Ab initio studies of transition-metal compounds: the nature of the chemical bond to a transition metal ‡

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"*Give us insight, not numbers*" (C. A. Coulson)

During the last two decades there has been a breathtaking development in the range and reliability of the methods of quantum chemistry that eventually lead to its applicability to chemically interesting problems even for heavy-atom molecules. In this way, it became possible to treat many-electron systems like transition-metal compounds in an accuracy challenging for the experimentalists.[1–4] It is now time to proceed to the second step of accurate quantum-chemical studies of heavy-atom molecules. After developing methods which predict reliably molecular geometries, bond energies,[1–3] vibrational frequencies[4] and even NMR chemical shifts[5] of transition-metal compounds, which is the necessary first step of quantum-chemical studies, the highly accurate but abstract sets of data need to be analysed and interpreted in terms of chemical models. Qualitative concepts have always been essential for the development of chemisry. We remind the reader of the influence of the concept of orbital symmetry and the Woodward–Hoffmann rules,[6] which had a strong impact on the headway of synthetic organic chemistry. The development of general concepts taken from the analysis of quantum-mechanical calculations is perhaps more important for the *understanding* of chemical phenomena than are numerically accurate results. On the other hand, quantitatively accurate theoretical methods are clearly the best basis for the development of reliable chemical models, which are not simply the result of a correlation of data. A correlation is not an explanation!

Comparatively few studies in modern theoretical chemistry have tried to develop the understanding of the chemical bond.[7] Important for the present work is the review article of Haaland,[8] who showed that it is not only possible but also useful to distinguish between covalent and donor–acceptor bonds in main-group chemistry. He demonstrated that this way of looking at the bonding is a good basis for understanding the structures of a large number of main-group compounds.

Covalent bonding in main-group chemistry is usually introduced and discussed in terms of two-electron bonds between two atoms, where each atom provides one electron. Compounds with donor–acceptor bonds (Lewis acid–base complexes), where one atom provides both bonding electrons, play a comparatively small role. The opposite situation exists in transition-metal chemistry. Donor–acceptor complexes of transition metals are ubiquitous, and this may be the reason why the bonding therein is mostly discussed within the donor–acceptor model. For example, the chemical bonds in WCl_6 and $W(CO)_6$ are usually described as the results of the interactions between closed-shell fragments, *i.e.* W^{6+} + 6 Cl^- in the case of WCl_6 and W + 6 CO in the case of $W(CO)_6$. Hardly anyone would discuss the bonding in CCl_4 in terms of interactions between C^{4+} + 4 Cl^-, but rather as covalent bonding with an sp^3-hybridised carbon atom. While sp^n hybridisation is an important model for the understanding of main-group chemistry, sd^n hybridisation in transition-metal chemistry has received little attention so far.

In this Perspective we want to show that, just as in the case of the main-group elements, it is not only possible but also very useful for the understanding of the structures of transition-metal compounds to distinguish between covalent and donor–acceptor types of bonds.§ This method for classifying transition-metal compounds has arisen from the analysis of high-level quantum-mechanical calculations. A pivotal role in the classification of a bond as being covalent or of donor–acceptor type is taken by the charge decomposition analysis (CDA)[9] of the calculated molecule, which can be applied to classical *ab initio* quantum-chemical methods based upon wavefunctions as well as to density functional theory (DFT) calculations. There are experimentally accessible criteria (structures, bond energies, vibrational frequencies) but also purely theoretical criteria (bond orders, partial charges) that justify such a classification. By presenting recent work on the quantum-chemical investigation of transition-metal compounds we try to demonstrate that this classification is helpful for an understanding of experimental as well as theoretical results.

How accurate are Modern *ab initio* Quantum-chemical Methods when applied to Transition-metal Compounds?

In the introduction we stated that modern quantum-chemical methods are able to predict molecular geometries, bond dissociation energies, vibrational frequencies and NMR chemical shifts of transition-metal compounds with good accuracy. The main reason for this achievement is the use of pseudopotentials (effective core potentials, ECPs), which replace the chemically inert core electrons with a set of parametrised functions that are derived from relativistic atomic calculations.[10] In this way it is possible drastically to reduce the large number of computationally cumbersome electrons and at the same time introduce the most important relativistic effects. The basic approaches of the most common ECPs and a comparison of the methods has been given in two recent reviews, which can also be used as a reference about the accuracy of ECP calculations of transition-metal compounds.[1,2] Effective core potentials can be used in conventional *ab initio* methods based on wave mechanics as well as in density functional theory, which are the two most important theoretical tools for calculating transition-metal compounds. We want to point out, however, that the statement

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‡ *Non-SI unit employed*: cal = 4.184 J; hartree, $E_h \approx 4.36 \times 10^{-18}$ J.

