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

Sergei F. Vyboishchikov and Gernot Frenking*

Abstract: Quantum mechanical ab initio calculations are reported for 13 low-valent (Fischer-type) and 13 high-valent (Schrock-type) tungsten carbyne complexes. The geometries have been optimized at the HF and MP2 levels of theory with relativistic effective core potentials for the heavy atoms with valence basis sets of DZP quality. Tungsten–carbyne bond dissociation energies are predicted at CCSD(T) with MP2 optimized geometries. The electronic structure of the complexes and the metal–ligand bonding have been analyzed with the help of the NBO method, the topological analysis of the electron-density distribution and the CDA method. The L_nW-CR bonds of the Fischer and Schrock carbyne complexes are much stronger than those of related carbene complexes. The strength of the L_nW-CR bond is strongly influenced by the nature of R. Substituents with p(π) lone-pair electrons yield lower bond dissociation energies. This can be explained by a bonding model that uses the $^1\Sigma^+$ ground state of CR^+ as reference state for the ligand of the Fischer complexes and the $^4\Sigma^-$ excited state of CR as reference state for the ligand of Schrock complexes.

Keywords: ab initio calculations · carbyne complexes · donor–acceptor interactions · metal–ligand interactions · tungsten

Introduction

In the preceding paper of this issue we presented a theoretical study about structure and bonding of transition metal (TM) carbene complexes in which the metal is in a low (Fischer-type) or high oxidation state (Schrock-type).[1] It happened that the same authors who introduced the two classes of TM compounds that have a metal–carbon double bond were also the first to report the synthesis of analogous TM compounds with metal–carbon triple bonds. In 1973, Fischer et al. succeeded in isolating $[Br(CO)_4W(CMe)]$.[2] Five years later, Schrock reported the synthesis of $[CpCl(PMe_3)Me-Ta(CPh)]$.[3] Although the distinction between the two types of carbyne or alkylidyne complexes is less clear-cut than in case of the carbene complexes, it has become a useful model to explain the differences in the chemical behaviour of Fischer and Schrock carbyne complexes. Generally, the carbyne ligand of Fischer complexes displays electrophilic behavior, while Schrock alkylidene complexes usually exhibit nucleophilic reactivity.[4] Again, the differences are not as pronounced as the in case of the carbene complexes. An important difference between Fischer-type carbene and carbyne complexes is that the latter compounds do not need a π-stabilizing substituent R at the carbyne ligand L_nMCR in order to become isolable.[6, 7]

Experimental research on carbyne complexes increased considerably after the discovery that $[(t\text{BuO})_3W(CMe)]$ is an active catalyst in alkyne metathesis reactions.[5] Fischer and Schrock carbyne complexes have now become versatile compounds for many synthetic and catalytic processes.[4, 6, 7] In contrast to the intensive experimental work on carbyne complexes, only few theoretical studies have been devoted to this important class of compounds. In particular, no accurate ab initio investigations of alkylidene complexes have been published so far. Kostic and Fenske have reported semiempirical Fenske–Hall type calculations for several Fischer-type carbyne complexes.[8] Nakatsuji published Hartree–Fock (HF) calculations for metal–carbon multiple–bonded molecules including the Fischer carbyne complexes $[(CO)_5Cr(CH)]^+$ and $[Cl(CO)_4Cr(CH)]$.[9] The most advanced study of carbyne complexes was published by Benard et al., who investigated $[Cl(CO)_4Cr(CH)]$ at the CASSCF level of theory.[10]

Most theoretical work has focused on the analysis and interpretation of the metal≡carbon triple bond.[8–10] R. Hoffmann has shown that valuable insight into the bonding situation of TM compounds can be won by use of the simple

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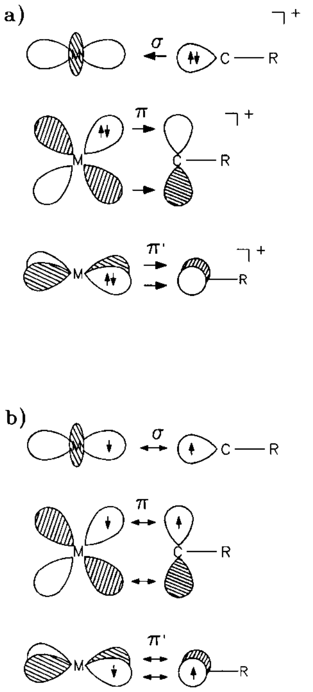
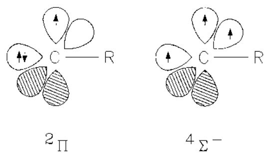
extended Hückel theory (EHT) method.[11] In spite of the qualitative nature of the method, important aspects of the bonding features can be revealed. The most detailed study in this spirit that focuses on carbyne complexes has been presented by P. Hofmann, who analyzed the metal–carbyne bonds in Fischer and Schrock complexes in terms of orbital interactions between the carbyne ligand and the metal fragment.[12] Because the neutral carbyne ligand is a radical, the discussion of carbyne complexes in terms of donor–acceptor interactions from the Dewar–Chatt–Duncanson (DCD) model[13] leads to a somewhat arbitrary choice of the appropriate closed-shell model ligand. P. Hofmann chose the positively charged CR^+ as a ligand model, because the orbital picture of the $^1\Sigma^+$ ground state[35] of CH^+ and related analogues (CR^+) is very convenient for an orbital interaction diagram with the orbitals of $[X(CO)_4M]^-$, which yields a model electronic structure for the Fischer carbyne complexes $[X(CO)_4M(CR)]$.[12] Also, the orbital interaction diagram becomes very similar to the DCD model for Fischer carbene complexes as discussed before.[1] Scheme 1a shows that the carbyne ligand CR^+ in the singlet electronic ground state has a σ-donor orbital and a degenerate p(π)-acceptor orbital; these are perfectly suited for symbiotic donation/back-donation interactions with the metal fragment.



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

We want to mention that an alternative model involves CR^{3-} as carbyne ligand; this ligand has the degenerate p(π) orbital occupied with four electrons and thus is a pure donor ligand. This model is sometimes used to describe the metal–carbon interactions in Schrock carbyne complexes.[4] We will use the $^1\Sigma^+$ ground state of CR^+ for the description of the metal–carbyne bond in Fischer complexes, because it is closely related to the model that was used for Fischer carbene complexes.[1] For the description of the Schrock carbyne complexes we have also chosen a model that is related to the carbene complexes. Guided by the results of charge-density analysis (CDA) that are described below, it became clear that the metal–carbyne bond of Schrock-type complexes should not be discussed in terms of closed-shell interactions. Homolytic cleavage of the M≡C triple bond in L_3MCR yields the metal fragment L_3M and CR in a quartet state. A quartet state is probably the electronic ground state for many L_3M fragments.[14] Scheme 1b shows the dominant orbital interactions in Schrock-type carbyne complexes. CH has a $^2\Pi$ ground state, but the electronically excited $^4\Sigma^-$ state (Scheme 2) is only 15.9 kcal mol^{-1} higher in energy.[15] As shown below, the strength of the metal–carbyne bonds is related to the $^2\Pi \rightarrow {}^4\Sigma^-$ excitation energy of CR; similarly the $^1A_1 \rightarrow {}^3B_1$ excitation energy of CR_2 is related to the $L_nM{=}CR_2$ bond strength in Schrock-type carbene complexes.[1, 16]



Scheme 2. Schematic representation of the $^2\Pi$ ground state and $4\Sigma^-$ excited state of carbynes CR.

