that the increase in the W−HCCH bond energy relative to CO between the 18- and 16-VE complexes ($\Delta E_2 - \Delta E_1 = -26.7$ kcal/mol, Table 1) is even higher than the W−CO BDE of [W(CO)$_5$(HCCH)], $D_e = 19.2$ kcal/mol.

The calculated structures of the three isomers of [W(CO)$_4$(HCCH)] lead to important conclusions about the stereoelectronic effects of CO loss from [W(CO)$_5$(HCCH)]. The results suggest that the labilizing influence of the acetylene ligand affects specifically the CO$_{cis1}$ ligands which are perpendicular to the W−HCCH plane, but not the CO$_{cis2}$ ligands. This could be an important result for alkyne complexes which have mixed ligands in the cis position to the alkyne group. We will explore this finding in a future study.

We investigated the influence of substituting one or two CH fragments by isoelectronic N in the acetylene ligand on the W−ligand bonding properties in [W(CO)$_5$L] and [W(CO)$_4$L]. Replacing one CH in HCCH by N leads to HCN. Figure 1a shows that CO loss from [W(CO)$_5$(π-NCH)] also gives a 16-VE compound which has the trans, cis1, and cis2 isomers as energy minima. The last isomer has two different forms, denoted as cis2a and cis2b, as energy minima where either N or CH is pointing toward the apical CO ligand. The cis2b form is clearly lower in energy than the cis2a form. The energetic ordering of the different isomers of [W(CO)$_4$(π-NCH)] is the same as found for the acetylene complex. Thus, the distorted-trigonal-bipyramidal form [W(CO)$_4$(π-NCH)](cis1) is clearly the energetically lowest lying isomer. The square-pyramidal forms with the π-NCH ligand in the basal position [W(CO)$_4$(π-NCH)](cis2) come next, followed by the isostructural isomer which has an apical π-NCH ligand [W(CO)$_4$(π-NCH)](trans) (Figure 2).

The explanation for the geometries and relative stabilities of the different isomers of [W(CO)$_4$(π-NCH)] is the same as for [W(CO)$_4$(HCCH)] and shall not be discussed in detail. There are two results which should be pointed out. First, the additional stabilization of π-NCH in [W(CO)$_4$(π-NCH)](cis1) compared to [W(CO)$_5$(π-NCH)] is 15.8 kcal/mol ($\Delta E_2 - \Delta E_1$, Table 1). This is clearly less than the value calculated for HCCH (26.7 kcal/mol). The CDA results given in Table 2 show that the W←(π)NCH donation in [W(CO)$_4$(π-NCH)](cis1) is only slightly larger (0.495 e) than in the parent compound [W(CO)$_5$(π-NCH)] (0.441 e). *The results clearly indicate that NCH, unlike HCCH, does not become an effective 4-electron donor in the 16-VE complex* [W(CO)$_4$L](cis1). The W→(π)NCH back-donation in [W(CO)$_4$(π-NCH)](cis1), however, is twice as large (0.364 e) as in the parent 18-VE complex (0.184 e). Note that also the W−L bond orders for [W(CO)$_4$(π-NCH)](cis1) are nearly twice as large as in [W(CO)$_5$(π-NCH)]. The electron deficiency at tungsten in [W(CO)$_4$(π-NCH)](cis1) is partly compensated by stronger interactions with the CO ligands in the cis1 position, which have very short W−CO distances (1.999 Å, Figure 2g). Note that the W−L bond orders of the cis1 and trans isomers of [W(CO)$_4$(π-NCH)] are nearly the same (Table 2 although the former isomer has significantly longer W−L bonds. This is very important information, which means that the much shorter W−L bonds in [W(CO)$_4$(π-NCH)](cis1) should not be taken as a hint of a much stronger bond than in the trans form.

Table 1 shows that the ligand NCH in [W(CO)$_4$(π-NCH)] is still 13.0 kcal/mol less tightly bound than CO. However, the change from a two-electron donor in [W(CO)$_5$(π-NCH)] to a partial four-electron donor in [W(CO)$_4$(π-NCH)] makes the π-donor strength of NCH as high as the σ-donor strength. Table 1 shows that the ΔE_2 values for σ-NCH (12.7 kcal/mol) and π-NCH (13.0 kcal/mol) are nearly identical.

The results for the π-N$_2$ complexes [W(CO)$_4$(π-N$_2$)] are somewhat different from those for the isoelectronic acetylene and π-NCH complexes. Figure 1a shows that only the trans and cis1 forms of [W(CO)$_4$(π-NCH)] are minima on the potential energy surface. The latter is 22.6 kcal/mol lower in energy than the former (Figure 2). However, the higher stability is not caused by enhanced W−N$_2$ bonding interactions in [W(CO)$_4$(π-N$_2$)](cis1). The energy gain comes, rather, from the stronger W−CO$_{cis}$ bonds, which are much shorter in [W(CO)$_4$(π-N$_2$)](cis1) (1.973 Å) than in [W(CO)$_4$(π-N$_2$)](trans) (2.049 Å, Figure 2k,l). The ΔE_1 and ΔE_2 values given in Table 1 show that the W−N$_2$ interactions in [W(CO)$_4$(π-N$_2$)] are only slightly enhanced by 4.0 kcal/mol compared with [W(CO)$_5$(π-N$_2$)]. The complex with π-bonded N$_2$ [W(CO)$_4$(π-N$_2$)](cis1) remains, therefore, clearly less stable than [W(CO)$_4$(σ-N$_2$)]. The CDA results given in Table 2 suggest that the W←(π)N$_2$ donation in [W(CO)$_4$(π-N$_2$)](cis1) is only slightly larger than in [W(CO)$_5$(π-N$_2$)], but the W→(π)N$_2$ back-donation in the former complex is twice as large as in the latter species. We want to draw attention to the calculated bond orders of the cis1 and trans isomers of [W(CO)$_4$(π-N$_2$)], which are also shown in Table 2. The P(W−N) value of the latter isomer is slightly larger (0.40) than for the cis1 form (0.38), although the W−N bond length in the cis1 species is clearly shorter (2.312 Å) than in the trans form (2.369 Å). This means that the shortening of the W−N distances from [W(CO)$_4$(π-N$_2$)](trans) to [W(CO)$_4$(π-N$_2$)](cis) does not indicate stronger W−N$_2$ interactions. The main differences in the bonding interactions between the two isomers take place in the W−CO(equatorial) bonds.