§ The terms 'covalent' and 'donor–acceptor' bonds are used in this work to distinguish between bonds where each bonding partner provides one electron to the two-electron bond ('covalent') and Lewis acid–base complexes ('donor–acceptor'). The term 'covalent' is *not* used to distinguish the bonding from ionic interactions. Donor–acceptor bonds are not necessarily ionic, they can have large covalent character.

about the high accuracy is only valid for electronically saturated or nearly saturated transition-metal compounds with an electronic ground state that is well separated from low-lying excited states. A much more complicated picture arises when one deals with electronically highly unsaturated species which are important in gas-phase organometallic chemistry.[11] Fortunately, the majority of the synthetically interesting transition-metal compounds belongs to the first class of molecules.
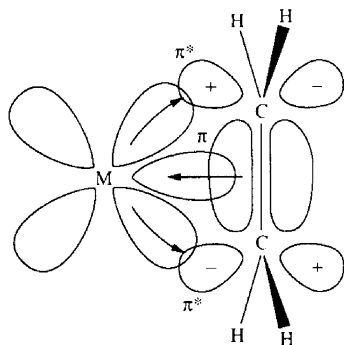
Bond lengths of transition-metal compounds can be predicted with an accuracy of ±0.05 Å, which is a rather conservative estimate. In most cases the agreement with experimental data is even better.[1,2,12] Owing to their high reliability, calculated metal–ligand bond lengths could be even used successfully to question experimental results.[13] Metal–ligand bond dissociation energies are very difficult to determine experimentally. It can be stated that theoretically predicted bond energies of transition-metal compounds are correct within ±5 kcal mol^{-1}, in most cases even better.[1,2,12–14] Systematic studies of the theoretically predicted vibrational frequencies of Jonas and Thiel[4] using DFT methods showed excellent agreement between theory and experiment. The most promising method for calculating NMR chemical shifts of ligand atoms in transition-metal compounds appears to be the sum-over-states individual gauge for localized orbitals (SOS-IGLO) approach of Malkin et al.,[5] which gives ^{13}C chemical shifts of carbonyl complexes that are in most cases within 10 ppm of the experimental values.[15] It should be noted that the experimental NMR chemical shifts are measured in solution, and obviously one cannot expect agreement of better than 5–10 ppm for ^{13}C shifts. Also, we want to point out that in most cases the *relative* numbers are more important for the interpretation and discussion of the experimental results than are the absolute data.

Distinguishing Covalent and Donor–Acceptor Bonds to a Transition Metal

Case study one: transition-metal complexes with side-on bonded π ligands

Transition-metal complexes with side-on bonded π ligands like ethylene or acetylene constitute an important class of organometallic compounds. They are frequently understood as donor–acceptor complexes and discussed within the framework of the Dewar–Chatt–Duncanson model,[16,17] according to which the bonding arises from two interdependent components (Fig. 1): electron donation from a filled π orbital of the ligand into a suitably directed vacant metal orbital and back donation from an occupied metal d orbital into the antibonding π* orbital of the ligand. However, in some cases an alternative interpretation of the bonding in these π complexes seems more appropriate: they can also be described as metallacyclopropanes or metallacyclopropenes, thus implying a true covalent bond between the metal and both of the ligand atoms.