In this paper we report the theoretical results for the Fischer carbyne complexes $[F(CO)_4W(CH)]$ (**1**), $[F(CO)_4W(CF)]$ (**2**), $[Cl(CO)_4W(CH)]$ (**3**), $[Br(CO)_4W(CH)]$ (**4**), $[Br(CO)_4W(CMe)]$ (**5**), $[Br(CO)_4W(CF)]$ (**6**), $[Br(CO)_4W\{C(NH_2)_2\}]$ (**7**), $[I(CO)_4W(CH)]$ (**8**), $[Me(CO)_4W(CH)]$ (**9**), $[Cl(PH_3)_4W(CH)]$ (**10**), $[Cl(PH_3)_4W(CMe)]$ (**11**), $[Me(PH_3)_4W(CH)]$ (**12**), $[Me(PH_3)_4W(CMe)]$ (**13**), and for the Schrock carbyne complexes $[F_3W(CH)]$ (**14**), $[F_3W(CMe)]$ (**15**), $[Cl_3W(CH)]$ (**16**), $[Cl_3W(CMe)]$ (**17**), $[Cl_3W(CF)]$ (**18**), $[Cl_3W\{C(NH_2)_2\}]$ (**19**), $[Me_3W(CH)]$ (**20**), $[Me_3W(CMe)]$ (**21**), $[(OH)_3W(CH)]$ (**22**), $[(OH)_3W(CMe)]$ (**23**), $[Cl_4W(CH)]^-$ (**24**), $[Cl_4W(CMe)]^-$ (**25**), and $[(OH)_4W(CH)]^-$ (**26**). The geometries of **1**–**26** were optimized at the HF and MP2 levels of theory and the metal–carbyne bond strengths of selected compounds are theoretically predicted at CCSD(T). The metal–carbyne bonding was analyzed by the topological analysis of the electron-density distribution[17] and natural bond orbital analysis (NBO).[18] Additional information about the tungsten–carbyne interactions was obtained from the charge-density analysis (CDA) of **1**–**26**.[19, 20] The performance of the CDA for analyzing donor–acceptor interactions has been reported in several studies of transition metal and main-group complexes.[21]

Concerning the classification of the carbyne complexes **1**–**26** as Fischer- or Schrock-type complexes, we refer to the Introduction of our work about carbene complexes in the preceding paper in this issue.[1] Using the same reasoning given there, we call the low-valent compounds **1**–**13** Fischer complexes and the high-valent compounds **14**–**26** Schrock complexes.

Computational Methods

The same theoretical methods were used in this study as in our previous work about TM carbene complexes.[1] Geometries were optimized at HF/I, HF/II, and MP2/II. Because more structures and larger molecules have been considered in this work than in the investigation of carbene complexes, the vibrational frequencies were only calculated at HF/I, and metal–carbyne bond dissociation energies could only be calculated for selected compounds. All structures reported here are minima on the potential energy surfaces at HF/I. Further details about the theoretical methods can be found in the preceding paper.[1]

Results and Discussion

Geometries and bond energies: The optimized structures of the carbyne complexes **1**–**26** are shown in Figure 1. Table 1

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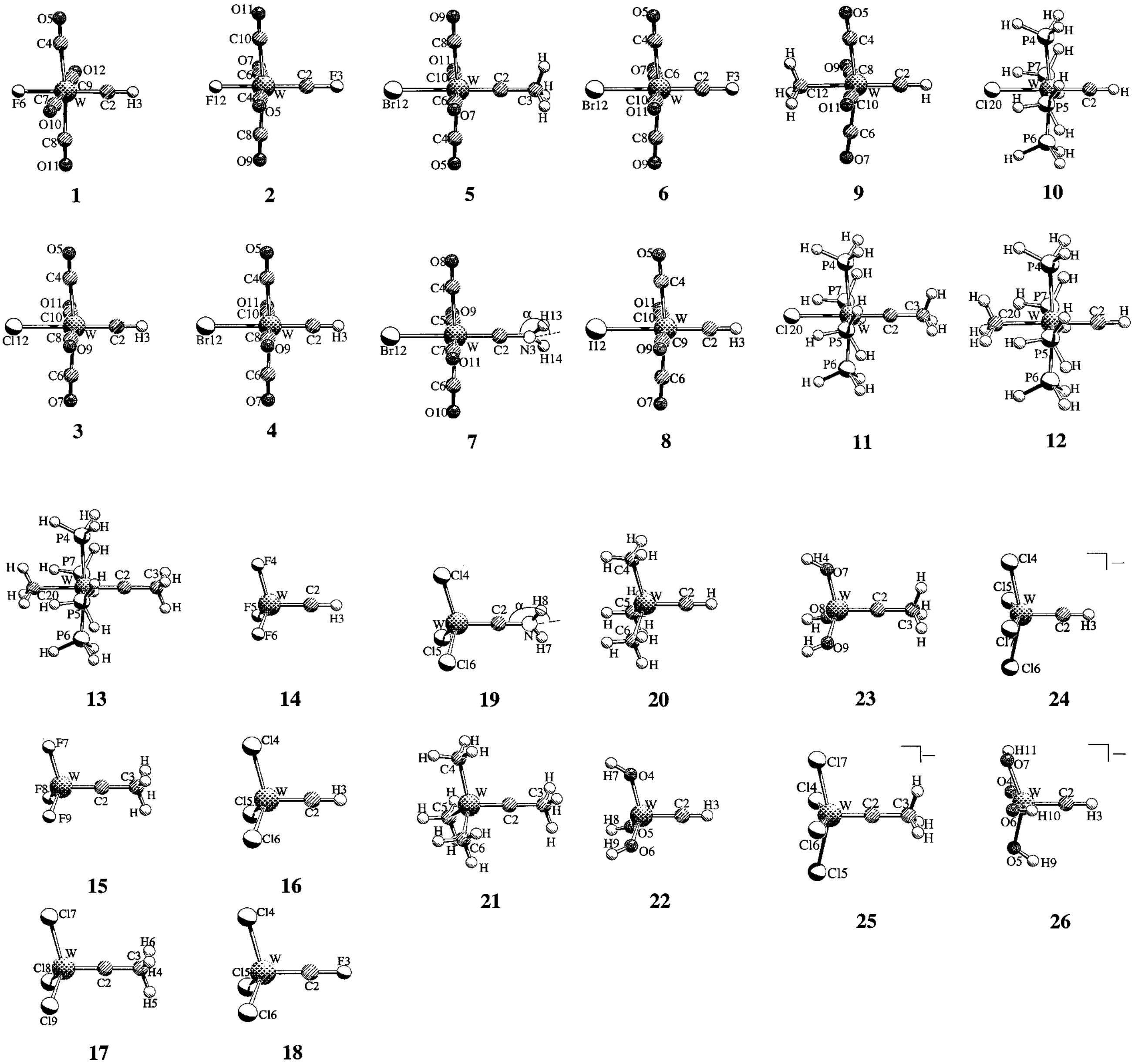


Figure 1. Optimized structures at MP2/II of the Fischer carbyne complexes **1**–**13** and the Schrock carbyne complexes **14**–**26**. For the geometrical data see Tables 1 and 2.

gives the most important geometrical variables at the three levels of theory for the Fischer complexes **1**–**13**. The geometries for the Schrock complexes **14**–**26** are listed in Table 2.