The fourth π-bonded ligand investigated by us is ethylene, which has only one π-bond that can serve as a strong electron donor via in-plane bonding interactions with tungsten. Figure 1a shows that the isomeric forms [W(CO)$_4$(C$_2$H$_4$)](trans), [W(CO)$_4$(C$_2$H$_4$)](cis1), and [W(CO)$_4$(C$_2$H$_4$)](cis2) are all minima on the potential energy surface. The energy ordering of the three isomers is the same as for the acetylene complexes [W(CO)$_4$(HCCH)]. This shows that the reason for the structural isomerism of the [W(CO)$_4$L] complexes cannot be seen in the ability of the ligand L to serve as a four-electron donor. Figure 1a shows that the most stable isomer, [W(CO)$_4$(C$_2$H$_4$)](cis1), is 15.5 kcal/mol lower in energy than [W(CO)$_4$(C$_2$H$_4$)](trans). This value shall be compared with the energy difference between the acetylene complexes [W(CO)$_4$(HCCH)](cis1) and [W(CO)$_4$(HCCH)](trans) (37.7 kcal/mol). The difference of 22.2 kcal/mol can mainly be attributed to the donor effect of the additional two π-electrons of the acetylene ligands. Note that the bond energies of [W(CO)$_5$L] with L = acetylene, ethylene which refer to the trans and cis2 isomers of [W(CO)$_4$L] are nearly the same! It is only in the distorted-trigonal-bipyramidal form [W(CO)$_4$(HCCH)]-

(cis1) that the ability of the acetylene ligand to act as a four-electron donor comes to the fore.

We want to point out an interesting difference between the calculated geometries of the [W(CO)$_4$(HCCH)] and [W(CO)$_4$(C$_2$H$_4$)] isomers. Figure 2 shows that the ethylene ligand in [W(CO)$_4$(C$_2$H$_4$)](cis1) has *longer* W−C bond lengths than in [W(CO)$_4$(C$_2$H$_4$)](trans), although the former is much lower in energy than the latter. This is opposite to the acetylene complexes. Here the W−C distances in [W(CO)$_4$(HCCH)](cis1) are much shorter than in [W(CO)$_4$(HCCH)](trans), which is another manifestation of acetylene becoming a four-electron donor in the former isomer.

3.2. Complexes with the σ-Bonded Ligands CO, NCH, N$_2$, OH$_2$, NH$_3$, SH$_2$, F$^-$, Cl$^-$, OH$^-$, SH$^-$. This section describes complexes with ligands L where the most important donor orbital has σ-symmetry. However, the ligands also have occupied π-orbitals which additionally may donate electronic charge into empty d(π)-orbitals of the metal. This can be important for the structure and stability of the 18- and 16-VE species, particularly when L is a negatively charged ligand because the occupied π-orbital is energetically high lying.

Figure 7 shows the optimized geometries of the 18- and 16-VE complexes with σ-bonded ligands L, [W(CO)$_5$L] and [W(CO)$_4$L], and the relative energies of the [W(CO)$_4$L] isomers. Experimental bond lengths are only known for W(CO)$_6$. The calculated W−CO distance (2.073 Å) is in very good agreement with the experimental value (2.058 Å).[30] The theoretically predicted first BDE of W(CO)$_6$, $D_e = 45.9$ kcal/mol, which gives after ZPE corrections $D_o = 43.8$ kcal/mol, conforms quite well with the experimental value 46 ± 2 kcal/mol.[31]

Figure 1b shows that the 16-VE complexes [W(CO)$_4$L] with σ-bonded neutral ligands L adopt a square-pyramidal structure as the energy minimum form, except for [W(CO)$_4$(OH$_2$)], which has the distorted-trigonal-bipyramidal form cis1 as the lowest lying isomer. The geometry of [W(CO)$_4$(NH$_3$)] is intermediate between distorted-trigonal-bipyramidal and the cis2 square-planar form. Figure 7m shows that the bond angles of the NH$_3$ group with the equatorial CO ligands are very different (122.2 and 150.3°). The energy minimum structure of [W(CO)$_4$(NH$_3$)] can be considered as a distorted-square-planar form where the C2O6 ligand is in the apical position. For all 16-VE complexes the isomers [W(CO)$_4$L](cis2), which have the ligand L in the basal position, are clearly lower in energy than the trans form, where L is in the apical position. This can be explained by the fact that CO is a stronger π-acceptor than the other σ-bonded ligands L. The CDA results for [W(CO)$_5$L] complexes given in Table 3 show that the largest W→L back-donation is calculated for L = CO. A trans form of [W(CO)$_4$(NH$_3$)] could not even be located as an energy minimum on the potential energy surface. In [W(CO)$_4$(L)](trans) the CO ligands are trans to each other and therefore compete with each other for metal→ligand π-back-donation. In [W(CO)$_4$(L)](cis2) one basal CO ligand is trans to L and the apical CO is trans to the hole. Figure 7 shows that the last two W−CO bonds in [W(CO)$_4$L](cis2) are much shorter than the W−CO bonds which are trans to each other.

