Structure and Bonding of Low-Valent (Fischer-Type) and High-Valent (Schrock-Type) Transition Metal Carbene Complexes**

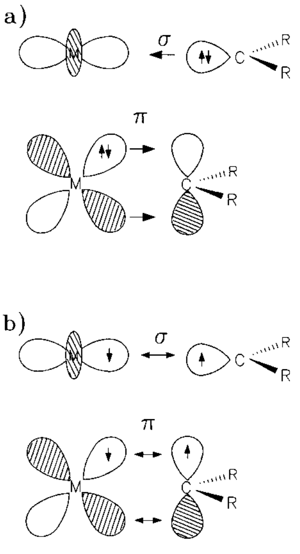
Sergei F. Vyboishchikov and Gernot Frenking*

Abstract: Quantum mechanical ab initio calculations are reported at the MP2 level of theory with effective core potentials for the heavy atoms of the low-valent carbene complexes $[(CO)_5WCH_2]$ (**1**), $[(CO)_5WCF_2]$ (**2**), $[(CO)_5WCHF]$ (**3**), and $[(CO)_5WCH(OH)]$ (**4**), and for the high-valent carbene complexes $[F_4W(CH_2)]$ (**5**), $[F_4W(CF_2)]$ (**6**), $[Cl_4W(CH_2)]$ (**7**), $[Br_4W(CH_2)]$ (**8**), $[I_4W(CH_2)]$ (**9**), $[(OH)_4W(CH_2)]$ (**10**), $[F_5W(CH_2)]^-$ (**11**), and $[F_5W(CF_2)]^-$ (**12**). Metal–carbene bond energies are predicted at CCSD(T) with MP2 optimized geometries. The bonding situation is analyzed with the help of Bader's topological theory of atoms in molecules, Weinhold's NBO-partitioning scheme and the CDA method for donor–acceptor interactions. The analysis of the calculated data shows that the chemical and physical properties of the two types of compounds can be understood when the electronic configuration at the metal is considered. The Taylor and Hall model is supported by the CDA results for the neutral compounds. This model suggests that the metal–carbene bonds in Fischer-type complexes are due to donor–acceptor interactions between the metal fragment and singlet carbenes, while Schrock-type complexes have normal covalent bonds between open-shell metal fragments and triplet carbenes. Donor–acceptor bonds are found for **1**–**4** and normal covalent bonds are found for **5**–**10**. The high-valent negatively charged complexes **11** and **12**, however, have donor–acceptor bonds.

Keywords: ab initio calculations • carbene complexes • donor–acceptor interactions • metal–ligand interactions • tungsten

Introduction

The first synthesis of a transition metal carbene complex by Fischer and Maasböl in 1964[1] introduced a new class of organometallic compounds into chemistry that soon proved very useful and versatile for organic and organometallic synthesis.[2–4] The metal–carbene bond of the Fischer complex is usually discussed[4] in terms of the familiar Dewar–Chatt–Duncanson model,[5] which considers the dominant bonding interactions to arise from ligand→metal σ donation and metal→ligand π back-donation. In the case of singlet ($^1A_1$) carbene as a ligand, the most important orbital interactions should be donation from the occupied a_1 orbital of CR_2 into the empty d_{z^2} metal orbital, and back-donation from the d_{xz} metal AO to the empty p(π) carbon orbital of CR_2. This is schematically shown in Scheme 1.



Scheme 1. Schematic representation of the dominant orbital interactions in a) Fischer-type carbene complexes and b) Schrock-type carbene complexes.

Ten years after Fischer's synthesis of $[(CO)_5WCMe(OMe)]$[1] another class of transition metal (TM) compounds with a metal–carbon double bond was introduced into organometallic chemistry by Schrock, who synthesized $[(Me_3CCH_2)_3Ta(CHCMe_3)]$.[6] Unlike the Fischer carbene complexes, Schrock's compound did not have a stabilizing substituent (usually OR or NR_2) at the carbene ligand. It was soon recognized that the latter type of carbene complex belongs to a class of transition metal compounds that behaves, chemically, very differently to the Fischer complexes.[7] The carbene ligand of Fischer complexes is usually electrophilic, while Schrock complexes have a nucleophilic carbene center. Also, Fischer complexes have transition metals that are usually in a low oxidation state, whereas

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Schrock complexes have transition metals in a high oxidation state. It has been pointed out, however, that the oxidation state is not a safe criterion for predicting electrophilic or nucleophilic reactivity.[8]

The different chemical behavior has been explained with a qualitatively different bonding situation between the two classes of compounds.[9, 10] The metal–carbene bonding in Schrock complexes was described as a covalent double bond between a triplet carbene and a triplet metal fragment (Scheme 1). Since the latter model does not employ donor–acceptor interactions between the metal and the carbene, the more appropriate name for the Schrock complexes is transition metal alkylidenes. Since the name Schrock complex is common in organometallic chemistry, we will use it in this paper.

The nature of the metal–carbene bond has been the subject of several theoretical studies, but most of the earlier work was carried out with use of either assumed geometries or Hartree–Fock (HF) optimized structures.[10–15] It is well known now that geometries of transition metal complexes in low oxidation states have to be optimized at correlated levels in order to get accurate geometries.[16] Nevertheless, some important theoretical results have been obtained. Taylor and Hall[10] studied the Fischer complexes [$(CO)_5MoCH_2$] and [$(CO)_5MoCH(OH)$] as well as the Schrock complexes [$CpCl_2NbCH_2$] and [$CpCl_2NbCH(OH)$]. They suggested in a pioneering study that the different chemical behavior of the two classes of TM compounds is not due to the carbene ligand, but rather that it is caused by the metal moiety. This work is important, because the different bonding models shown in Scheme 1 were suggested for the first time. A dominant influence of the metal fragment on the metal–carbene bond has also been postulated by Cundari and Gordon,[11] who reported a configuration interaction (CI) study of several Schrock complexes using HF-optimized geometries. Goddard et al.[9] employed the GVB method for an analysis of Schrock and Fischer complexes. The electronic and molecular structure of the Fischer complex and higher analogues [$(CO)_5MoAH_2$] (A = C, Si, Ge, Sn) have been studied by Márquez and Fernandez Sanz[12] at the CASSCF level with HF-optimized geometries. The most recent theoretical work on Fischer complexes was carried out by Ziegler et al.,[13] who reported DFT calculations of [$(CO)_5MCH_2$] (M = Cr, Mo, W),[13a] and later [$(CO)_5CrAH_2$] (A = C, Si, Ge, Sn) and [$(CO)_5MCH_2$] (M = Mo, W, Mn^+).[13b] We want to point out that theoretical work has also been carried out on naked metal carbenes MCH_2.[17]

In this paper we report our theoretical studies of the low-valent carbene complexes [$(CO)_5WCH_2$] (**1**), [$(CO)_5WCF_2$] (**2**), [$(CO)_5WCHF$] (**3**) and [$(CO)_5WCH(OH)$] (**4**), and the high-valent alkylidenes [$F_4W(CH_2)$] (**5**), [$F_4W(CF_2)$] (**6**), [$Cl_4W(CH_2)$] (**7**), [$Br_4W(CH_2)$] (**8**), [$I_4W(CH_2)$] (**9**), [$(OH)_4W(CH_2)$] (**10**), [$F_5W(CH_2)$]$^-$ (**11**), and [$F_5W(CF_2)$]$^-$ (**12**). We present theoretically predicted geometries and tungsten–carbene bond dissociation energies of **1**–**12**. The bonding situation of the compounds has been analyzed with the topological analysis of the electron-density distribution[18] and the natural bond orbital analysis (NBO).[19] Additional information about the tungsten–carbene interactions has been obtained from the charge-density analysis (CDA) of **1**–**12**.[20, 21]