The theoretically predicted W–carbyne bond lengths of the Fischer carbyne complexes **1**–**13** at MP2/II are between 1.840 Å (for **10**) and 1.873 Å (for **13**). This is significantly shorter than the calculated W–carbene distances for the Fischer carbene complexes reported in the preceding paper (2.029–2.088 Å).[1] There is an interesting difference between the computational results at different levels of theory for the Fischer carbyne and carbene complexes. While the W–carbene bond lengths at MP2/II are always significantly shorter than at the HF level,[1] the MP2/II distances for the W–carbyne bonds are always clearly longer than the HF values (Table 1). This computational result has some relevance for the interpretation of the chemical bond. It is known that bond lengths of donor–acceptor bonds are always shorter at the MP2 level than at HF with the same basis set,[22] while classical covalent multiple bonds become longer when going from HF to MP2.[23] The results for the W–carbyne bond lengths at HF and MP2 indicate that the bond has more the character of a normal multiple bond than a donor–acceptor bond. We remind the reader that a model for the W–carbyne bond as donor–acceptor bond necessitates the use of charged fragments such as L_nM^- and CR^+, while the model fragments for the W–carbene bond L_nW, and CR_2, are the actual dissociation products.

Table 2 shows that the W–carbyne bond lengths of the Schrock complexes **14**–**26** are clearly shorter (1.757 Å–1.795 Å) than those of the Fischer complexes **1**–**13**. They are also ≈0.1 Å shorter than the calculated W–carbene bond lengths of the Schrock complexes.[1] Like the Fischer com-

Table 1. Optimized geometries of the Fischer carbyne complexes **1**–**13**. Bond lengths in Å, angles in degrees.

	Symmetry	Geometrical parameter	HF/I	HF/II	MP2/II
[F(CO)$_4$W(CH)] (**1**)	C_{4v}	W–C2	1.816	1.809	1.861
		W–F	1.981	2.021	2.023
		W–C4	2.137	2.159	2.097
		∢C2-W-C4	90.0	932	92.2
[F(CO)$_4$W(CF)] (**2**)	C_{4v}	W–C2	1.817	1.818	1.870
		W–F	1.972	2.010	2.007
		W–C4	2.134	2.155	2.093
		∢C2-W-C4	91.2	94.0	92.9
[Cl(CO)$_4$W(CH)] (**3**)	C_{4v}	W–C2	1.806	1.794	1.845
		W–Cl	2.526	2.553	2.514
		W–C4	2.139	2.156	2.095
		∢C2-W-C4	92.8	93.9	94.1
[Br(CO)$_4$W(CH)] (**4**)	C_{4v}	W–C2	1.804	1.805	1.843
		W–Br	2.706	2.712	2.674
		W–C4	2.139	2.156	2.094
		∢C2-W-C4	92.8	93.9	94.1
[Br(CO)$_4$W{C(CH$_3$)}] (**5**)	C_s	W–C2	1.811	1.801	1.849
		W–C4	2.131	5.150	2.090
		W–C6	2.132	2.149	2.090
		W–C8	2.132	2.150	2.090
		W–Br	2.713	2.736	2.677
		C2–C3	1.477	1.477	1.473
		∢C2-W-C4	92.6	93.8	93.9
		∢C2-W-C6	92.7	93.7	93.8
		∢C2-W-C8	92.7	93.8	93.8
		∢C2-W-Br	180.0	180.0	180.0
[Br(CO)$_4$W(CF)] (**6**)	C_{4v}	W–C2	1.815	1.805	1.854
		W–Br	2.677	2.712	2.652
		W–C4	2.133	2.151	2.088
		∢C2-W-C4	93.8	94.3	94.5
[Br(CO)$_4$W{C(NH$_2$)}] (**7**)	C_s	W–C2	1.854	1.843	1.849
		W–C4	2.123	2.141	2.083
		W–C5	2.123	2.141	2.081
		W–C7	2.123	2.141	2.078
		W–Br	2.707	2.729	2.674
		C2–N	1.313	1.313	1.353
		∢C2-W-C4	92.7	93.6	94.3
		α[a]	180	180	144.0
[I(CO)$_4$W(CH)] (**8**)	C_{4v}	W–C2	1.802	1.790	1.841
		W–I	2.952	2.947	2.880
		W–C4	2.136	2.154	2.093
		∢C2-W-C4	92.8	93.6	94.1
[(CH$_3$)(CO)$_4$W(CH)] (**9**)	C_s	W–C2	1.835	1.819	1.870
		W–C4	2.118	2.137	2.076
		W–C6	2.120	2.139	2.077
		W–C8	2.119	2.138	2.077
		W–C12	2.307	2.365	2.355
		∢C2-W-C4	93.4	94.2	96.5
		∢C2-W-C6	94.2	94.7	97.1
		∢C2-W-C8	93.7	94.4	96.5
		∢C2-W-C12	179.3	179.2	180.7
[Cl(PH$_3$)$_4$W(CH)] (**10**)	C_{4v}	W–C2	1.804	1.790	1.840
		W–Cl	2.601	2.618	2.536
		W–P	2.523	2.530	2.454
		∢C2-W-P	93.5	93.9	93.2
[Cl(Ph$_3$)$_4$W{C(CH$_3$)}] (**11**)	C_s	W–C2	1.807	1.795	1.844
		W–P4	2.519	2.525	2.449
		W–P5	2.520	2.524	2.449
		W–P6	2.519	2.524	2.449
		W–Cl	2.609	2.624	2.538
		∢C2-W-P4	93.7	94.2	93.2
		∢C2-W-P6	93.6	94.1	92.9
		∢C2-W-P8	93.5	94.1	92.7
		∢C2-W-Cl	179.9	180.0	179.8
[(CH$_3$)(Ph$_3$)$_4$W(CH)] (**12**)	C_s	W–C2	1.834	1.818	1.868
		W–P4	2.505	2.513	2.438
		W–P5	2.507	2.513	2.439
		W–P6	2.506	2.514	2.440
		W–C20	2.338	2.377	2.328
		∢C2-W-P4	92.2	92.9	93.6
		∢C2-W-P6	92.6	93.2	93.6
		∢C2-W-P8	93.4	93.9	94.7
		∢C2-W-C20	179.3	179.0	179.6
[(CH$_3$)(Ph$_3$)$_4$W{C(CH$_3$)}] (**13**)	C_s	W–C2	1.837	1.823	1.873
		W–P4	2.500	2.508	2.433
		W–P5	2.501	2.510	2.434
		W–P6	2.502	2.510	2.436
		W–C20	2.341	2.329	2.329
		∢C2-W-P4	92.40	92.7	92.7
		∢C2-W-P6	92.8	93.5	93.5
		∢C2-W-P8	93.5	94.9	94.9
		∢C2-W-C20	179.1	180.0	180.0

[a] Tilting angle of the amino group, see Figure 1.

plexes, the W–carbyne distances of **14**–**26** are significantly longer at MP2/II than at the HF level. The results at HF/I and HF/II are not very different. The L$_n$W-C-R bond angle of the carbyne ligand of **1**–**26** is always 180°. Experimental data shows that most carbyne complexes have a linear or nearly linear M-C-R moiety.[4, 6, 7] Deviations from a linear geometry are probably the result of solid-state effects or intermolecular interactions. Calculation of a recently reported[24] tungsten methylidyne complex with a W-C-H angle of 162.3° showed that the free compound has a linear methylidyne ligand.[25]