It is surprising that a distorted-trigonal-bipyramidal form was found as the energy minimum form only for [W(CO)$_4$(OH$_2$)](cis1), but not for the other σ-bonded neutral ligands. We carried out several geometry optimizations using distorted-trigonal-bipyramidal forms of [W(CO)$_4$(L)] as starting geometries for L = CO, σ-N$_2$, σ-NCH, SH$_2$, NH$_3$ in order to verify the result. The calculations gave always the cis2 form (which is identical with the trans form when L = CO) as the energy minimum. We think that the p(π)-lone-pair donor orbital of OH$_2$ is the reason that the cis1 form [W(CO)$_4$(OH$_2$)](cis1) is an energy minimum. The ligands CO, σ-N$_2$, σ-NCH, and NH$_3$ do not have a p(π)-donor lone-pair orbital at the ligand. SH$_2$ does have a p(π)-donor lone-pair orbital, but donation from a third-row element seems to be less effective than that from a second-row element. Table 1 clearly shows that OH$_2$ labilizes a cis CO ligand more ($\Delta E_2 - \Delta E_1 = -5.7$ kcal/mol) than SH$_2$ ($\Delta E_2 - \Delta E_1 = -1.8$ kcal/mol). Stronger energetic effects of a second-row ligand compared to those of the third row also become obvious from the results which have been obtained for the negatively charged ligands. Previous theoretical studies have shown that π-donor ligands L$^-$ destabilize the 18-VE complexes but stabilize the 16-VE complex.[12a,20] Our results show that this holds also for neutral ligands L. The π-donor strength could be the factor which determines if a complex [W(CO)$_4$L] has a distorted-trigonal-bipyramidal structure or a square-planar geometry.

The calculations predict that the negatively charged complexes with the σ-donor ligands F$^-$, Cl$^-$, OH$^-$, and SH$^-$ *always* adopt a distorted-trigonal-bipyramidal form [W(CO)$_4$L]$^-$(cis1) where the ligand L$^-$ occupies an equatorial position. Only for L$^-$ = Cl$^-$ did we find an energetically high lying square-pyramidal isomer [W(CO)$_4$Cl]$^-$(trans) as the second energy minimum form. We want to point out that the equatorial W−CO bonds of [W(CO)$_4$L]$^-$(cis1) are very short. CDA analyses showed that the W→CO π-back-donation is significantly enhanced in the equatorial bonds of [W(CO)$_4$L]$^-$(cis1).

Table 1 shows that the neutral σ-donor ligands N$_2$, NH$_3$, and SH$_2$ have hardly any labilization effect on the W−CO bond. The $\Delta E_2 - \Delta E_1$ values are very small. Slightly higher $\Delta E_2 - \Delta E_1$ values are calculated for OH$_2$ and σ-NCH, but the W−CO bond weakening effect remains small. A much stronger labilization of the W−CO bond is predicted for the negatively charged σ-donor complexes [W(CO)$_5$L]$^-$. Table 1 shows that the W−L$^-$ bonds, which are clearly stronger than the W−CO bonds in [W(CO)$_5$L]$^-$, become even further strengthened with respect to the W−CO bonds in the 16-VE complexes [W(CO)$_4$L]$^-$. This becomes obvious by the calculated reaction energies ΔE_1 and ΔE_2. The strongest W−CO labilization effect is calculated for OH$^-$, followed by F$^-$, SH$^-$, and Cl$^-$ (see the $\Delta E_2 - \Delta E_1$ values in Table 1). We want to point out that the labilization effect of the second-row ligands F$^-$ and OH$^-$ is clearly higher than that of the third-row ligands Cl$^-$ and SH$^-$. It is noteworthy, however, that the W−CO bond labilization of OH$^-$ (−25.7 kcal/mol) is still 1 kcal/

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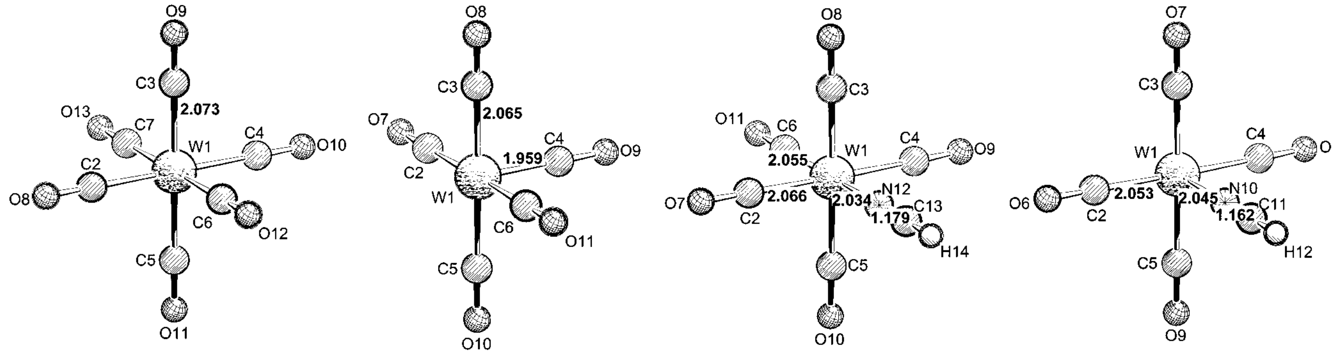
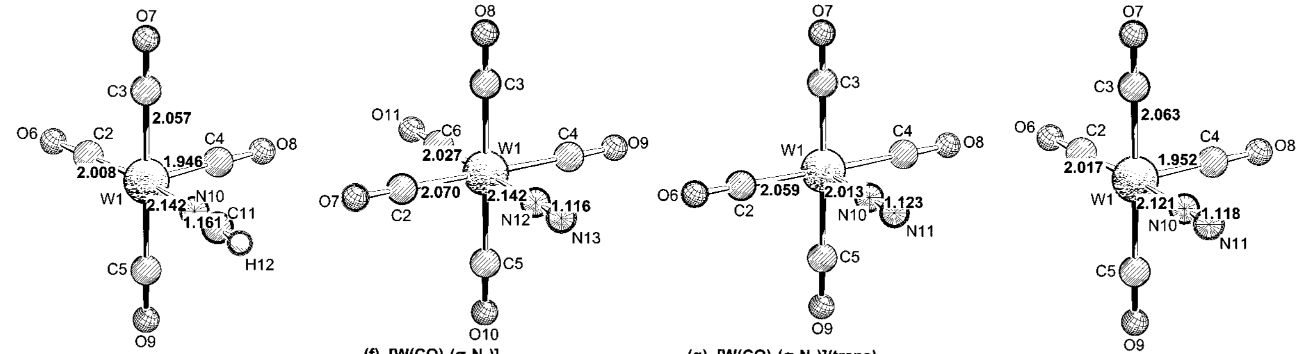