The very helpful comments of two referees made it clear that we should clarify the unconventional use of some terms in our work, which otherwise might lead to some confusion. In particular, the classification of carbene complexes as Fischer and Schrock type is somewhat different from that used in many textbooks of organometallic chemistry. The name *Fischer carbene complexes* is normally used for compounds that have a heteroatom linked to the carbenoid carbon; they usually have a metal in a low oxidation state, π-acceptor ligands, and electrophilic character at the carbene carbon atom. *Schrock carbene complexes* (better: alkylidenes) are those with alkyl groups or hydrogen atoms at the carbene center; these usually present higher oxidation states of the metal atom, a variety of ligands, which are usually not closed-shell species as free molecules, and they have nucleophilic character at the carbene carbon atom. Such criteria are easy to use for classifying a carbene complex to belong to one or the other type, but sometimes it becomes difficult and arbitrary to label a compound in this way. For example, the osmium carbene complex [$(PPh_3)_2Cl(NO)OsCH_2$] should be labelled as Fischer-type, because of the low oxidation state of Os^{II}, but the carbene ligand reacts with a variety of electrophilic reagents at the carbene carbon, which is typical for Schrock carbenes.[8]

In this paper we decided to use the terms Schrock and Fischer carbenes strictly for complexes that have metals in a high or low oxidation state, respectively. Thus, **1**–**4** are called Fischer-type complexes and **5**–**12** are termed Schrock complexes. The results of the calculations showed that, for example, the bonding properties of **1**, which has a CH_2 (Schrock-type) ligand and **4**, which has a CH(OH) (Fischer-type) ligand are very similar, while the differences between the methylene complexes **1** and **5** are striking. If the terms Fischer and Schrock carbene complexes are used for compounds in which the carbene ligand has electrophilic or nucleophilic character, then neither the oxidation state nor the ligand type gives a clear answer to which category a particular complex belongs. We want to emphasize, however, that our analysis of the metal–carbene binding in **1**–**12** focuses on the model of Taylor and Hall,[10] who suggested that the electronic configuration at the metal center must be taken into consideration to explain the different reactivity of the two types of carbene complexes. We were interested to see if the low-valent complexes **1**–**4** all have metal–carbene bonds that are formed through donor–acceptor interactions (Scheme 1a), and if the high-valent complexes **5**–**12** all have bonds that are formally formed from two open-shell fragments (Scheme 1b). It will be shown below that the analysis of the bonding situation by means of the CDA method makes it possible to distinguish between the two bonding types. It was found that the assumption about different bonding situations in high-valent and low-valent complexes is justified for the neutral compounds **1**–**10**. In case of the negatively charged complexes **11** and **12**, however, the CDA finds donor–acceptor interactions for the tungsten–carbene bonds, although these are high-valent compounds. We are currently investigating by theoretical methods if ligands other than carbenes show a similar dual-binding-type behavior.

Another source of possible confusion are the terms that we use for the different binding types shown in Scheme 1. The bonding situation typical for a Lewis acid–base pair depicted in Scheme 1a is termed a *donor–acceptor bond*. In textbooks it is sometimes called a semicovalent bond, because the nature of the bonding interaction is partly covalent and partly ionic. The name dative bond has also been suggested.[22] Donor–acceptor bonds dissociate in a heterolytic way. The homolytically formed bond shown in Scheme 1b we call a *normal covalent bond*, in order to distinguish it from the term semicovalent bond. We want to point out that donor–acceptor and normal covalent bonds may both have covalent and ionic contributions.

Finally we want to emphasize that, although the present work deals only with carbene complexes of tungsten, the conclusions made from the results should hold for other metals as well. We are aware that complexes of the early and late transition metals are quite different, mainly because of the number of d electrons; this gives rise to the fact that for some transition metals only one type of carbene complex has been synthesized so far. However, the focus on the electronic configuration at the metal will always be a good way to understand the nature and reactivity of the metal–carbene bond.

Computational Methods

Two different basis sets I and II were used in this study. Basis set I has a quasirelativistic small-core effective-core potential (ECP) with a (441/41/21) valence basis set for W,[23a] an ECP with a (21/21/1) valence basis set for Cl, Br, and I[23b] and 3-21G all-electron basis sets for the other atoms.[24] Basis set II has the same ECPs as in basis set I. However, a less contracted (441/2111/21) valence basis set for W and 6-31G(d) all-electron basis sets[25] for H, C, F, O were employed in basis set II. The valence basis sets for Cl, Br, and I in II are the same as in I. The performance of basis sets I and II was studied systematically for calculating transition metal compounds.[16] The geometries of **1**–**12** were optimized at the Hartree–Fock (HF) level of theory with basis sets I and II, and at the level of second-order Møller–Plesset perturbation theory (MP2)[26] with basis set II. Vibrational frequencies and the zero-point energies (ZPE) were calculated only at HF/I. All structures reported here are minima on the potential energy surface at HF/I (number of imaginary frequencies $i = 0$). The tungsten–carbene bond dissociation energies were calculated at the CCSD(T)/II level with MP2/II optimized geometries. For computational reasons we could not carry out CCSD(T) calculations of **2**, **3**, and **4**. In these cases bond dissociation energies at CCSD(T)/II have been estimated from isostructural reactions.[27] It has been shown that estimated bond energies from isostructural reactions are very similar to directly calculated values.[27] The calculations were performed with the program packages Gaussian 92,[28] Turbomole,[29] and ACES II.[30] The topological analysis of the electron-density distribution was carried out with the programs EXTREME, PROAIM, and BONDER.[31]

Inspection of the tungsten–carbene interactions was performed by charge-density analysis (CDA).[20] In the CDA method the molecular orbitals (canonical, natural, or Kohn–Sham) of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the natural orbitals (NO) of the MP2/II wavefunctions are formed in the CDA calculations as a linear combination of the MOs of the carbene ligand and those of the remaining fragment WL_n [$W(CO)_5$ for the Fischer complexes, WL_4 or WL_5^- for the Schrock complexes] in the geometry of the carbene complex. The orbital contributions are subdivided into four parts: i) the mixing of the occupied MOs of the carbene ligand and the unoccupied MOs of the fragment (carbene $\rightarrow WL_n$ donation); ii) the mixing of the unoccupied MOs of the carbene and the occupied MOs of the fragment ($L_nW \rightarrow$carbene back-donation); iii) the mixing of the occupied MOs of the carbene and the occupied MOs of the fragment (carbene $<\rightarrow WL_n$ repulsive polarization); and iv) the residue term arising from the mixing of unoccupied orbitals. It has been shown that the residue term is ≈ 0 for closed-shell interactions, while shared interactions have values for the residue terms that are significantly different from zero.[32a–c] A more detailed presentation of the method and the interpretation of the results is given in refs. [20] and [32]. The CDA calculations were performed with the program CDA 2.1.[21]

Results and Discussion

Geometries and bond energies: The optimized structures of the carbene complexes **1**–**12** are shown in Figure 1. The theoretically predicted metal–ligand bond lengths and angles for the Fischer complexes **1**–**4** are presented in Table 1. The calculated geometries of the Schrock complexes **5**–**12** are shown in Table 2. Table 3 gives the theoretically predicted metal–carbene bond dissociation energies.