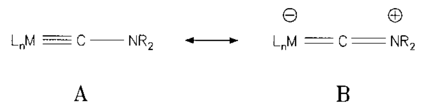
The agreement between the theoretically predicted geometries at MP2/II level and the experimental results is very good. The experimental W–carbyne distances of Fischer complexes taken from X-ray structure analysis are $\mathrm{W{-}C} = 1.82 \pm 0.04$ Å for **5** and $\mathrm{W{-}C} = 1.77 \pm 0.04$ Å for the CMe derivative of **8**.[26] An analysis of the vibrational spectra of [X(CO)$_4$(CMe)] (X = Cl, Br, I) showed that the W–carbyne stretching mode has nearly the same frequency in all three compounds.[27] This is in agreement with the calculated W–carbyne bond lengths of **3**, **4**, and **8**, which are very similar (Table 1). Other experimental values conform with the MP2/II data. For **5** the experimental value for the W–Br bond is 2.648 ± 0.006 Å (calcd 2.677 Å), the average W–CO bond length is 2.11 ± 0.05 Å (calcd 2.090 Å), and the C–Me bond length is 1.44 ± 0.06 Å (calcd 1.473 Å).[26] The W–I bond length of the CMe derivative of **8** is 2.867 ± 0.003 Å (calcd 2.880 Å). Theory and experimental are also in accord with the lengthening of the W–carbyne distance when the carbonyl ligands are substituted by phosphane. The experimental W–carbyne bond length of [Me(PMe$_3$)$_4$W(CMe)][28] is 1.891 ± 0.025 Å, the calculated value for the related Fischer complex **13** is 1.873 Å (Table 1). The experimental value for the W–carbyne bond length of [Cl(PMe$_3$)$_4$W(CH)][29] $\mathrm{W{-}C} = 1.84$ Å is the same as the theoretical value for **10** $\mathrm{W{-}C} = 1.840$ Å. The perfect agreement is of course fortuitous, but it shows that the theoretical results are quite reliable.

Table 2. Optimized geometries of the Schrock carbyne complexes **14–26**. Bond lengths in Å, angles in degrees.

	Symmetry	Geometrical parameter	HF/I	HF/II	MP2/II
$[F_3W(CH_2)]$ (**14**)	C_{3v}	W–C	1.713	1.717	1.761
		W–F	1.845	1.861	1.863
		∢C-W-F	102.9	105.9	104.6
$[F_3W\{C(CH_3)\}]$ (**15**)	C_{3v}	W–C	1.716	1.722	1.762
		W–F	1.85	1.869	1.868
		∢C-W-F	102.7	105.6	104.4
$[Cl_3W(CH)]$ (**16**)	C_{3v}	W–C	1.731	1.718	1.761
		W–Cl	2.269	2.291	2.265
		∢C-W-Cl	103.9	105.0	104.0
$[Cl_3W\{C(CH_3)\}]$ (**17**)	C_{3v}	W–C	1.735	1.725	1.758
		W–Cl	2.280	2.301	2.270
		∢C-W-Cl	103.1	104.3	103.5
$[Cl_3W(CF)]$ (**18**)	C_{3v}	W–C	1.747	1.738	1.767
		W–Cl	2.271	2.296	2.266
		∢C-W-Cl	103.2	104.4	104.2
$[Cl_3W\{C(NH_2)\}]$ (**19**)	C_1	W–C	1.782	1.766	1.757
		W–Cl4	2.286	2.305	2.267
		W–Cl5	2.286	2.306	2.276
		W–Cl6	2.302	2.322	2.276
		C–N	1.301	1.305	1.376
		∢C-W-Cl4	104.3	105.4	104.4
		∢C-W-Cl5	104.3	1.05.5	103.3
		∢C-W-Cl6	98.6	100.2	103.1
		α[a]	180	180	132.7
$[(CH_3)_3W(CH)]$ (**20**)	C_{3v}	W–C2	1.742	1.730	1.775
		W–C4	2.216	2.144	2.117
		∢C2-W-C4	103.8	104.4	102.8
$[(CH_3)_3W\{C(CH_3)\}]$ (**21**)	C_{3v}	W–C2	1.744	1.735	1.776
		W–C4	2.132	2.149	2.118
		∢C2-W-C4	103.3	104.0	102.6
$[(OH)_3W(CH)]$ (**22**)	C_{3v}	W–C	1.723	1.720	1.767
		W–O	1.887	1.925	1.928
		∢C-W-O	103.6	104.5	102.4
		∢W-O-H	135.7	118.7	114.9
$[(OH)_3W\{C(CH_3)\}]$ (**23**)	C_{3v}	W–C2	1.724	1.724	1.766
		W–O	1.898	1.932	1.931
		∢C-W-O	102.7	103.9	101.9
		∢W-O-H	131.9	117.7	114.5
$[Cl_4W(CH)]^-$ (**24**)	C_{4v}	W–C	1.725	1.714	1.764
		W–Cl	2.387	2.412	2.380
		∢C-W-Cl	101.8	102.6	101.5
$[Cl_4W\{C(CH_3)\}]^-$ (**25**)	C_s	W–C2	1.726	1.717	1.760
		W–Cl4	2.397	2.420	2.382
		W–Cl5	2.397	2.420	2.382
		W–Cl6	2.397	2.420	2.382
		W–Cl7	2.396	2.420	2.383
		∢C2-W-Cl4	101.3	102.0	100.9
		∢C2-W-Cl5	101.3	102.2	100.8
		∢C2-W-Cl6	101.0	102.0	101.1
		∢C2-W-Cl7	101.1	101.7	101.3
$[OH_4W(CH)]^-$ (**26**)	C_1	W–C	1.743	1.740	1.795
		W–O4	1.969	2.023	2.030
		W–O5	1.940	1.991	1.996
		W–O6	1.919	1.968	1.973
		W–O7	1.942	1.996	2.015
		∢C-W-O4	105.9	107.6	104.3
		∢C-W-O5	103.0	104.3	101.6
		∢C-W-O6	104.2	104.3	102.9
		∢C-W-O7	107.3	108.0	109.3
		∢W-O4-H8	120.9	109.9	108.2
		∢W-O5-H9	128.7	113.9	110.1
		∢W-O6-H10	132.2	116.2	111.8
		∢W-O7-H11	119.1	108.7	104.7

[a] Tilting angle of the amino group, see Figure 1.

The calculated structures for the aminocarbyne complexes **7** and **19** are very interesting. The aminocarbyne ligand of both compounds is planar at the HF level with both basis sets I and II, but it becomes pyramidal at MP2/II ($\alpha = 144.0°$ for **7**, $\alpha = 132.7°$ for **19**, Figure 1, Tables 1 and 2). This seems to be in conflict with experimental results. The X-ray structure analysis of the related complex $[Br(CO)_4Cr(CNEt_2)]$ has a planar structure for the carbyne ligand.[30] However, the energy difference between the planar and pyramidal forms of **7** and **19** calculated at MP2/II is very small. Constrained optimizations of **7** and **19** at MP2/II with planar aminocarbyne ligands gave structures that are only 0.5 and 2.0 kcal mol^{-1} higher in energy, respectively, than the pyramidal form. It is possible that the pyramidal equilibrium structures of **7** and **19** are artefacts of the MP2/II level of theory, or that the experimentally observed planar geometries of related compounds are caused by solid-state effects. The N-C-W π conjugation is not very large, but it is strong enough to enforce (at HF/II) or to lower (at MP2/II) the inversion barrier at the amino groups of **7** and **19**. We want to point out that the inversion barrier for NH_3 is only 5.24 kcal mol^{-1}.[40] Note that the W–C carbyne bonds of **7** and **19** even at HF/II are not much longer than in the other carbynes (Tables 1 and 2). This indicates that there is little conjugation between the nitrogen lone-pair orbital and the W–C π bonds in aminocarbyne complexes. In the language of resonance theory form **A** contributes significantly more to the description of **7** and **19** than **B** (Scheme 3). The same conclusion has been drawn before from EHT calculations.[12, 31]



Scheme 3. Schematic representation of the most important resonance structures **A** and **B** for aminocarbyne complexes. **A** is more important than **B** in **7** and **19** (see text).