(a) [W(CO)$_6$]
∠C2–W–C4: 180.0
∠C3–W–C5: 180.0

(b) [W(CO)$_5$](trans)
∠C2–W–C4: 90.7
∠C3–W–C5: 178.6

(c) [W(CO)$_5$(σ-NCH)]
∠C2–W–C4: 178.6
∠C3–W–C5: 178.6

(d) [W(CO)$_4$(σ-NCH)](trans)
∠C2–W–C4: 178.5
∠C3–W–C5: 178.5
E_{rel} = 0.0 kcal/mol

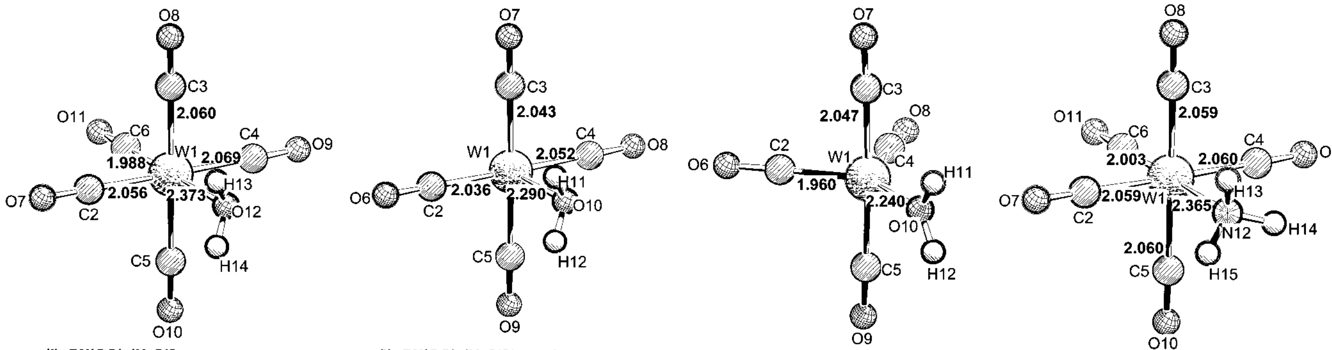


(e) [W(CO)$_4$(σ-NCH)](cis2)
∠C2–W–C4: 90.4
∠C3–W–C5: 177.7
E_{rel} = -14.5 kcal/mol

(f) [W(CO)$_5$(σ-N$_2$)]
∠C2–W–C4: 179.5
∠C3–W–C5: 179.5

(g) [W(CO)$_4$(σ-N$_2$)](trans)
∠C2–W–C4: 177.9
∠C3–W–C5: 177.9
E_{rel} = 0.0 kcal/mol

(h) [W(CO)$_4$(σ-N$_2$)](cis2)
∠C2–W–C4: 90.4
∠C3–W–C5: 178.4
E_{rel} = -11.0 kcal/mol

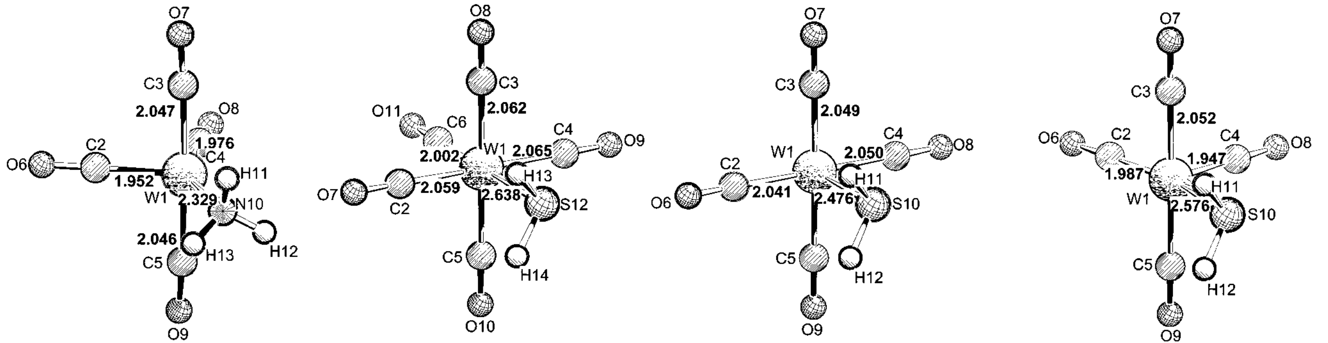


(i) [W(CO)$_5$(H$_2$O)]
∠C2–W–C4: 180.0
∠C3–W–C5: 179.1
∠H–O–H: 106.1
OH torsion: 30.8

(j) [W(CO)$_4$(H$_2$O)](trans)
∠C2–W–C4: 178.4
∠C3–W–C5: 177.9
∠H–O–H: 106.2
OH torsion: 32.0
E_{rel} = 0.0 kcal/mol

(k) [W(CO)$_4$(H$_2$O)](cis1)
∠C2–W–C4: 87.3
∠C3–W–C5: 175.8
∠H–O–H: 109.3
OH torsion: 0.0
E_{rel} = -26.5 kcal/mol

(l) [W(CO)$_5$(NH$_3$)]
∠C2–W–C4: 179.8
∠C3–W–C5: 179.6
NH$_3$ torsion: 15.0

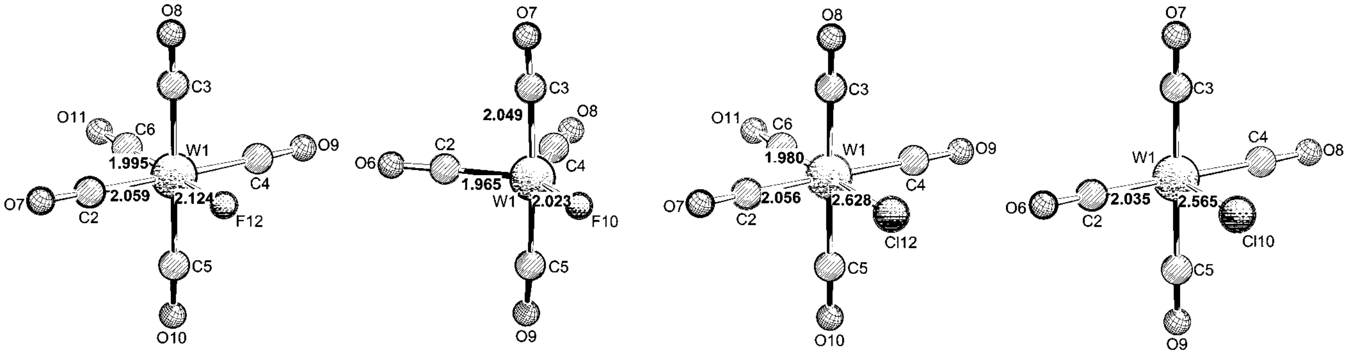


(m) [W(CO)$_5$(NH$_3$)](cis2)
∠C2–W–C4: 87.5
∠C3–W–C5: 176.1
NH$_3$ torsion: 4.1
∠N–W–C4: 150.3
∠N–W–C2: 122.2