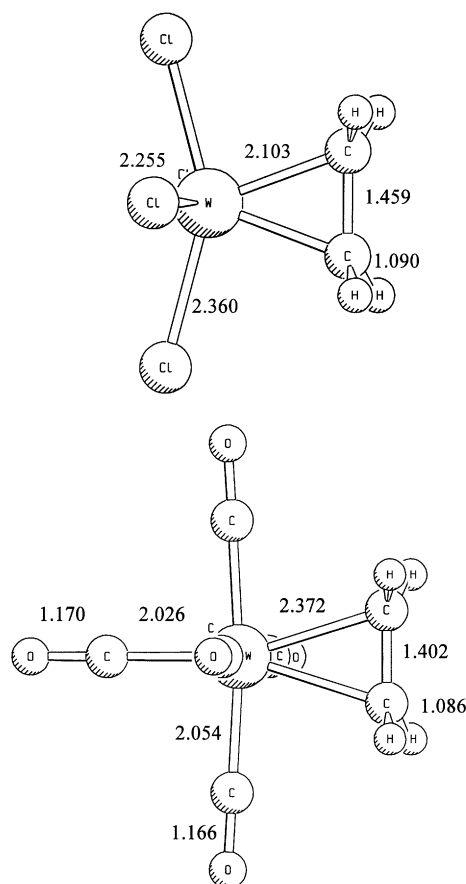Is it possible to classify transition-metal complexes with side-on bonded π ligands unequivocally to one or the other bonding scheme? Are there objective criteria to decide whether a ligand is bonded covalently or in a donor–acceptor way? In order to address these questions we investigated two typical series of transition-metal compounds, WCl$_4$L and W(CO)$_5$L with L = C$_2$H$_2$, C$_2$H$_4$, CO$_2$, CS$_2$ or CH$_2$O.[18] We fully optimised the geometries at the second-order Møller-Plesset perturbation (MP2) level of theory using an effective core potential at tungsten and valence basis sets of double-ζ plus polarisation quality; improved energies were obtained at the coupled cluster with singles, doubles and estimated triples [CCSD(T)] level. The determined structures and bond energies are in good agreement with experimental data, indicating that the methods chosen should be appropriate for a theoretical description of this class of compounds. From the calculations one can deduce a rather clear bonding picture: the complexes W(CO)$_5$L are typical donor–acceptor complexes, while the WCl$_4$L compounds are better described as metallacycles with polar covalent bonds.[18]

What are the criteria that lead to such a classification? We want to demonstrate the differences between the two series using the ethylene complexes as an example; however, the same conclusions can be drawn for the other compounds under investigation. A first, very strong criterion is given by the structures of the complexes which can, in principle, also be determined by experiment. Fig. 2 shows the calculated geometries of WCl$_4$(C$_2$H$_4$) **1** and W(CO)$_5$(C$_2$H$_4$) **2**.
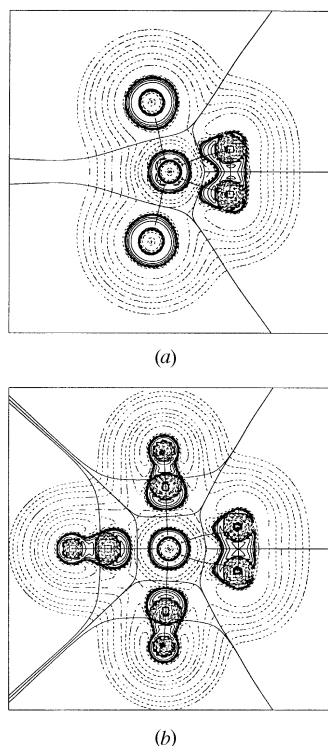
The first thing to notice is the co-ordination number. In a real donor–acceptor complex the ligand should occupy just one co-ordination site at the metal, which holds perfectly well in the octahedral complex **2**. In the case of WCl$_4$(C$_2$H$_4$) the co-ordinative situation at the tungsten atom is not so clear, but it is obvious that the ethylene ligand is bonded more tightly than in W(CO)$_5$(C$_2$H$_4$). The W–C distance is just 2.103 Å in **1**, as opposed to 2.372 Å in **2**, an indication of a difference in the type of bonding. In the same way, the calculated C–C distance

Fig. 1 Dewar–Chatt–Duncanson model of the bonding between a transition metal and a side-on bonded π ligand. Note that the ligand π orbital has σ symmetry in the complex

Fig. 2 Optimised geometries of WCl$_4$(C$_2$H$_4$) **1** and W(CO)$_5$(C$_2$H$_4$) **2**. Bond lengths in Å at the MP2/II level

Table 1 Calculated bond orders and energy densities H_b (hartree Å^{-3}) at the bond critical points

	Molecule	Bond	Order	H_b
1	$WCl_4(C_2H_4)$	W–C	0.91	−0.391
		C–C	1.11	−1.694
2	$W(CO)_5(C_2H_4)$	W–C	0.39	−0.094
		C–C	1.61	−2.078

Table 2 Charge decomposition analysis of the complexes in their MP2 geometries *

	1 $WCl_4(C_2H_4)$	**2** $W(CO)_5(C_2H_4)$
d	−0.263	0.225
b	−0.194	0.148
r	−0.318	−0.422
Δ	0.351	−0.025

* Donation d, back donation b, repulsive part r and residual term Δ.