The theoretically predicted shortening of the W–carbyne bond lengths of the Schrock complexes **14–26** with respect to **1–13** is in agreement with experimental data. The typical range of W≡C triple bond distances in $[L_3W(CR)]$ complexes is 1.74–1.80 Å.[4, 6] An X-ray structure analysis of $[(t\mathrm{BuO})_3W(CMe)]$ shows that the compound is a dimer that has two long W–OR bridges.[32] The experimental W–carbyne bond length of 1.759 ± 0.006 Å agrees very well with the calculated MP2/II value for **23** W–C = 1.766 Å (Table 2). Please note that the addition of Cl^- to **16** and **17**, yielding the anions **24** and **25**, respectively, has hardly any influence on the W–carbyne bond length, while the addition of OH^- to **22** gives a somewhat longer W–carbyne bond in **26**. We included the negatively charged Schrock complexes **24–26** in our study, because neutral carbyne complexes in high oxidation states are strong Lewis acids, and negatively charged complexes can easily be prepared. An example is the complex $[N(Et)_4]^+[Cl_4W(Ct\mathrm{Bu})]^-$.[33] Unfortunately no experimental geometries of negatively charged carbyne complexes are known to us.

Table 3 gives the tungsten–carbyne bond dissociation energies for selected compounds. Calculations at the CCSD(T)/II level of theory could not be carried out for **4**, **6**, and **7** because of the size of the molecules. The CCSD(T)/II bond energies have been estimated from the MP2/II values and the ratio of the CCSD(T)/II and MP2/II values for **16**, **18**, **19**, and **24**. Systematic studies have shown that MP2 overestimates the bond energies of transition metal–ligand bonds, but the trend of the bond energies is in agreement with CCSD(T) results.[36] The previous paper about carbene complexes supports this conclusion.[1]

Table 3. Dissociation energies of selected carbyne complexes **4>**, **6**, **7**, **16**, **18**, **19**, and **24** (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
4	160.8	155.0	133.9	128.1
6	126.1	122.5	105.0	101.4
7	114.4	110.9	95.2	91.7
16	183.0	177.5	154.5	149.0
18	136.2	133.0	111.7	106.2
19	128.0	124.0	104.9	100.9
24	209.0	205.9	176.5	173.4

[a] Doublet state of $WBr(CO)_4$, CH, CF, $C(NH_2)$, WCl_4^-, quartet state of WCl_3. The CCSD(T) values of **4**, **6**, and **7** have been estimated, see text.

The theoretically predicted bond energy of the tungsten–carbyne bond of the Fischer complex **4** ($D_e = 133.9$ kcal mol^{-1}) is much higher than that of the tungsten–carbene bond of $[(CO)_5W{=}CH_2]$ ($D_e = 78.9$ kcal mol^{-1}).[1] The W–CH bond becomes significantly weaker when the hydrogen atom of the carbyne ligand is substituted by fluorine. The calculated W–CF bond dissociation energy of **6** is $D_e = 105.0$ kcal mol^{-1}. The trend is similar to the carbene complexes. The calculated bond dissociation energy of $[(CO)_5W{=}CF_2]$ is $D_e = 60.6$ kcal mol^{-1}.[1] The weaker tungsten–carbyne bond of **6** compared with **4** can be explained by the effect of the fluorine atom on the relevant donor and acceptor orbitals of CR^+ (Scheme 1). The carbon lone-pair σ orbital of CR^+ becomes lower in energy when R = F, which makes it a weaker donor than CH^+. The fluorine lone-pair p(π) orbitals donate electronic charge into the formally empty p(π) orbitals of carbon, which weakens the acceptor strength of CF^+. Both factors reduce the donor–acceptor interactions of CF^+ with a transition metal. The tungsten–carbyne bond of the aminocarbyne complex **7** is even weaker ($D_e = 95.2$ kcal mol^{-1}) than that of **6** (Table 3). $C(NH_2)_2^+$ is a better σ donor than CF_2^+, but the π-acceptor strength of $C(NH_2)_2^+$ is lower compared with CF_2^+, because nitrogen is a better p(π) donor than fluorine. The calculated bond strengths of **6** and **7** indicate that the W→CR π back-bonding is more important for the metal–carbyne bond than the RC→W σ donation. The same conclusion has been drawn in an analysis of metal–ligand bonding in carbonyl complexes.[37]

The W–carbyne bond of the Schrock complex **16** is stronger ($D_e = 154.5$ kcal mol^{-1}) than that of the Fischer complex **4**, and it is also much stronger than the W–carbene bond of the Schrock-carbene complex $[Cl_4W{=}CH_2]$ ($D_e = 75.3$ kcal mol^{-1}).[1] Substitution of the hydrogen atom in **16** by fluorine lowers the strength of the W–carbyne bond significantly as seen in the Fischer complexes **4** and **6**. The W–CF bond energy of **18** is only $D_e = 111.7$ kcal mol^{-1} (Table 3). This can be explained by the effect of the fluorine atom on the $(^2\Pi) \rightarrow (^4\Sigma^-)$ excitation energy of CR from the $^2\Pi$ ground state to the $^4\Sigma^-$ excited state of CR, which is the electronic reference state for Schrock carbyne complexes (Schemes 1b and 2). The $^4\Sigma^-$ state of CF is 61.3 kcal mol^{-1} higher than the $^2\Pi$ ground state,[38] while the $(^2\Pi) \rightarrow (^4\Sigma^-)$ excitation energy of CH is only 15.9 kcal mol^{-1}.[35] The calculations show that the aminocarbyne complex **19** has an even lower W–CR bond dissociation energy ($D_e = 104.9$ kcal mol^{-1}) than **18**. The energy difference between the doublet ground state and quartet excited state of $C(NH_2)$ has not been studied yet. If the bonding model shown in Scheme 1b is correct, $C(NH_2)$ should have an even higher lying quartet state than CF.[39]

From the comparison of the theoretical and experimental geometries it follows that the theoretically predicted structures at MP2/II for the Fischer and Schrock carbyne complexes **1**–**26** are quite reliable. The optimized molecules will now be used to analyze the W–carbyne bonding situation.

Bonding analysis: Table 4 gives the results of the topological analysis of the electron-density distribution of **1**–**26**. Figure 2 shows the contour line diagrams of the Laplacian distribution of selected compounds.