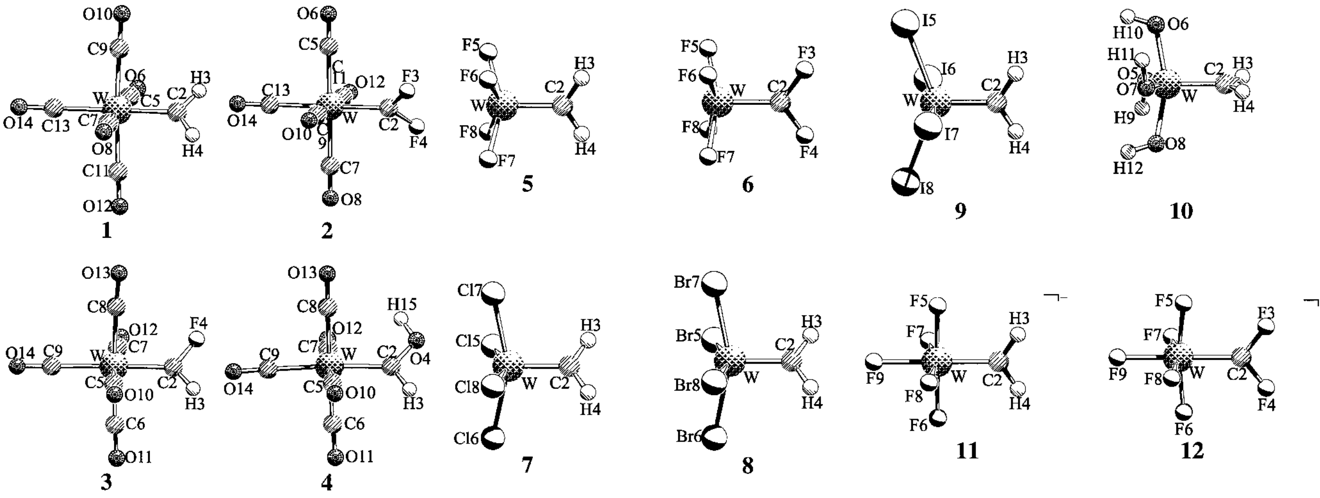

Figure 1. Optimized structures at MP2/II of the Fischer complexes **1**–**4** and the Schrock complexes **5**–**12**. For the geometrical data see Tables 1 and 2.

Table 1. Optimized geometries of the Fischer carbene complexes **1**–**4**. Bond lengths in Å, angles in degrees.

	Symmetry	Geometrical parameter	HF/I	HF/II	MP2/II
$[(CO)_5W(CH_2)]$ (**1**)	C_{2v}	W–C2 (carbene)	2.045	2.053	2.031
		W–C5 (*cis*)	2.095	2.11	2.064
		W–C13 (*trans*)	2.139	2.151	2.119
		∢C2-W-C5	88.8	89.0	88.3
$[(CO)_5W(CF_2)]$ (**2**)	C_{2v}	W–C2 (carbene)	2.077	2.105	2.057
		W–C5 (*cis*)	2.094	2.106	2.060
		W–C13	2.111	2.121	2.083
$[(CO)_5W(CHF)]$ (**3**)	C_s	W–C2 (carbene)	2.047	2.062	2.029
		W–C5 (*cis*)	2.090	2.102	2.059
		W–C7 (*cis*)	2.099	2.113	2.065
		W–C9 (*trans*)	2.133	2.149	2.114
		∢C2-W-C5	89.6	89.3	88.3
		∢C2-W-C7	89.5	89.5	88.1
		∢C2-W-C9	180.2	179.4	179.1
$[(CO)_5W(CH(OH))]$ (**4**)	C_s	W–C2 (carbene)	2.128	2.151	2.088
		W–C5 (*cis*)	2.089	2.105	2.059
		W–C7 (*cis*)	2.082	2.093	2.051
		W–C9 (*trans*)	2.098	2.107	2.085
		C2–O4	1.333	1.301	1.333
		∢C2-W-C5	88.1	88.0	86.5
		∢C2-W-C7	92.0	91.5	91.8
		∢C2-W-C9	177.6	177.3	176.0

Table 2. Optimized geometries of the Schrock carbene complexes **5**–**12**. Bond lengths in Å, angles in degrees.

	Symmetry	Geometrical parameter	HF/I	HF/II	MP2/II
$[F_4W(CH_2)]$ (**5**)	C_{2v}	W–C	1.830	1.845	1.860
		W–F	1.833	1.852	1.856
		C–H	1.080	1.081	1.091
		∢C-W-F	103.3	103.2	103.4
$[F_4W(CF_2)]$ (**6**)	C_{2v}	W–C	1.928	1.946	1.892
		W–F	1.840	1.863	1.854
		C–H	1.314	1.277	1.339
		∢C-W-F	99.0	99.4	99.3
$[Cl_4W(CH_2)]$ (**7**)	C_{2v}	W–C	1.867	1.859	1.850
		W–Cl	2.300	2.323	2.301
		C–H	1.081	1.081	1.081
		∢C-W-Cl	101.5	101.6	102.7
$[Br_4W(CH_2)]$ (**8**)	C_{2v}	W–C	1.872	1.863	1.851
		W–Br	2.475	2.502	2.472
		C–H	1.081	1.081	1.094
		∢C-W-Br	101.2	101.3	102.4
$[I_4W(CH_2)]$ (**9**)	C_{2v}	W–C	1.885	1.870	1.844
		W–I5	2.629	12.667	2.661
		W–I6	2.762	2.784	2.731
		C–H	1.083	1.083	1.097
		∢C-W-I5	114.1	110.0	111.8
		∢C-W-I6	91.8	94.7	95.8
		∢H-C-H	114.4	115.2	118.0
$[(OH)_4W(CH_2)]$ (**10**)	C_{2v}	W–C	1.864	1.865	1.886
		W–O5	1.840	1.896	1.922
		W–O6	1.890	1.953	1.941
		W–O7	1.855	1.896	1.921
		∢C-W-O5	101.4	110.3	109.5
		∢C-W-O6	105.6	99.2	99.6
		∢C-W-O7	100.2	110.3	109.5
		∢C-W-O8	107.0	99.2	99.6
$[F_4W(CH_2)]^-$ (**11**)	C_{2v}	W–C	1.896	1.924	1.934
		W–F5	1.862	1.856	1.861
		W–F7	1.844	1.916	1.907
		W–F9	1.880	1.949	1.974
		C–H	1.081	1.082	1.093
		∢C-W-F5	82.9	89.0	89.6
		∢C-W-F7	94.9	97.3	97.6
$[F_4W(CF_2)]^-$ (**12**)	C_{2v}	W–C	1.984	2.005	1.966
		W–F5	1.834	1.853	1.851
		W–F7	1.897	1.938	1.961
		W–F9	1.896	1.920	1.934
		C–F	1.338	1.304	1.374
		∢C-W-F5	82.9	84.3	85.3
		∢C-W-F7	94.9	95.9	97.7
		∢F-C-F	105.6	106.0	106.1