(n) [W(CO)$_5$(SH$_2$)]
∠C2–W–C4: 180.5
∠C3–W–C5: 179.6

(o) [W(CO)$_4$(SH$_2$)](trans)
∠C2–W–C4: 179.3
∠C3–W–C5: 178.2
E_{rel} = 0.0 kcal/mol

(p) [W(CO)$_4$(SH$_2$)](cis2)
∠C2–W–C4: 89.3
∠C3–W–C5: 176.4
∠S–W–C4: 104.5
E_{rel} = -16.8 kcal/mol

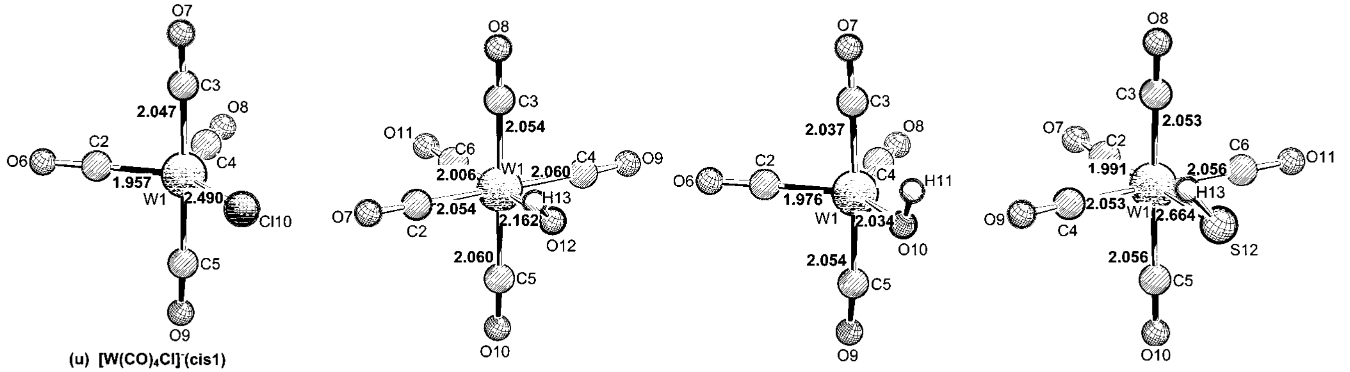


(q) $[W(CO)_5F]^-$
∠C2–W–C4: 179.2
∠C3–W–C5: 179.2

(r) $[W(CO)_4F]^-$(cis1)
∠C2–W–C4: 87.1
∠C3–W–C5: 175.2

(s) $[W(CO)_5Cl]^-$
∠C2–W–C4: 183.0
∠C3–W–C5: 183.0

(t) $[W(CO)_4Cl]^-$(trans)
∠C2–W–C4: 181.2
∠C3–W–C5: 181.2
E_{rel} = 0.0 kcal/mol

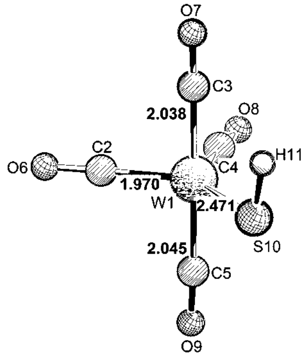


(u) $[W(CO)_4Cl]^-$(cis1)
∠C2–W–C4: 88.0
∠C3–W–C5: 177.8
E_{rel} = -41.1 kcal/mol

(v) $[W(CO)_5(OH)]^-$
∠C2–W–C4: 179.0
∠C3–W–C5: 179.0
∠W–O–H: 108.0
OH torsion: 45.0

(w) $[W(CO)_4(OH)]^-$(cis1)
∠C2–W–C4: 88.7
∠C3–W–C5: 174.7
∠W–O–H: 111.9
OH torsion: 0.0

(x) $[W(CO)_5(SH)]^-$
∠C2–W–C4: 184.5
∠C3–W–C5: 184.3
∠H–S–W: 99.0
SH torsion: 45.0



(y) $[W(CO)_4(SH)]^-$(cis1)
∠C2–W–C4: 90.3
∠C3–W–C5: 178.3
∠H–S–W: 103.5
SH torsion: 0.0

Figure 7. Optimized geometries (B3LYP/II) of the complexes $[W(CO)_5L]$ and $[W(CO)_4L]$ with σ-bonded monodentate ligands L. Bond distances are given in Å, bond angles in deg, and relative energies of the $[W(CO)_4L]$ isomers in kcal/mol.

mol less than the bond weakening effect of the neutral ligand HCCH (−26.7 kcal/mol).