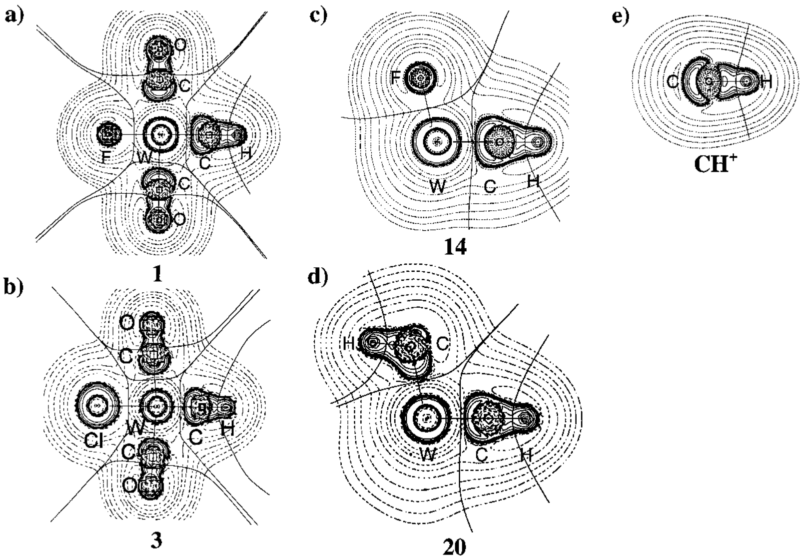


Figure 2. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/II of a) **1**; b) **3**; c) **14**; d) **20**; e) free ($^1\Sigma^-$) CH^+. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$); solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$). 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 $\mathbf{r}_c$.

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]	d_c[c]
1	W–C2	1.162	10.867	-0.646	0	1.87	0.451
	W–F	0.670	13.291	-0.071	0	0.48	
	W–C4	0.654	8.811	-0.164	0.36	0.70	
2	W–C2	1.017	13.394	-0.476	0	1.72	0.447
	W–CF	0.685	13.660	-0.071	0	0.50	
	W–C4	0.659	8.949	-0.168	0.28	0.72	
3	W–C2	1.210	10.650	-0.699	0	1.96	0.450
	W–Cl	0.395	4.400	-0.051	0	0.49	
	W–C4	0.658	8.818	-0.168	0.37	0.71	
4	W–C2	1.218	10.442	-0.708	0	1.97	0.449
	W–CBr	0.354	2.940	-0.064	0	0.50	
	W–C4	0.660	8.832	-0.170	0.37	0.71	
5	W–C2	1.197	10.581	-0.685	0	1.91	0.450
	W–C4	0.665	8.919	-0.173	0.32	0.72	
	W–C6	0.665	8.926	-0.173	0.32	0.72	
	W–C8	0.665	8.932	-0.173	0.32	0.73	
	W–Br	0.351	2.925	-0.063	0	0.50	
	C–C	1.796	-16.081	-1.633	0	1.03	
6	W–C2	1.072	12.847	-0.536	0	1.79	0.448
	W–Br	0.367	3.031	-0.066	0	0.53	
	W–C4	0.671	8.897	-0.178	0.28	0.74	
7	W–C2	1.132	12.533	-0.597	0.01	1.80	0.463
	W–Br	0.680	9.135	-0.183	0.24	0.75	
	W–C4	0.349	2.944	-0.060	0.02	0.51	
	C2–N	2.189	-18.787	-3.650	0.18	1.06	
8	W–C2	1.234	9.855	-0.728	0	1.98	0.447
	W–I	0.310	1.739	-0.068	0	0.51	
	W–C4	0.666	8.745	-0.175	0.35	0.72	
9	W–C2	1.139	10.794	-0.621	0	1.85	0.451
	W–C4	0.686	8.943	-0.188	0.31	0.74	
	W–C6	0.685	8.950	-0.187	0.31	0.73	
	W–C8	0.745	8.954	-0.187	0.31	0.73	
	W–C12	0.504	2.827	-0.141	0	0.53	
10	W–C	1.215	10.617	-0.704	0	2.07	0.450
	W–Cl	0.370	4.362	-0.042	0	0.49	
	W–P	0.499	4.092	-0.139	0.83	0.73	
11	W–C2	1.284	15.082	-0.758	0	1.98	0.471
	W–P4	0.422	4.824	-0.081	4.29	0.70	
	W–P5	0.422	4.823	-0.081	4.32	0.72	
	W–P6	0.422	4.819	-0.081	4.35	0.72	
	W–Cl	0.295	3.739	-0.019	0	0.50	
12	W–C2	1.217	14.355	-0.684	0	1.94	0.470
	W–P4	0.427	4.954	-0.082	4.55	0.73	
	W–P5	0.427	4.948	-0.082	4.50	0.72	
	W–P6	0.427	4.924	-0.082	4.41	0.72	
	W–C20	0.482	3.479	-0.113	0	0.56	
13	W–C2	1.196	14.845	-0.657	0	1.90	0.470
	W–P4	0.429	5.037	-0.083	4.07	0.71	
	W–P5	0.428	5.024	-0.082	4.06	0.71	
	W–P6	0.428	5.003	-0.082	4.01	0.71	
	W–C20	0.530	3.562	-0.110	0	0.59	
14	W–C	1.509	7.674	-1.116	0	2.50	0.426
	W–F	0.979	19.905	-0.212	0.07	0.74	
15	W–C	1.488	8.833	-1.084	0	2.47	0.429
	W–F	0.960	20.012	-0.195	0.08	0.73	
16	W–C	1.522	7.110	-1.127	0	2.52	0.431
	W–Cl	0.678	6.482	-0.181	0.08	0.93	
17	W–C	1.526	7.363	-1.137	0	2.51	0.433
	W–Cl	0.669	6.456	-0.175	0.09	0.92	
18	W–C	1.360	12.315	-0.902	0	2.33	0.441
	W–Cl	0.678	6.489	-0.182	0.09	0.95	
19	W–C	1.458	11.018	-1.031	0.04	2.43	0.454
	W–Cl4	0.663	6.658	-0.169	0.09	0.93	
	W–Cl5	0.651	6.565	-0.161	0.11	0.92	
	W–Cl6	0.650	6.564	-0.161	0.11	0.92	
	C–N	2.070	-23.22	-3.216	0.14	1.06	
20	W–C2	1.446	8.338	-1.009	0	2.43	0.436
	W–C4	0.823	2.645	-0.350	0.10	0.84	
21	W–C2	1.448	7.955	-1.019	0	2.40	0.436
	W–C4	0.819	2.660	-0.343	0.11	0.83	
22	W–C	1.475	7.874	-1.061	0	2.47	0.430
	W–O	0.910	15.626	-0.229	0.02	0.84	
23	W–C2	1.471	8.239	-1.058	0	2.45	0.431
	W–O	0.01	15.509	-0.222	0.01	0.83	
24	W–C	1.506	7.033	-1.129	0	2.48	0.428
	W–Cl	0.535	5.072	-0.102	0.21	0.70	
25	W–C2	1.517	7.248	-1.125	0	2.45	0.429
	W–Cl4	0.530	5.079	-0.099	0.22	0.70	
	W–Cl5	0.530	5.081	-0.099	0.22	0.69	
	W–Cl6	0.530	5.079	-0.099	0.22	0.69	
	W–Cl7	0.529	5.077	-0.099	0.22	0.69	
	C2–C3	1.729	-14.868	-1.533	0	1.02	
26	W–C	1.362	8.781	-0.906	0.02	2.29	0.431
	W–O4	0.740	11.461	-0.131	0.19	0.61	
	W–O5	0.793	12.875	-0.156	0.08	0.69	
	W–O6	0.831	13.835	-0.177	0.03	0.72	
	W–O7	0.778	11.673	-0.160	0.25	0.64	

[a] Electron density at the bond critical points in the carbyne 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 $\varepsilon_c(\varepsilon_c = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 are negative eigenvalues of electron density Hessian). [b] Bond order according to Cioslowski and Mixon.[34] [c] Position of the bond critical point given by $d_c = (\mathbf{r}_c - \mathrm{C}_{carbyne})/(\mathrm{C}_{carbyne} - \mathrm{W})$.