(a)

(b)

Fig. 3 Contour-line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ at the MP2/II level of (a) $WCl_4(C_2H_4)$ and (b) $W(CO)_5(C_2H_4)$ in the respective molecular plane. Dashed lines indicate charge depletion $[\nabla^2\rho(r) > 0]$, solid lines indicate charge concentration $[\nabla^2\rho(r) < 0]$. The solid lines connecting the atomic nuclei are the bond paths; those separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and the zero-flux surfaces are the bond critical points r_b

of the co-ordinated C_2H_4 amounts to only 1.402 Å in **2**, not much longer than in free ethylene (1.336 Å), while the C–C distance of 1.459 Å in **1** approaches a typical C–C single bond (1.54 Å), as expected for a metallacyclopropane. The structures in Fig. 2 clearly show that the C_2H_4 ligand mainly keeps its ethylene character in $W(CO)_5(C_2H_4)$, but that the C atoms are largely rehybridised in $WCl_4(C_2H_4)$.

Can these conclusions drawn from structural observations also be verified by an electronic analysis of the quantum-chemical wavefunction? Are there thus also purely theoretical criteria that help to distinguish between covalent and donor–acceptor types of bonds to transition metals? Fig. 3 shows the contour-line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ of complexes **1** and **2** in the respective plane of symmetry. Bader[19] has demonstrated that the Laplacian distribution, which indicates relative charge depletion $[\nabla^2\rho(r) > 0]$ or relative charge concentration $[\nabla^2\rho(r) < 0]$, correlates nicely with the Lewis picture of the distribution of electrons in a molecule. The main difference between the two diagrams in Fig. 3 is in the co-ordinated C_2H_4. The Laplacian distribution of C_2H_4 has a marked distortion toward the metal in $WCl_4(C_2H_4)$, indicating a substantial degree of covalent W–C bonding in **1**, as was already inferred from the structural data. On the other hand, the electronic density distribution of free ethylene changes only slightly when it is co-ordinated to $W(CO)_5$.

The visual impression of the Laplacian distributions is supported by the calculated energy densities H_b at the bond critical points (Table 1). The value for H_b at the W–C bond critical point is clearly negative for $WCl_4(C_2H_4)$, while it is about zero in the case of $W(CO)_5(C_2H_4)$. It has been shown that a negative value for H_b indicates covalent character for the bond and that $H_b \geqslant 0$ is typical for closed-shell interactions.[20]

Another theoretical indicator for a more covalent W–L bond in the WCl_4L compounds is the covalent bond order. In the framework of the topological analysis of the electron density we calculated covalent bond orders according to the definition of Cioslowski and Mixon[21] (Table 1). The W–C bond in $WCl_4(C_2H_4)$ has a bond order near 1, typical for a normal covalent bond. The W–C bond in **2** does also have some covalent character, but a bond order of only 0.39 indicates that another type of bonding is present. In the same way, the calculated C–C bond orders show that the C_2H_4 ligand in **2** still has some double-bond character, while it has been reduced to a normal single bond in **1**.

An unequivocal answer to the question whether a metal–ligand bond shall be classified as covalent or of donor–acceptor type is given by the charge decomposition analysis.[9,22] The CDA method considers the bonding in a complex in terms of (fragment) molecular orbital interactions between two closed-shell fragments. In the present case, the fragments are $W(CO)_5$ and L for the $W(CO)_5L$ complexes and WCl_4 and L for the WCl_4L complexes. In principle, there are three kinds of interactions which describe the electronic structure of the complex: (i) the mixing of the occupied orbitals of the ligand and the empty orbitals of the metal fragment leading to the electron-donation term d; (ii) the mixing of the unoccupied orbitals of L and the occupied orbitals of the metal fragment giving the back donation b; (iii) the interaction between the occupied orbitals of both fragments leading to the repulsive polarisation r. The non-classical rest term Δ resulting from the mixing of unoccupied orbitals on the two fragments should be virtually zero in a donor–acceptor complex, because all interactions between the fragments should arise from the mixing of occupied and unoccupied orbitals. If the mixing of the unoccupied orbitals of the fragments gives a significant contribution to the charge interaction it can be taken as an indication of bond formation involving electron promotion from the ground state to an excited state of one or both fragments. The conclusion would be that the bond is formed from open-shell fragments, *i.e.* that the bond is a 'normal' covalent bond.¶ In this way, the CDA can be used as a tool to distinguish between the two types of bonding and, at the same time, as a quantitative expression of the familiar Dewar–Chatt–Duncanson model. The wavefunction of a quantum-chemical calculation is translated in a well defined way into a chemical model that has proved to be useful for an understanding of the chemical bonding.