Table 3. Dissociation energies of the carbene complexes **1**–**12** (kcal mol^{-1}) with respect to the electronic ground states of the respective fragments.[a]

	MP2/II		CCSD(T)	
	D_e	D_o	D_e	D_o
1	81.3	75.7	78.9	73.3
2	67.5	65.7	60.6[b]	58.8[b]
3	86.9	84.1	80.0[b]	77.2[b]
4	81.9	78.0	75.0[b]	71.1[b]
5	127.7	125.6	118.2	116.1
6	65.3	63.7	57.5	55.9
7	91.2	89.5	75.3	73.6
8	87.9	86.4	74.2	72.7
9	82.5	81.4	70.5	69.4
10	119.0	116.5	108.0	105.5
11	110.0	104.5	101.3	95.8
12	70.7	68.6	62.8	60.7

[a] Singlet state of $W(CO)_5$, triplet state of WX_4, singlet state of WF_5^-, triplet state of CH_2, singlet state of CHF, CF_2, and CH(OH). [b] The CCSD(T) values were estimated from isostructural reactions.[27]

The tungsten–carbene bond lengths of the Fischer complexes **1**–**4** become slightly longer at the HF level when the basis set is improved from BS I to II (Table 1). The $(CO)_5W$–CXY bonds are clearly shorter at MP2/II compared to the HF values. It is well known that bond lengths of donor–acceptor complexes are generally predicted to be too long at HF, while MP2 gives values that are in good agreement with experiment. This holds for complexes of main-group elements[33] and for transition metal complexes.[16]

Although transition metal carbene complexes with CH_2 as the carbene ligand have frequently been used to mimic Fischer complexes,[12, 13, 15] compound **1** is not a particularly good model for these molecules, because it is well known that a π-stabilizing substituent (usually O or N) at the carbene ligand is necessary in order to make the complexes stable enough to become isolable.[2, 3] Otherwise the carbene carbon atom in Fischer complexes is too reactive for nucleophilic attack to be isolable. Table 1 shows that two fluorine atoms and the even better π-donor substituent OH yield longer W–carbene bonds in **2** and particularly in **4** than in **1**. The bond dissociation energies of the W–carbene bonds of the Fischer complexes with π-donor substituents at the carbene ligand in **2** and **4** are also lower than that of **1** (Table 3). Please note that the bond dissociation energies are calculated with respect to the electronic ground state of the fragments. CHF, CF_2, and CHOH have (^1A or $^1A_1$) singlet ground states, while CH_2 has a ($^3B_1$) triplet ground state, which is 9.0 kcal mol^{-1} lower in energy than the ($^1A_1$) singlet state.[34] Since the electronic reference state of the Fischer complexes for the carbene ligand is the singlet state, the binding interactions between $W(CO)_5$ and CH_2 in **1** are 9.0 kcal mol^{-1} higher than the dissociation energy given in Table 3. It follows that the higher stability of π-donor-substituted Fischer carbene complexes is not caused by stronger metal–carbene bonds, but rather by the electronic structure at the carbene ligand. This will be discussed in more detail below.

The theoretically predicted W–carbene bond length of **4** (2.088 Å) is in excellent agreement with the experimentally derived value of 2.086 Å for the related compound $[(CO)_5W-C(OMe)(cy-C_5H_7)]$.[35] A slightly longer W–carbene bond length of 2.15 Å has been reported for $[(CO)_5WC(Ph)_2]$.[36] Although fluorocarbene complexes of transition metals have been synthesized,[37] we do not know of any experimental geometry of a tungsten–fluorocarbene complex. The calulations show that the W–CO bond of **1**–**4**, which is *trans* to the carbene ligand, is always longer than the $W-CO_{cis}$ bond. The $W-CO_{trans}$ bond length shows that the order with respect to the carbene ligands is $CH_2 > CHF > CF_2 > CHOH$. This is in agreement with experimental evidence, which shows that decreasing π-acceptor properties of a carbene ligand decreases the bond length of a *trans* metal–CO bond.[38]

The planar carbene ligand has a staggered conformation with regard to the *cis* carbonyl groups in **1**–**4**. However, the barrier for rotation about the W–carbene bond is very low. The eclipsed conformations of **1**–**4**, which are transition states, are only ≤ 0.5 kcal mol^{-1} (MP2/II) higher in energy than the staggered ground-state forms. The hydroxyl group of **4** has a *trans* conformation. Geometry optimization with a *cis* conformation of the OH group leads to a higher lying form **4a**, which is 5.6 kcal mol^{-1} less stable than **4**. Experimental evidence shows that, in the absence of steric interactions, the *trans* form is usually the more stable form of $[(CO)_5M-C(OR)X]$ (M = Cr, Mo, W) complexes, but the *cis* form may also be present.[3a, 38]

The calculations suggest that the carbene ligands in **1**–**4** are much more strongly bound to the metal than CO in tungsten hexacarbonyl. The theoretically predicted W–carbene dissociation energies of the hydroxycarbene ligand in **4** are $D_e = 75.0$ kcal mol^{-1} and $D_o = 71.1$ kcal mol^{-1} (Table 3). The first bond dissociation energies of $[W(CO)_6]$ calculated at CCSD(T)/II are $D_e = 48.0$ kcal mol^{-1} and $D_o = 45.7$ kcal mol^{-1}.[39] The experimental value is $D_o = 46 \pm 2$ kcal mol^{-1}.[40] The calculated bond energies demonstrate that a stonger bond does not lead to lower reactivity. The carbene ligand is usually more reactive than CO, because the carbene reacts further in exothermic processes, which makes the overall reaction thermodynamically favorable.

A comparison of the optimized geometries of the Fischer complexes **1**–**4** (Table 1) with the structures of the Schrock complexes **5**–**12** (Table 2) shows that the latter have much shorter metal–carbene bonds than the Fischer complexes. This holds particularly for the neutral Schrock complexes **5**–**10**, which have W–carbene bond lengths between 1.844 Å (for **9**) and 1.892 Å (for **6**). The calculated W–carbene bonds of the Fischer complexes **1**–**4** are between 2.029 Å (for **3**) and 2.088 Å (for **4**). This is in agreement with the results of X-ray structure analyses, which show that typical Schrock complexes have shorter metal–carbene bonds than Fischer complexes.[2, 7] An example that comes close to our model compounds **8** and **10** is $[WBr_2(OCH_2tBu)_2(=C(CH_2)_4]$, which has an experimentally observed W–carbene bond length of 1.890 Å.[41] The calculated W–carbene interatomic distances are 1.851 Å and 1.886 Å for **8** and **10**, respectively (Table 2).

Two reasons can be given to explain the different bond lengths between Fischer and Schrock carbene complexes. One is the smaller radius of the metal atom in the Schrock complexes in which the metal is in a high oxidation state. The second reason is the different type of metal–carbene bonding interactions, which will be discussed below. The longer W–carbene bonds of the anions **11** and **12** are intermediate between those of the neutral Schrock complexes **5** and **6** and the respective Fischer complexes **1** and **2** (Tables 1 and 2). We will show below that the analysis of the bonding situation suggests that **11** and **12** have metal–carbene bonds that are more similar to those of the Fischer complexes **1**–**4** than those of the neutral Schrock complexes **5**–**10**.