We show only two examples each for the Laplacian distribution of Fischer (**1** and **3**) and Schrock complexes (**14** and **20**), because there are little visible differences among the carbyne ligands of the two classes of carbyne complexes. The most important aspect of the shape of the Laplacian distribution is the area of electron depletion ($\nabla^2\rho(\mathbf{r}) > 0$) in the valence shell of free CH$^+$ (Figure 2e, dashed lines). This hole in the valence-electron concentration indicates the spatial distribution of the empty p(π) orbitals in free ($^1\Sigma^+$) CH$^+$. The important point is that this hole is filled or nearly filled in the methylidyne complexes of the Schrock type and the Fischer type (Figure 2a–d). This is different from the carbene complexes, where the Fischer-type complexes have a large area of electron depletion in the π direction of the carbene ligand.[1] The Laplacian distribution shown in Figure 2 indicates that the carbyne ligands of Fischer complexes should be less reactive towards nucleophilic agents than the Fischer carbene complexes, and that the chemical behaviour of Fischer and Schrock carbyne complexes should be less different than in case of the carbene complexes.

The W–carbyne bonds of the Fischer complexes **1**–**13** have a much higher covalent character than the Fischer-type W–carbene bonds. This becomes evident by the energy densities at the W–carbyne critical points $H(\mathbf{r}_c)$ for **1**–**13**, which are clearly more negative than $H(\mathbf{r}_c)$ for W–carbene bonds of Fischer complexes.[1] Also the bond orders for the W–carbyne bonds of the Fischer complexes, which have values between 1.72 (for **2**) and 2.07 (for **10**), are clearly higher than the results for the Fischer W–carbene bonds (0.93–1.18).[1] Even higher bond orders between 2.29 (for **26**) and 2.52 (for **16**) and more negative $H(\mathbf{r}_c)$ values have been calculated for the Schrock carbyne complexes **14**–**26** (Table 4). Thus, while there are three W–C bonds in **1**–**26** (one σ bond and one degenerate π bond), the topological analysis of the electron-density distribution suggests that the covalent-bond strength of the Fischer carbyne complexes **1**–**13** is that of a double bond, while the covalent-bond strengths of the Schrock complexes **14**–**26** are intermediate between a double and a triple bond.

Table 5 shows the results of the NBO analysis. The electron configuration at tungsten has a significantly higher 5d occupation in the low-valent complexes **1**–**13** (between 5.42 for **1** and 6.12 for **10**) than in the high-valent complexes **14**–**26** (between 3.62 for **14** and 4.52 for **18**). Thus, the notation high valent and low valent is justified by the calculated electron configuration. It is interesting to see that the partial charges at tungsten in the Fischer and Schrock carbyne complexes are very similar to the Fischer and Schrock carbene complexes,

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

	AO occupation of the tungsten atom			W–C bond[a]					Charge		p(π)
	6s	5d	6p	Occup.	%W	%s	%p	%d	W	CX[b]	$C_{carbyne}$[c]
1	0.46	5.42	0.03	σ: 1.91	28.13	28.6	0	71.4	+0.07	−0.19	1.70
				π: 1.72	54.71	0	18.5	81.5			
2	0.47	5.52	0.03	σ: 1.90	19.79	26.3	0	73.7	−0.03	−0.07	1.72
				π: 1.86	64.74	0	0	100.0			
3	0.49	5.67	0.02	σ: 1.90	28.08	35.7	0	64.3	−0.19	−0.08	1.65
				π: 1.87	58.94	0	12.1	87.9			
4	0.50	5.71	0.02	σ: 1.95	29.45	29.4	0	70.6	−0.24	−0.07	1.64
				π: 1.88	61.90	0	0	100.0			
5	0.50	5.71	0.02	σ: 1.95	28.70	33.3	0	66.7	−0.23	−0.04	1.64
				π: 1.80	61.84	0	6.1	93.9			
6	0.54	5.80	0.02	σ: 1.95	27.58	29.4	0	70.6	−0.38	+0.04	1.67
				π: 1.86	64.44	0	0	100.0			
7	0.50	5.80	0.02	σ: 1.95	27.67	37.0	0	63.0	−0.33	+0.12	1.65
				π: 1.79	53.06	0	10.6	89.4			
8	0.54	5.73	0.02	σ: 1.87	33.23	21.3	0	78.7	−0.31	−0.06	1.63
				π: 1.78	60.09	0	0	100.0			
9	0.48	5.63	0.02	σ: 1.89	30.80	26.3	0	73.7	−0.11	−0.07	1.59
				π: 1.72	58.70	0	0	100.0			
10	0.45	6.12	0.04	σ: 1.90	32.24	22.7	0	77.3	−0.67	−0.17	1.73
				π: 1.81	57.90	0	0	100.0			
11	0.41	6.08	0.02	σ: 1.94	28.47	25.0	0	75.0	−0.53	−0.23	1.75
				π: 1.89	56.60	0	0	100.0			
12	0.40	6.07	0.02	σ: 1.94	28.00	28.6	0	71.4	−0.49	−0.29	1.77
				π: 1.90	55.08	0	0	100.0			
13	0.39	6.10	0.02	σ: 1.94	27.87	28.7	0	71.3	−0.52	−0.25	1.74
				π: 1.89	56.15	0	0	100.0			
14	0.29	3.62	0.06	σ: 1.93	34.45	35.7	0	64.3	+2.03	−0.42	20.7
				π: 1.89	49.83	0	0	100.0			
15	0.29	3.62	0.05	σ: 1.93	34.14	3507	0	64.3	+2.04	−0.41	20.7
				π: 1.88	50.00	0	0	100.0			
16	0.37	4.33	0.06	σ: 1.98	29.91	29.4	0	70.6	+1.06	−0.22	1.90
				π: 1.94	60.36	0	0	100.0			
17	0.41	4.44	0.04	σ: 1.93	36.79	29.4	0	70.6	+1.07	−0.21	1.92
				π: 1.87	55.29	0	0	100.0			
18	0.42	4.52	0.05	σ: 1.99	26.21	31.3	0	68.7	+0.98	−0.15	1.89
				π: 1.94	63.51	–	0	100.0			
19	0.41	4.48	0.04	σ: 1.93	35.74	31.2	0	69.7	+1.04	−0.13	1.99
				π: 1.90	55.80	0	0	100.0			
20	0.42	4.04	0.01	σ: 1.99	29.96	27.0	0	73.0	+1.39	−0.26	1.96
				π: 1.997	52.96	0	0	0			
21	0.46	4.17	0.02	σ: 1.94	35.90	26.3	0	73.7	+1.40	−0.26	1.97
				π: 1.86	51.02	0	0	100.0			
22	0.29	3.68	0.02	σ: 1.99	30.50	28.6	0	71.4	+2.02	−0.32	2.03
				π: 1.92	54.34	0	0	100.0			
23	0.35	3.88	0.04	σ: 1.95	37.96	26.3	0	73.7	+1.74	−0.31	2.03
				π: 1.73	45.90	0	0	100.0			
24	0.43	4.49	0.04	σ: 1.94	36.28	25.0	0	75.0	+0.95	−0.26	1.92
				π: 1.82	52.02	0	14.5	85.5			
25	0.43	4.48	0.04	σ: 1.93	36.01	27.0	0	73.0	+0.98	−0.27	1.94
				π: 1.75	50.20	0	13.9	86.1			
26	0.33	3.79	0.07	σ: 1.92	31.49	35.7	0	64.3	+1.71	−0.76	2.18
				π: 1.76	42.05	0	16.3	83.7			

[a] Only one component of a degenerate or nearly degenerate carbyne π bond is given. [b] The sum of atomic charges of the atoms comprising the carbyne ligand. [c] The sum of the occupations of the $2p_x$ and $2p_y$ orbitals of the carbyne atom is given.

respectively, which are given in the preceding paper. The similar partial charges at the metal for the Fischer carbene and carbyne complexes indicate that the formulation of $[(X^-)(CO)_4W(CR^+)]$ is a valid qualitative description for the Fischer carbynes, which supports the use of the donor–acceptor model between $[X(CO)_4M]^-$ and CR^+. Although there is no direct connection between partial charges and formal-oxidation state, the charge distribution suggests that the Fischer carbyne complexes $[X(CO)_4W(CR)]$ should be considered as W^0 compounds.[41]

Table 6. CDA results for the carbyne complexes **1**–**26** at the MP2/II level.