Does the W←L donation and W→L back-donation change significantly between $[W(CO)_5L]$ and $[W(CO)_4L]$? What is the mechanism through which the negatively charged ligands L^- labilize the W−CO bonds in $[W(CO)_5L]^-$? Does electron donation from the p(π)-lone-pair donor orbitals become so important that F^-, Cl^-, OH^-, and SH^- become effectively four-electron donors in $[W(CO)_4L]^-$(cis1)? Table 3 shows the results of the CDA and NBO partitioning. The CDA values for CO, σ-NCH, and σ-N_2 suggest that the ligands have donor and acceptor properties in the 18- and 16-VE complexes. The W→L back-donation becomes, as expected, stronger upon CO loss in the trans forms of $[W(CO)_4L]$ with L = CO, σ-NCH, σ-N_2. The ligands OH_2, NH_3, and SH_2 are pure donors in the 18- and 16-VE complexes. The donation of L = SH_2 becomes slightly higher in $[W(CO)_4(SH_2)]$ than in $[W(CO)_5(SH_2)]$, while the donation of OH_2 and NH_3 remains the same in the 18- and 16-VE species. This apparently contradicts the above conclusion that OH_2 is a better π-donor than SH_2. However, the CDA data in Table 3 give the total donation. It is not possible to calculate the σ- and π-contributions in the 18-VE complexes with L = OH_2, SH_2 because the ligand lone pair orbitals do not have π-symmetry in the compounds. We want to point out that the ligand OH_2 in $[W(CO)_4(OH_2)]$(cis1) is coplanar with the axial CO ligands, which

Table 3. CDA and NBO Results of the $W(CO)_nL$ and $W(CO)_{n-1}L$ Complexes with σ-Bonded Ligands L: $(CO)_nW\leftarrow L$ Donation (*d*), $(CO)_nW\rightarrow L$ Back-Donation (*b*), NBO Partial Charges (*q*), and Wiberg Bond Indices (*P*(W−L))

L	complex	*d*	*b*	*q*(W)	*q*(L)	*P*(W−L)
CO	$W(CO)_5L$	0.455	0.246	−0.773	0.128	0.80
	$W(CO)_4L$(trans)[a]	0.519	0.362	−0.361	0.059	1.27
	$W(CO)_4L$(trans)[b]	0.448	0.252	−0.361	0.075	0.83
N_2	$W(CO)_5L$	0.128	0.127	−0.625	0.047	0.46
	$W(CO)_4L$(trans)	0.174	0.223	−0.156	−0.032	0.77
	$W(CO)_4L$(cis2)	0.148	0.137	−0.211	−0.003	0.48
NCH	$W(CO)_5L$	0.210	0.124	−0.544	0.078	0.51
	$W(CO)_4L$(trans)	0.246	0.178	−0.134	0.047	0.70
	$W(CO)_4L$(cis2)	0.229	0.103	−0.169	0.061	0.42
OH_2	$W(CO)_5L$	0.250	−0.011	−0.513	0.152	0.19
	$W(CO)_4L$(trans)	0.250	−0.016	−0.068	0.180	0.32
	$W(CO)_4L$(cis1)	0.248	−0.011	−0.092	0.161	0.24
NH_3	$W(CO)_5L$	0.274	−0.015	−0.569	0.209	0.25
	$W(CO)_4L$(cis2)	0.271	−0.008	−0.134	0.178	0.25
SH_2	$W(CO)_5L$	0.398	0.027	−0.715	0.261	0.34
	$W(CO)_4L$(trans)	0.430	0.066	−0.334	0.300	0.66
	$W(CO)_4L$(cis2)	0.423	0.055	−0.316	0.223	0.37
F^-	$W(CO)_5L$	0.461	−0.034	−0.308	−0.730	0.31
	$W(CO)_4L$(cis1)	0.493	−0.014	0.125	−0.687	0.41
Cl^-	$W(CO)_5L$	0.568	−0.041	−0.562	−0.631	0.36
	$W(CO)_4L$(trans)	0.554	−0.044	−0.224	−0.590	0.62
	$W(CO)_4L$(cis1)	0.666	−0.014	−0.159	−0.586	0.48
OH^-	$W(CO)_5L$	0.599	−0.018	−0.395	−0.592	0.40
	$W(CO)_4L$(cis1)	0.619	−0.022	0.021	−0.515	0.60
SH^-	$W(CO)_5L$	0.698	−0.002	−0.623	−0.505	0.40
	$W(CO)_4L$(cis1)	0.853	0.030	−0.265	−0.436	0.63
$O_2C_2H_2^{2-}$	$W(CO)_4L$	0.969	−0.017	0.079	−1.419	0.32
	$W(CO)_3L$(cis)	0.938	−0.019	0.399	−1.380	0.41/0.35[c]
$S_2C_2H_2^{2-}$	$W(CO)_4L$	1.254	0.034	−0.483	−1.166	0.39
	$W(CO)_3L$(cis)	1.386	0.074	−0.166	−1.119	0.54/0.47[c]

[a] Apical ligand. [b] Basal ligand. [c] The first value refers to the equatorial bond and the second to the axial bond.

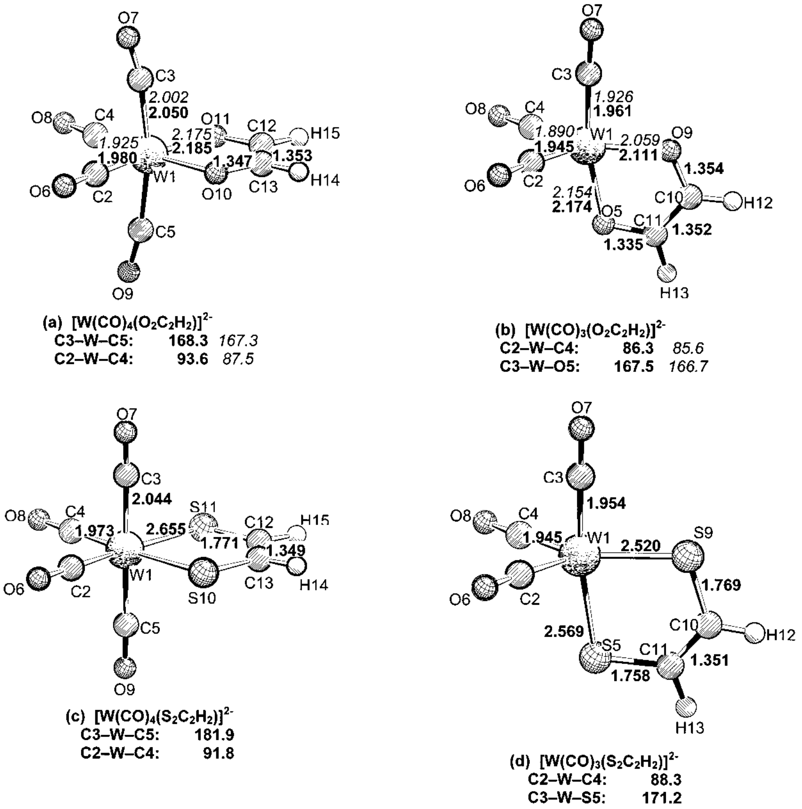
indicates enhanced π-donor interactions with the metal. It seems, however, that the most important change toward stronger bonding interactions takes place in the W−CO(equatorial) bonds of $[W(CO)_4(OH_2)]$(cis1) and *not* in the $W-OH_2$ bond. Table 3 shows that the bond order $P(W-OH_2)$ of $[W(CO)_4(OH_2)]$(cis1) (0.24) is significantly *smaller* than in $[W(CO)_4(OH_2)]$(trans) (0.32), although the $W-OH_2$ bonds of the former are clearly shorter than in the latter isomer (Figure 7j,k). The same result was found for the complexes with the ligand L = π-N_2 (see above) and with L = Cl^- (see below). There is a push−pull π-interaction in the equatorial moiety of the distorted-trigonal-bipyramidal structures $[W(CO)_4L]$(cis1), where L is the pushing π-donor and the CO ligands are π-accepting ligands.