A comparison of the geometries of **5**–**12** obtained at different levels of theory shows that at MP2/II the W–carbene bond becomes on the one hand shorter and on the other hand longer than at HF/II. This is different to the Fischer complexes, where MP2/II always gives shorter bonds than HF/II. Note that the CF_2 complexes **6** and **12** at MP2/II have significantly shorter W–carbene and longer C–F bonds than at HF/II.

Table 3 gives the W–carbene bond dissociation energies of the Schrock complexes **5**–**12**. The dissociation of the neutral complexes **5**–**10** is given with respect to the triplet electronic ground states of WX_4. The ground states of the carbene ligands are $^3B_1$ for CH_2 and $^1A_1$ for CF_2. This is important for a comparison of the W–carbene bond strengths of **5** and **6**. Table 3 shows that **5** has a much stronger bond ($D_e = 118.2$ kcal mol^{-1}) than **6** ($D_e = 57.5$ kcal mol^{-1}), although the W–carbene bond lengths are not very different (Table 2). However, the reference electronic state of CF_2 in **6** is not the singlet ground state, but the $^3B_1$ first excited state (Scheme 1). The experimentally observed $^3B_1 \rightarrow {}^1A_1$ excitation energy of CF_2 is 56.7 kcal mol^{-1}.[42] This leads to a bond dissociation energy **6** ($^3B_1$, CF_2) of $D_e = 114.2$ kcal mol^{-1}, which is a better estimate of the bonding interaction energy of the W–carbene bond. The higher value of the binding interactions also explains the rather short F_4W-CF_2 bond (Table 2).

The effect of substituting hydrogen with fluorine at the carbene ligand on the bond energies between the Fischer complexes (**1**→**2**) and the Schrock complexes (**5**→**6**), shows the usefulness of the approach to consider the different bonding situation of the two types of compounds (Scheme 1), and to explain the properties of these compounds. The W–carbene bond energy of **6** is much lower than that of **5**, because CH_2 has a triplet ground state, while CF_2 has a singlet ground state and a large singlet→triplet excitation energy. The bond energy of **2** is only slightly lower than in **1**, because singlet CF_2 has a low-lying lone-pair orbital and thus is a weaker Lewis base than singlet CH_2. This compensates the triplet→singlet excitation energy of CH_2.

The W–carbene bond strength of the methylene complexes X_4WCH_2 increases with higher electronegativity of the substituent X: $F > OH \gg Cl > Br > I$. This is an interesting result that might be helpful for experimental studies. Compounds $[F_4W(CH_2)]$ (**5**) and $[(OH)_4W(CH_2)]$ (**10**) have higher W–carbene bond dissociation energies than the Fischer complexes, but the bond energies of **6**–**9** are comparable in magnitude with those of **1**–**4** (Table 3). This also shows that the stability of the Schrock complexes is not primarily due to the metal–carbene bond strength, but is caused by the electronic structure at the carbene carbon atom as discussed below. Addition of F^- to **5** and **6** yields the negatively charged complexes **11** and **12**, respectively. Table 3 shows that the metal–carbene bond energy of **11** is a little less than that of **5**, while **12** has a bond energy which is slightly higher than that of **6**.

Analysis of the bonding situation: Table 4 gives the results of the topological analysis of the electron-density distribution of **1**–**12**. Figure 2 shows the contour line diagrams of the Laplacian of selected compounds.

A comparison of the Laplacian distributions of the carbene complexes with CH_2 ligands **1**, **5**, and **11**, and free CH_2 shows clearly the difference between the Fischer and Schrock complexes. There are few changes at the carbene ligand when the contour line diagrams in the CH_2 plane are compared (Figures 2a, 2e, 2g, 2i, 2k). The area of charge concentration at the carbene carbon atom pointing towards the tungsten atom, which corresponds to the carbon lone-pair electrons of CH_2, is not much distorted by the presence of the metal fragment in both types of carbene complexes. Significant differences are found when the Laplacian distribution in the π plane of the carbene ligand are examined. The Fischer complex **1** shows an area of charge depletion (dashed lines) in the direction of the p(π) orbitals of the carbene carbon atom, which are indicated by arrows in Figure 2b. These holes in the electron concentration, which are visible signs for the direction of a possible nucleophilic attack at the carbene ligand, are still present in **4** (Figure 2d) although the carbene ligand has a π-stabilizing OH group. In contrast to the Fischer complexes, the carbene carbons atoms of the Schrock complexes **5** and **11** are shielded by continous areas of charge concentration (Figures 2f and 2h). The carbene ligands of **5** and **11** have Laplacian distributions that are similar to those of ($^3B_1$) CH_2, while the carbene ligand of **1** resembles ($^1A_1$) CH_2.