	Carbyne(+) → WL_n(−) donation[a]	L_nW(−) → Carbyne(+) back-donation[a]	L_nW(−) ↔ Carbyne(+) repulsion[a]	Residue term
1	0.478	0.870	−0.228	0.053
2	0.517	0.767	−0.231	0.097
3	0.451	0.856	−0.261	0.069
4	0.403	0.753	−0.203	−0.029
5	0.492	0.798	−0.262	0.068
6	0.500	0.742	−0.252	0.112
7	0.524	0.726	−0.283	0.069
8	0.451	0.843	−0.255	0.076
9	0.455	0.852	−0.243	0.082
10	0.513	0.970	−0.196	0.014
11	0.558	0.947	−0.217	−0.001
12	0.538	1.012	−0.216	0.018
13	0.563	0.946	−0.221	0.019
14	0.024	0.346	+0.246	0.518
15	0.034	0.286	+0.307	0.393
16	0.061	0.267	+0.188	0.621
17	0.051	0.192	+0.289	0.518
18	0.014	0.212	+0.257	0.618
19	0.017	0.213	+0.295	0.554
20	0.095	0.309	+0.167	0.534
21	0.081	0.272	+0.242	0.493
22	0.032	0.317	+0.296	0.426
23	0.035	0.307	+0.329	0.416
24	−0.016	0.339	+0.259	0.381
25	0.110	0.328	+0.171	0.363
26	0.126	0.281	+0.189	0.427

[a] WL_n^{2-} for **24**–**26**.

The optimal Lewis structure for all complexes **1**–**26** given by the NBO-partitioning scheme has a $L_nW{\equiv}CR$ triple bond, that is, one σ bond and a degenerate (or nearly degenerate) π bond. The two π components become slightly different in some complexes, because of the break in symmetry caused by the substituents. Because the differences are very small, only one component of the W–carbyne π bond is shown in Table 5. The W–carbyne π bond of the Fischer complexes **1**–**13** is always slightly polarized towards the metal end, while the σ bond is clearly polarized towards carbon. The σ and π contributions to the W–carbyne bonds of the Schrock complexes **14**–**26** are both less polarized than in case of the Fischer complexes. The opposite shift of the W–carbyne σ and π bonds when one goes from Fischer to Schrock complexes explains the similar partial charges of the carbyne ligands in both classes of compounds. The CR ligand carries in most cases a small negative charge, although it can become slightly positive in the Fischer complexes (**6** and **7**). The partial charges at the carbyne ligands of **1**–**26** are similar to those of the carbene ligands in the Fischer and Schrock complexes in our preceding study.[1] Note that the p(π) occupation of the carbyne carbon atom given in Table 5 is the sum of the two p(π) orbitals. Because neutral ($^2\Pi$) CH has one electron in the p(π) orbital, the W → carbon π back-donation of **1**–**13** is between 0.59 e (for **9**) and 0.72 e (for **2**). These values are very similar to the p(π) occupation of the carbene carbon atom in Fischer carbene complexes.[1] The same holds true for the Schrock complexes **14**–**26**. The W–carbon π back-donation is between 0.89 e (for **18**) and 1.18 e (for **26**), which is similar to the values for the investigated Schrock carbene complexes.[1]

Table 6 shows the CDA results of the carbyne complexes. The metal–carbyne orbital interactions are calculated from L_nW^- (or L_nW^{2-} in case of the anions **24**–**26**) and CR^+ as fragments. The CDA results for the Fischer complexes **1**–**13** show that the chosen model makes it possible to discuss the metal–carbyne bonding in the framework of the DCD model. There is strong $RC^+ \rightarrow WL_n^-$ σ donation and twice as much $L_nW^- \rightarrow CR^+$ back-donation. The calculated donation/back-donation ratio is reasonable because of the charges of the fragments. The values for the residue terms of **1**–**13** are small, but the deviations from zero are in some cases higher than one would expect for a donor–acceptor complex. This is another indication that the W–carbyne bonds of the Fischer complexes have more the character of a normal covalent bond than the Fischer carbene complexes.

The results for the Schrock complexes **14**–**26** show that the metal–carbyne bonding should not be discussed in terms of orbital interactions between closed-shell species Wl_n^- and CR^+. The residue term is always very big. This means that electronically excited states of WL_n^- and CR^+ or other reference species should be used to describe the W–carbyne bonding in **14**–**26**. A possible model to describe the bonding in Schrock-type carbyne complexes, which is analogous to the model suggested for high-valent carbene complexes,[16] uses the $^4\Sigma^-$ state of CR which interacts with the quartet ground state of L_3M (Scheme 3). Whichever model is used, the CDA results show clearly that the W–carbyne bonds of the Schrock complexes **14**–**26** should not be discussed in terms of donor–acceptor interactions.

Summary and Conclusion

The theoretically predicted geometries of the Fischer and Schrock-type carbyne complexes **1**–**26** are in very good agreement with experimental results. The W–carbyne bonds of the Fischer complexes **1**–**13** are ≈0.2 Å shorter than the W–carbene bonds of the previously reported Fischer carbene complexes. The Schrock complexes have W–carbyne distances that are ≈0.1 Å shorter than the Fischer carbyne complexes. The analysis of the bonding situation shows that the W–carbyne bonds of Fischer and Schrock complexes are less different than the W–carbene bonds of these two classes of compounds. The bond order of the W–carbyne bond of the

Fischer complexes indicates a covalent double bond, while the Schrock complexes have a W–carbyne bond with a covalent bond order that is intermediate between a double and a triple bond. The CDA results suggest that the metal–carbyne bonds of the Fischer complexes **1**–**13** should be discussed as donor–acceptor bonds between a positively charged closed-shell carbyne ligand CR^+ and the negatively charged metal fragment, while bonding in the Schrock complexes **14**–**26** is due to electron pairing between the carbyne ligand and the metal fragment in the quartet states.

The W–carbyne bond strengths of the Fischer and Schrock carbyne complexes are significantly higher than those of related carbene complexes. The $L_nW{-}CR$ bond dissociation energies depend strongly on the nature of R. Substituents with p(π) lone-pair electrons lower the bond strength of the Fischer and Schrock carbyne complexes. This is because the π-acceptor strength of the carbyne ligand CR in Fischer complexes is reduced by the π-donor substituents R. π-donor ligands also lead to higher $(^2\Pi) \rightarrow (^4\Sigma^-)$ excitation energies of the free carbyne. Since the excited $^4\Sigma^-$ state of CR is the electronic reference state in Schrock-type carbyne complexes, higher excitation energies yield lower bond dissociation energies.

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