The negatively charged species F^-, Cl^-, OH^-, and SH^- are, as expected, only donor ligands in $[W(CO)_5L]^-$ and $[W(CO)_4L]^-$. The $W\leftarrow L^-$ donation in $[W(CO)_4L]^-$(cis1) is higher than in $[W(CO)_5L]^-$. This becomes obvious from the CDA results and from the atomic partial charges (Table 3). However, the total $W\leftarrow L^-$ donation does not say if the enhanced donation comes from the σ-orbital or from the p(π)-lone-pair orbitals of L^-. We examined the CDA results for L = F^-, Cl^- concerning contributions coming from orbitals which have different symmetry. The $W\leftarrow L^-$ donation in $[W(CO)_5L]^-$ comes nearly only from orbitals which have a_1 symmetry: i.e., from the σ-donor orbital of L^-. The largest contribution from a π-donor orbital which has b_2 symmetry is very small (<0.05 e). However, in $[W(CO)_4F]^-$ and $[W(CO)_4Cl]^-$(cis1) there is one b_2 orbital that contributes significantly (0.161 e in $[W(CO)_4F]^-$ and 0.180 e in $[W(CO)_4Cl]^-$) to the total $W\leftarrow L^-$ donation. This is a clear manifestation of the $W\leftarrow p(\pi)L^-$ donation for L^- = F^-, Cl^-. We also carried out CDA analyses of $[W(CO)_5L]^-$ and $[W(CO)_4L]^-$ with L^- = OH^-, SH^- where the XH^- ligands are staggered with the axial W−CO bonds (C_s symmetry). The C_s structures were less than 0.1 kcal/mol higher in energy than the energy minimum geometries shown in Figure 7. The CDA results showed that the $W\leftarrow XH^-$ donation coming from a″ orbitals in $[W(CO)_4(XH)]^-$ is significantly higher (0.284 e for X = O; 0.275 e for X = S) than in $[W(CO)_5(XH)]^-$ (0.184 e for X = O; 0.098 e for X = S). We conclude that the complexes $[W(CO)_4L]^-$ with L^- = F^-, Cl^-, OH^- SH^- become stabilized by $W\leftarrow p(\pi)L^-$ donation. This is in agreement with previous work.[12a,20] However, the main effect of the stabilization of the cis1 form of $[W(CO)_4L]$ comes from the strengthening of the equatorial W−CO bonds through push−pull π-interactions as discussed above.

Finally, we want to point that the axial W−CO bond lengths in $[W(CO)_4(XH)]^-$ are quite different from each other (Figure 7). The $W-CO_{axial}$ distance of the CO ligand which is syn to the XH bond and anti to the in-plane lone-pair orbital at X is clearly shorter than the other $W-CO_{axial}$ bond length. This can be explained by the $W\leftarrow XH$ electron donation of the in-plane lone-pair orbital of atom X, which enhances the $W\rightarrow CO_{axial}$ π-back-donation toward the CO ligand that is anti to the lone pair orbital.

3.3. Complexes with the Bidentate ligands $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$.

Figure 1c shows the types of equilibrium structures of $[W(CO)_4(X_2C_2H_2)]^{2-}$ and $[W(CO)_3(X_2C_2H_2)]^{2-}$ (X = O, S) which have theoretically been found and the calculated W−CO BDEs of the former species. The bond energies are rather small. The W−CO BDE of the 18-VE oxygen complex is a bit lower



(a) $[W(CO)_4(O_2C_2H_2)]^{2-}$
C3–W–C5: 168.3 *167.3*
C2–W–C4: 93.6 *87.5*

(b) $[W(CO)_3(O_2C_2H_2)]^{2-}$
C2–W–C4: 86.3 *85.6*
C3–W–O5: 167.5 *166.7*

(c) $[W(CO)_4(S_2C_2H_2)]^{2-}$
C3–W–C5: 181.9
C2–W–C4: 91.8

(d) $[W(CO)_3(S_2C_2H_2)]^{2-}$
C2–W–C4: 88.3
C3–W–S5: 171.2

Figure 8. Optimized geometries (B3LYP/II) of the complexes $[W(CO)_4(X_2C_2H_2)]^{2-}$ and $[W(CO)_3(X_2C_2H_2)]^{2-}$ with σ-bonded bidentate ligands L. Bond distances are given in Å, bond angles in deg, and relative energies of the $[W(CO)_4L]$ isomers in kcal/mol. Experimental values (in italics) for the geometries of $[W(CO)_4(O_2C_2H_2)]^{2-}$ and $[W(CO)_3(O_2C_2H_2)]^{2-}$ have been taken from the related 3,5-*tert*-butylcatecholate complexes.[10]

(D_o = 20.6 kcal/mol) than the value for the sulfur complex (D_o = 23.2 kcal/mol). This suggests that 16-VE complexes with catecholate ligands should be slightly more stable than species with thiocatecholate ligands. 16-VE complexes of tungsten with both ligands have been synthesized,[10,11] but the experimental data are not conclusive which ligand stabilizes the formally electron deficient metal more strongly.