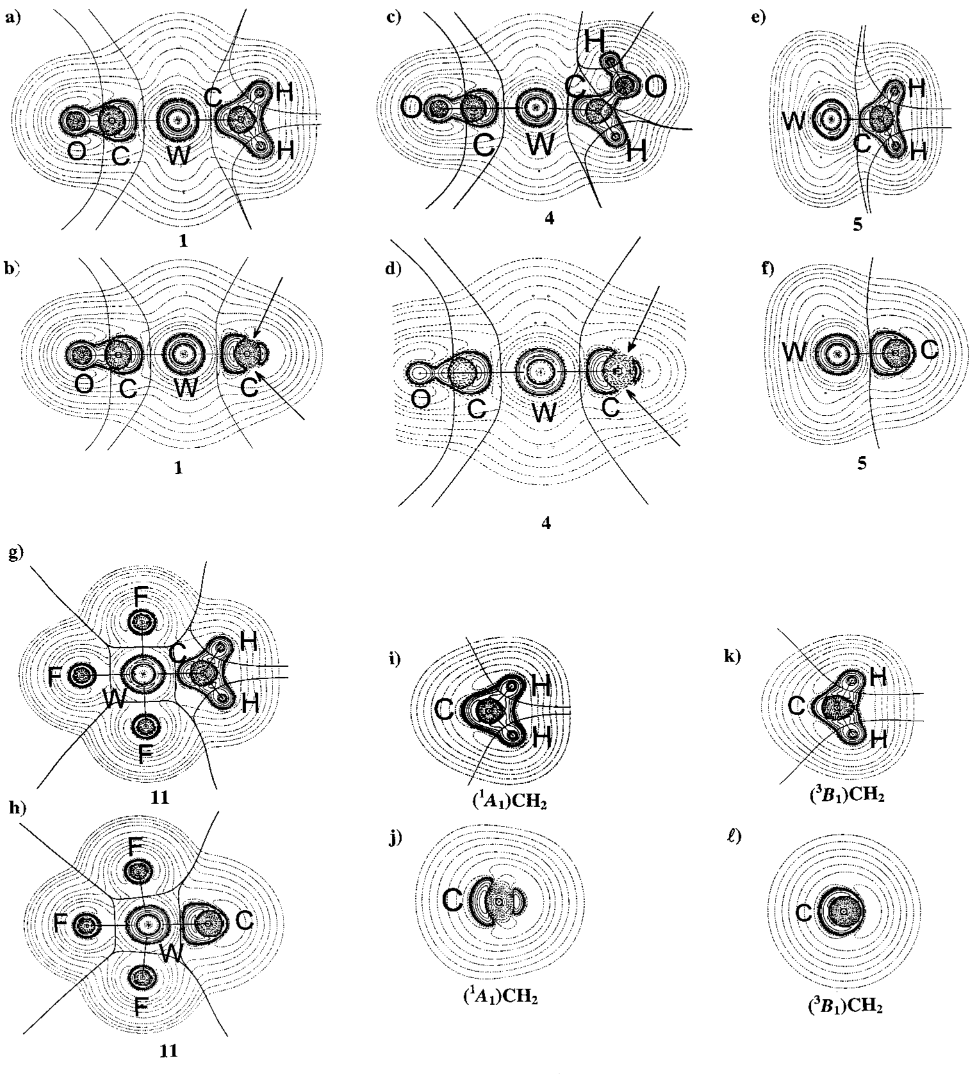

Figure 2. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/II of a) **1** in the plane of the carbene ligand; b) **1** perpendicular to the plane of the carbene ligand; c) **4** in the plane of the carbene ligand; d) **4** perpendicular to the plane of the carbene ligand; e) **5** in the plane of the carbene ligand; f) **5** perpendicular to the plane of the carbene ligand; g) **11** in the plane of the carbene ligand; h) **11** perpendicular to the plane of the carbene ligand; i) free ($^1A_1$) CH_2 in the molecular plane; j) free ($^1A_1$) CH_2 perpendicular to the molecular plane; k) free ($^3B_1$) CH_2 in the molecular plane; l) free ($^3B_1$) CH_2 perpendicular to the molecular plane. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$); solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$). The solid lines connecting the atomic nuclei are the bond paths; the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points $\mathbf{r}_c$. The large arrows in b) and d) show the hole in the valence sphere of the carbene ligand that is prone to attack by a nucleophilic agent.

A closer examination of Figure 2 shows that the position of the bond critical point ($\mathbf{r}_c$) of the W–carbene bond is, in case of the Schrock complexes **5** and **11**, closer to the charge concentration of the carbene carbon atoms compared with the Fischer complexes **1** and **4**. This is important, because the calculated values at the bond critical point can be used to analyze and classify the bond.[18, 43] The calculated values given in Table 4 show that the W–carbene bonds of the Fischer and Schrock complexes are very different. Firstly, the energy density at the bond critical point $H(\mathbf{r}_c)$ of the W–carbene bond has much higher

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Table 4. Results of the topological analysis of the electron density distribution at the MP2/II level.[a]

	Bond	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	$H(\mathbf{r}_c)$	ε_c	Bond order[b]	dc[c]
1	W–C2	0.885	6.580	–0.382	0.122	1.18	0.481
	W–C5	0.700	9.453	–0.198	0.115	0.82	–
	W–C13	0.632	8.327	–0.164	0.512	0.76	–
2	W–C2	0.775	9.446	–0.256	0.154	0.93	0.489
	W–C5	0.700	9.809	–0.197	0.032	0.84	–
	W–C13	0.667	9.376	–0.178	0.291	0.81	–
3	W–C2	0.873	8.216	–0.355	0.127	1.10	0.515
	W–C5	0.702	9.757	–0.199	0.072	0.84	–
	W–C9	0.629	8.652	–0.159	0.383	0.75	–
4	W–C2	0.770	7.464	–0.272	0.123	0.93	0.490
	W–C5	0.701	9.769	–0.198	0.044	0.86	–
	W–C9	0.670	9.139	–0.184	0.224	0.82	–
5	W–C	1.374	0.920	–0.940	0.549	1.71	0.444
	W–F	1.018	20.417	–0.242	0.093	0.72	–
6	W–C	1.267	3.969	–0.793	1.147	1.54	0.464
	W–F	1.024	20.669	–0.247	0.140	0.74	–
7	W–C	1.404	0.576	–0.973	0.500	1.82	0.440
	W–Cl	0.655	5.639	–0.172	0.080	0.90	–
8	W–C	1.392	1.099	–0.956	0.486	1.85	0.441
	W–Br	0.553	3.195	–0.159	0.063	0.97	–
9	W–C	1.412	1.371	–0.978	0.450	1.87	0.443
	W–I5	0.484	1.178	–0.155	0.053	1.11	–
	W–I6	0.427	1.453	–0.126	0.018	1.03	–
10	W–C	1.289	1.991	–0.831	0.530	1.67	0.451
	W–O5	0.958	14.665	–0.273	0.195	0.82	–
	W–O6	0.911	14.997	–0.237	0.105	0.79	–
	W–O7	0.958	14.665	–0.274	0.195	0.78	–
11	W–C	1.184	3.589	–0.702	0.666	1.48	0.464
	W–F5	0.992	20.212	–0.212	0.036	0.66	–
	W–F7	0.897	17.427	–0.168	0.104	0.49	–
12	W–C	1.043	7.044	–0.530	0.393	1.57	0.476
	W–F5	0.934	18.769	–0.181	0.094	0.60	–
	W–F9	0.830	16.998	–0.134	0.240	0.58	–

[a] Electron density at the bond critical points in the carbene complexes $\rho(\mathbf{r}_c)$(e Å^{-3}), Laplacian of electron density at the bond critical point $\nabla^2\rho(\mathbf{r}_c)$ (e Å^{-5}), electron energy density $H(\mathbf{r}_c)$ (Hartree Å^{-3}), and ellipticity ε_c. [b] Bond order according to Cioslowski and Mixon.[45] [c] Position of the bond critical point given by $dc = (\mathbf{r}_c - \mathrm{C}_{\mathrm{carbene}})/(\mathrm{C}_{\mathrm{carbene}} - \mathrm{W})$.

negative values for **5**–**12** than for **1**–**4**. It has been shown that shared-electron (covalent) bonds have negative energies at the bond critical point, while closed-shell interactions (ionic bonds or van der Waals interactions) have $H(\mathbf{r}_c)$ values ≥ 0.[43] The $H(\mathbf{r}_c)$ values of the W–carbene bonds of **1**–**4** are comparable in magnitude with the W–CO donor–acceptor bonds, while the W–carbene bonds of **5**–**12** have much more negative $H(\mathbf{r}_c)$ values than the W–X bonds (X = halogen or oxygen), thereby indicating a larger degree of bond covalency.

Secondly, the calculated ellipticities (ε_c), which are a measure of the double-bond character,[44] show that the W–carbene bonds of the Schrock complexes **5**–**12** have a much higher double-bond character than the Fischer complexes **1**–**4**. The higher W–carbene double-bond character of the Schrock complexes is supported by the calculated bond orders, which have values between 1.48 (for **11**) and 1.87 (for **9**), while the Fischer complexes have bond orders for the W–carbene bonds between 0.93 (for **2** and **4**) and 1.18 (for **1**). Also the values for the electron densities $\rho(\mathbf{r}_c)$ and the Laplacian $\nabla^2\rho(\mathbf{r}_c)$ at the bond critical points are clearly different for the Fischer and Schrock complexes.

Additional information about the W–carbene bonds is given by the results of the NBO analysis, which are listed in Table 5. Again, there are typical differences between the Fischer and Schrock complexes. The optimal Lewis structure predicted by the NBO-partitioning scheme for the Fischer complexes **1** and **3** has a W–carbene σ and a π bond, while **2** and **4**, which are more realistic models for a Fischer complex, have only a σ bond. The W–carbene σ bond of **1**–**4** is clearly polarized towards the carbon end (only 23%–28% are at the tungsten end), while the W–carbene π bond of **1** and **3** is polarized (63% and 67%) toward W. The NBO-bonding pattern for **2** and **4** suggests that the W–carbene π bond is even more polarized towards the metal end, because the optimal Lewis structure has a tungsten lone-pair d(π) orbital rather than a π bond. The calculated hybridization shows that the σ bond has mainly d character at the tungsten end, while the π bond at tungsten is purely d(W). The carbene ligand of the Fischer complexes carries only a small partial charge between −0.13 and +0.13.

It is interesting to note that the population of the p(π) AO of the CH_2 carbene carbon atom in **1** (0.67) is very similar to those of the CHF, CF_2, and CHOH ligands in **2**–**4** (Table 5). This is in agreement with the Laplacian of **1** and **4** in the π plane of the carbene ligands, which showed holes in the electron concentration of both molecules. This is surprising, because **4** is experimentally a clearly more stable Fischer complex than **1**, which is usually explained with the stabilization of the p(π) orbital of the carbene carbon atom by the substituent. The NBO results suggest that the higher stability of **4** relative to **1** is a kinetic effect. Breaking the W–carbene bond of **4** retains the electronic stabilization of the carbene ligand by donation of the OH substituent into the p(π) orbital, while the only stabilization of the carbene through metal →carbene π back-donation is lost when the W–carbene bond of **1** is stretched. This makes the reaction of the carbene ligand of **1** with a nucleophilic agent more favorable compared with that of **4**.

The NBO results of the Schrock complexes **5**–**12** are very different to those of the Fischer complexes **1**–**4**. i) All Schrock complexes have W–carbene σ and π bonds that are both polarized towards the carbon end. The calculated polarization of the π bond is in agreement with the previous study of Taylor and Hall, who found that the π electrons in Fischer complexes are polarized towards the metal, while in the Schrock complex they are more equally distributed.[10] The d(W) AOs contribute the largest parts of the W–carbene σ and π bonds at the tungsten end. It is interesting to see that the polarization of the σ bonds of the neutral Schrock complexes **5**–**10** is very similar to that of the respective π bonds. ii) The carbene ligands of **5**–**12** carry a distinct negative partial charge. iii) The population of the p(π) orbital of the carbene carbon atoms is significantly higher (1.09–1.20) in the Schrock complexes than in the Fischer complexes. This explains why the Laplacian of the electron-density distribution of the Schrock complexes have an area of electron concentration around the carbene carbon atoms, while the Fischer complexes have a hole in the π direction. Thus, the NBO analyses of **1**–**12** complement nicely the results of the topological analysis of the electron-density

Table 5. Results of the NBO analysis of the tungsten carbene complexes at the MP2/II level.

	AO occupation of the tungsten atom			W–C bond					Charge		p(π)
	6s	5d	6p	Occup.	%W	%s	%p	%d	W	CXY[a]	$C_{carbene}$[b]
1	0.53	5.86	0.02	σ:1.77	24.51	11.5	11.1	77.4	−0.41	−0.13	0.67
				π:1.68	62.90	0	0	100			
2	0.50	6.06	0.02	σ:1.91	28.19	31.6	0	68.4	−0.57	+0.04	0.67
3	0.49	5.97	0.02	σ:1.77	22.66	10.3	16.3	73.4	−0.48	−0.04	0.67
				π:1.66	67.27	0	0	100			
4	0.49	6.02	0.02	σ:1.90	27.95	30.8	0	69.2	−0.54	+0.13	0.61
5	0.33	3.16	0.05	σ:1.94	38.77	29.7	0	70.3	+2.41	−0.38	1.20
				π:1.74	33.82	0	29.2	70.8			
6	0.37	3.22	0.07	σ:1.94	34.75	29.3	0	70.7	+2.32	−0.33	1.13
				π:1.73	39.33	0	21.5	78.5			
7	0.45	4.37	0.05	σ:1.94	41.47	18.0	0	81.6	+1.06	−0.24	1.11
				π:1.95	48.63	0	9.9	89.9			
8	0.50	4.72	0.07	σ:1.94	41.10	19.5	0	80.5	+0.63	−0.24	1.10
				π:1.80	42.43	0	21.4	78.6			
9	0.57	4.97	0.10	σ:1.94	41.11	15.0	0	85.0	+0.27	−0.25	4.09
				π:1.90	45.67	0	10.1	89.9			
10	0.36	3.46	0.04	σ:1.77	30.13	21.7	5.80	72.5	+2.10	−0.40	1.17
				π:1.68	33.27	0	29.0	71.0			
11	0.31	3.06	0.07	σ:1.94	27.71	35.3	0	64.7	+2.45	−0.63	1.19
				π:1.94	42.70	0	0	100			
12	0.32	3.16	0.07	σ:1.93	24.38	35.0	0	65.0	+2.34	−0.54	1.12
				π:1.75	40.85	0	0	0			

[a] Partial charge of the carbene ligand. [b] Natural occupation of the 2p-π orbital of C.

distribution. This is gratifying, because the NBO analysis focuses on the orbital structure of the molecules, while the topological analysis considers the total electron-density distribution.

A final difference between the Fischer complexes **1**–**4** and the Schrock complexes **5**–**12** concerns the electronic configuration and the atomic partial charge at the metal. The tungsten 5d-shell population in the Fischer complexes is ≈ 6 electrons, and the small negative partial charges ≈ -0.5 are due to the population of the 6s orbital (Table 5). The calculated 5d population agrees with the formal notation of these compounds as W(6d) compounds with the oxidation state zero (i.e., W^0).[46] However, the concept of oxidation state is based on a formal assigments of the bonding electrons to the metal and the ligand. The NBO results for the Schrock complexes show that the formal charge is as low as +0.27 for **9**, which is very different to the formal charge of +6 for a W^{VI} compound. Nevertheless, the calculated partial charges indicate that the tungsten atom of the Schrock complexes is more positively charged and has a lower 5d population than the Fischer complexes. Please note that the negatively charged complexes **11** and **12** have practically the same partial charge at the metal as the respective neutral compounds **5** and **6**. This is because the fluorine atoms carry most of the additional charge.

A bonding model that is very popular in the transition metal community, and which is frequently used to discuss the metal–ligand interactions in transition metal complexes, is the donor–acceptor bonding scheme introduced by Dewar, Chatt, and Duncanson.[5] This model considers the bonding interactions to arise from ligand → metal σ donation and metal → ligand π back-donation. Ligands are often classified with regard to their ability to act as a donor and/or an acceptor in a complex. The strength of the relative σ donation and π back-donation is usually estimated from experimental results, such as the shift of vibrational frequencies or rotational barriers of the metal–ligand bond. We developed the CDA method as a theoretical tool to quantify the relative amount of σ donation and π back-donation. Details about the method and its application are given in Computational Methods and in the literature.[20, 32]

Table 6. CDA results for the carbene complexes **1**–**12** at the MP2/II level.

	Carbene → WL_n donation	L_nW → Carbene back-donation	LnW ↔ Carbene repulsion	Residue term
1	0.314	0.282	−0.370	0.016
2	0.369	0.219	−0.289	0.027
3	0.324	0.268	−0.325	0.017
4	0.417	0.177	−0.285	0.032
5	0.013	−0.084	0.209	0.380
6	0.440	0.223	−0.311	0.351
7	−0.031	−0.058	0.141	0.416
8	−0.014	−0.074	0.113	0.406
9	0.343	−0.044	−0.271	0.423
10	0.016	−0.069	0.221	0.396
11	0.451	0.234	−0.334	−0.006
12	0.440	0.223	−0.311	0.005
$[W(CO)_6]$[a]	0.315	0.233	−0.278	

[a] Ref. [32d]. CO → $W(CO)_5$ donation, $W(CO)_5$ → CO back-donation, and $W(CO)_5$ ↔ CO repulsive polarizations are given.