Figure 8 shows the calculated equilibrium structures and the most important geometrical parameters. The calculated values for the oxygen complexes are in very good agreement with the experimental values for the related 18-VE catecholate complex $[W(CO)_4(O_2C_6H_4)]^{2-}$ and the 16-VE complex $[W(CO)_3(O_2C_6H_2R_2)]^{2-}$ (R_2 = 3,5-di-*tert*-butyl).[10] Theory and experiment agree that the axial W−O bond in the 16-VE complex is clearly longer than the equatorial W−O bond and that both W−O bonds are shorter than in the 18-VE complex.

Table 1 shows that $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$ are significantly more strongly bonded than two CO ligands in the 18-VE complexes and particularly in the 16-VE complexes. However, the increase in the bond strength relative to 2 CO ($\Delta E_2 - \Delta E_1 = -23.6$ kcal/mol for $O_2C_2H_2^{2-}$ and −20.4 kcal/mol for $S_2C_2H_2^{2-}$) is nearly the same as the bond strengths calculated for one OH^- (−25.7 kcal/mol) and one SH^- (−19.1 kcal/mol) ligand, respectively. This is surprising, because the ligands $O_2C_2H_2^{2-}$ and $S_2C_2H_2^{2-}$ occupy *two* positions which may be used for electron donation from p(π)-lone-pair donor orbitals of X. There is one significant difference between the complexes with the ligands $X_2C_2H_2^{2-}$ and those with XH^-. The axial W−CO distance of the 16-VE complexes $[W(CO)_3(X_2C_2H_2)]^{2-}$ become much shorter than in $[W(CO)_4(X_2C_2H_2)]^{2-}$, while the W−CO$_{\text{axial}}$ bonds of $[W(CO)_4(OH)]^-$ remain nearly as long as in $[W(CO)_5(OH)]^-$.

The CDA results of the bidentate complexes are very interesting. Table 3 shows that the total $(CO)_3W \leftarrow O_2C_2H_2^{2-}$ donation (0.938 e) is even less than the $(CO)_4W \leftarrow O_2C_2H_2^{2-}$ donation (0.969 e). The $W \leftarrow S_2C_2H_2^{2-}$ donation becomes higher in the 16-VE complex (1.386 e) than in the 18-VE species (1.254 e), but the increase is less than for the complexes with the monodentate ligand SH^-. Inspection of the donation from the a′ (σ) orbitals and a″ (π) orbitals revealed a surprising result. The 18-VE complexes $[W(CO)_4(X_2C_2H_2)]^{2-}$ have large contributions from orbitals with a″ symmetry (0.345 e when X = O and 0.536 e when X = S) which become, however, significantly *smaller* in the 16-VE complexes $[W(CO)_3(X_2C_2H_2)]^{2-}$ (0.292 e when X = O and 0.333 e when X = S). The results suggest that W←L π-donation is already operative in the 18-VE complexes and that the π-donation by the ligand lone-pair orbitals is not the main reason for the stability of $[W(CO)_3(X_2C_2H_2)]^{2-}$. The high stability of the latter species may, rather, come from the very short and strong equatorial *and* axial W−CO bonds in the distorted-trigonal-bipyramidal structure, which has also rather short W−X bonds. It follows that the particular effect of the ligands $X_2C_2H_2^{2-}$ in the 16-VE complexes $[W(CO)_3(X_2C_2H_2)]^{2-}$ is that they enhance the W−CO bonds, which stabilize the formally electron-deficient tungsten atom.

4. Summary and Conclusion

The most important results of this study can be summarized as follows. Three different structural isomers have been found as energy minima on the potential energy surfaces of the formal 16-VE complexes $[W(CO)_4L]$ with σ-bonded and π-bonded ligands L = N_2, NCH, C_2H_2, C_2H_4, OH_2, SH_2, NH_3, F^-, Cl^-, OH^-, SH^-, which are all weaker π-acceptors than CO. Square-planar structures (trans) with L in the apical position are energetically high-lying forms of $[W(CO)_4L]$. All complexes $[W(CO)_4L]$ have either distorted-trigonal-bipyramidal structures with L in the equatorial position (cis1) or square-based-pyramidal forms with L in the basal position (cis2) as the global energy minimum. Analysis of the electronic structure of $[W(CO)_4(HCCH)]$, which has trans, cis1, and cis2 isomers, shows that the trans and cis1 forms belong to different electronic states. The ligand HCCH becomes a 4-electron donor in $[W(CO)_4(HCCH)]$(cis1) via donation from the out-of-plane π-orbital of acetylene, which significantly stabilizes the 16-VE complex and thus labilizes the cis-CO ligand which is orthogonal to the W−HCCH plane in $[W(CO)_5(HCCH)]$. This mechanism is much weaker in the π-NCH complex, and it is not operative in the π-bonded dinitrogen and ethylene complexes.

The negatively charged ligands F^-, Cl^-, OH^-, and SH^- have also a strong CO-labilizing effect in $[W(CO)_5L]^-$ because the ligands stabilize the formal 16-VE species $[W(CO)_4L]^-$ by electron donation from the p(π) lone-pair donor orbital. The stabilization by the negatively charged ligands was found to be slightly weaker than that of neutral HCCH, which indicates the special character of acetylene as a CO-labilizing ligand. The neutral σ-bonded ligands SH_2, NH_3, and N_2 stabilize $[W(CO)_4L]$ very poorly, and the ligands OH_2 and σ-NCH are weakly stabilizing. The high stability of the 16-VE complexes with bidentate ligands $[W(CO)_3(X_2C_2H_2)]^{2-}$ (X = O, S) cannot solely be explained with strong $W \leftarrow X_2C_2H_2{}^{2-}$ π-donation, which is already operative and even stronger in the 18-VE parent complexes $[W(CO)_4(X_2C_2H_2)]^{2-}$. An important additional reason for the stability of the 16-VE species $[W(CO)_3(X_2C_2H_2)]^{2-}$ lies in the ability of the ligands $X_2C_2H_2{}^{2-}$ to enhance the bond strength of the three W−CO bonds.

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