Table 6 shows the CDA results of **1**–**12**. The result for the carbonyl ligand in $[W(CO)_6]$ is given for comparison. The data for the Fischer complexes **1**–**4** indicate that the carbene ligand is a stronger electron donor than electron acceptor. We want to emphasize that the *absolute* numbers of the L → metal donation and metal → ligand back-donation are not important, but rather the *relative* values. The donation/back-donation ratio for **1**–**4** suggests that the carbene ligands have the order of acceptor strength $CH_2 < CHF < CF_2 < CHOH$. The repulsive polarization term is always negative. This is reasonable, because it gives the amount of electronic charge that is removed from the overlapping area of occupied orbitals of the ligand and the metal fragment. The residue term is ≈ 0. This means that the complexes **1**–**4** can be reasonably interpreted as complexes between the closed-shell fragments $W(CO)_5$ and CXY.

A comparison of the relative donor/acceptor ability of the CHOH ligand of **4**, which is a realistic model for a carbene ligand of a Fischer complex, and CO is very interesting. Fischer concluded from the observed C–O stretching frequencies of $[(CO)_5CrL]$ (where L = CO or $C(OCH_3)(Ph)$) that the carbene ligand possesses a substantially larger σ-donor/π-acceptor ratio than CO.[38] Table 6 shows that the CDA results are in agreement with Fischer's suggestion. The calculated σ-donor/π-acceptor ratio of CHOH in **4** is 0.417/0.177 = 2.36, the value for CO in $[W(CO)_6]$ is 0.315/0.233 = 1.35.

The CDA results may lead to the conclusion that the carbene →metal σ donation is clearly more important for the binding energy than the metal →carbene π back-donation. This is not correct. The carbene lone-pair orbital overlaps not only with empty metal orbitals, but also with occupied metal d orbitals, which leads to repulsive interactions. Jacobsen and Ziegler[13b] gave a breakdown of the binding energies in $[(CO)_5M(CH_2)]$ (M = Cr, Mo, W); this shows that the π contribution to the $(CO)_5W{=}CH_2$ bond is 51.8 kcal mol^{-1}, the σ contribution is 54.7 kcal mol^{-1}, and the calculated total bond energy of 71.8 kcal mol^{-1}. It follows that most of the σ-type bonding between the carbene ligand and the metal is compensated by repulsive interactions. However, there are very stable transition metal carbene complexes in which the carbene ligand acts mainly as σ donor. N-heterocyclic carbenes,[47] which were first isolated by Arduengo,[48] form very stable transition metal complexes with various early and late transition metals.[49] Analysis of the peculiar bonds in these complexes has shown that there is little metal →carbene π back-donation and yet the calculated bond strengths may be as high as 82.8 kcal mol^{-1} in ClAu–$C_{carbene}$.[50]

The CDA results for the neutral Schrock complexes **5**–**10**, which are calculated from the interactions between closed-shell fragments WL_4 and carbene ligand, differ substantially from the data for the Fischer complexes. The donation and back-donation terms are in some cases negative, which is a physically unreasonable result. More striking are the results for the residue term, which gives the contributions of the unoccupied orbitals of the fragments to the electronic structure of the respective complex. The residue terms are in all cases large positive numbers! This means that the electronic structure of **5**–**10** should *not* be discussed in terms of donor–acceptor interactions between the closed-shell carbene ligand and the metal fragment. Inspection of the orbitals that make up the residue term shows that the p(π) AO of the carbene carbon atom, which is unoccupied in the CH_2 fragment, is a large contributor to the metal–carbene interactions. This means that the W–carbene bonds of **5**–**10** should be discussed in terms of interactions between the ($^3B_1$) triplet state of the carbene and the triplet ground state of WCl_4. The CDA result for **5**–**10** are in agreement with the bonding model suggested by Taylor and Hall for Schrock complexes.[10]

The CDA results for the negatively charged Schrock complexes **11** and **12** suggest that the metal–carbene bonding in these compounds can be interpreted as donor–acceptor interactions between the closed-shell fragments WCl_5^- and CX_2. This is not very surprising, because WCl_5^- has a singlet ground state, while WCl_4 is a triplet. The residue term of **11** and **12** is ≈ 0. CH_2 and CF_2 are even better donor ligands in **11** and **12** than in **1** and **2** (Table 6). The CDA results for **11** and **12** show that a transition metal in a Schrock-type high oxidation state may have a donor–acceptor carbene bond just like a Fischer-type carbene complex, which has a metal in a low oxidation state. We want to point out that a similar situation exists for transition metal complexes with π-bonded ligands such as ethylene or acetylene. The analysis of the bonding situation in $[W(CO)_5L]$ complexes (L = ethylene, acetylene) with the CDA method showed that these compounds should be considered as donor–acceptor complexes, while $[WCl_4L]$ compounds should be interpreted as metallacyclic molecules.[32a,b] The corresponding anions $[WCl_5L]^-$ can be considered as donor–acceptor complexes.

Summary and Conclusion

The calculated geometries of **1**–**12**, which are in very good agreement with experimental values of related compounds, show that the W–carbene bonds of the Fischer complexes **1**–**4** are significantly longer than those of the Schrock complexes **5**–**12**. The metal–carbene bond dissociation energies are rather high. The Schrock complexes have slightly higher or similar bonding energies to those of the Fischer complexes. The shorter W–carbene bonds of the Schrock complexes are explained by the smaller atomic radius of W^{VI} compared with W^0, and from the different bonding interactions. The higher stability of the Fischer carbene complexes with π-donor substituents at the carbene ligand has a kinetic origin and is not due to stronger metal–carbene bonding. The $(CO)_5W$–CH_2 bond in **1** is shorter and stronger than the $(CO)_5W$–CH(OH) bond in **4**.

The analysis of the bonding situation shows significant differences between Fischer and Schrock complexes. The topological analysis of the electron-density distribution reveals that the W–carbene bonds of Fischer complexes are less covalent, and have lower double-bond character and bond orders; this is an indication of W–carbene single bonds. The Schrock complexes have a much more covalent W–carbene bond and a larger bond order with a higher double-bond character. The Fischer complexes have carbene carbon atoms that are electron deficient in the p(π) direction. This is shown by the Laplacian distribution, which shows an area of electron depletion in the p(π) direction, and by the occupation of the p(π) of the carbene carbon atom of **1**–**4**. The Schrock complexes **5**–**12** have a significantly higher p(π) population at the carbene carbon atom. The NBO analysis of the Schrock complexes gives W–carbene σ and π bonds that are both polarized towards the carbon end.

The CDA results suggest that the Fischer complexes **1–4** can be interpreted as metal–carbene donor–acceptor complexes, in which the carbene ligand has a substantially larger σ-donor/π-acceptor ratio than CO. The W–carbene bonds of the neutral Schrock complexes **5–10** should be discussed in terms of interactions between triplet WX$_4$ and ($^3B_1$) carbene. The bonding in the negatively charged Schrock complexes **11** and **12**, however, can be interpreted in terms of donor–acceptor interactions between singlet WCl$_5^-$ and ($^1A_1$) CX$_2$.

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