Table 2 shows the CDA results for $W(CO)_5(C_2H_4)$ and $WCl_4(C_2H_4)$. In the case of $W(CO)_5(C_2H_4)$ **2** the results are just as expected for a typical donor–acceptor complex: for the

¶ In principle, it is possible that a doubly excited closed-shell electronic state is involved in the bond formation. This is unlikely, but it can be checked by analysing the CDA result.

Table 3 Calculated bond dissociation energies D_e (kcal mol^{-1}) at the CCSD(T)/II//MP2//II level for the complexes WCl$_4$L and W(CO)$_5$L

Molecule	D_e	Molecule	D_e
WCl$_4$(C$_2$H$_2$)	36.6	W(CO)$_5$(C$_2$H$_2$)	35.3
WCl$_4$(C$_2$H$_4$)	12.1	W(CO)$_5$(C$_2$H$_4$)	41.4
WCl$_4$(CO$_2$)	-17.7	W(CO)$_5$(CO$_2$)	10.7
WCl$_4$(CS$_2$)	-3.2	W(CO)$_5$(CS$_2$)	24.6
WCl$_4$(CH$_2$O)	18.7	W(CO)$_5$(CH$_2$O)	27.2

(C$_2$H$_4$)→W donation d as well as the W→(C$_2$H$_4$) back donation b small positive numbers are found. The negative value for the repulsive polarisation r indicates that charge is depleted from the overlapping area of the occupied orbitals. As expected, the residual term Δ nearly vanishes. A completely different picture is obtained for the complex WCl$_4$(C$_2$H$_4$) **1**: the values for the donation and back donation are negative, indicating that electronic charge is *removed* from the overlapping region between occupied and unoccupied orbitals. Obviously, this is a physically absurd result. It follows that the electronic structure of WCl$_4$(C$_2$H$_4$) cannot reasonably be described by the Dewar–Chatt–Duncanson model. This conclusion is supported by the large value found for the residual term Δ. The analysis makes clear that the closed-shell fragments WCl$_4$ and C$_2$H$_4$ are not proper reference systems for the metal–ligand bond in **1**. This is in agreement with the information gained by the optimised geometries and the topological analysis of the electron-density distribution. The bonding in WCl$_4$L should not be considered as donor–acceptor type. Rather, it is a normal covalent bond between two open-shell fragments and a description as a metallacycle is more appropriate. In this way, the charge decomposition analysis is not just a useful tool for a quantitative understanding of donor–acceptor complexes, but it may also serve as a theoretical indicator to distinguish between covalent and donor–acceptor types of bonds to a transition metal.

Now that we have shown that there are objective experimental as well as purely theoretical criteria that allow a distinction between covalent and donor–acceptor types of bonds to a transition metal, we have to address the question whether such a classification is of any use. Are there molecular properties which can only be understood if one presumes two different types of bonding in two compounds? To answer this question, we show in Table 3 the calculated bond dissociation energies of the complexes WCl$_4$L and W(CO)$_5$L with respect to the fragments WCl$_4$ or W(CO)$_5$ and L in their respective electronic ground states.

The first thing to notice is that the bond energies in the W(CO)$_5$L series are clearly higher than the corresponding bond energies for the WCl$_4$L compounds, except for L = C$_2$H$_2$ where nearly the same bond dissociation energies are predicted. This is in apparent contradiction to the much shorter W–L bonds in the WCl$_4$L series. Obviously, one has to distinguish carefully between the strength of the metal–ligand interactions, as expressed by the bond length or the distortion of the fragments, and the bond dissociation energy. This distinction becomes important when one deals with two basically different types of bonding, as in the present case. The W–L interactions are clearly stronger in the WCl$_4$L series, but in order to form these strong covalent bonds the ligands formally have to be electronically excited into their respective triplet states. As a result, the net bond energies that can be obtained from an interaction between WCl$_4$ and the ligands L are rather small, because the excitation energies from the singlet to the triplet state of the ligands are very high. The vertical excitation energy from the singlet ground state to the lowest-lying triplet state of C$_2$H$_4$ is 100.5 kcal mol^{-1}.[23] Thus, the interaction energy between WCl$_4$ and

|| The adiabatic excitation energy of C$_2$H$_4$ will be lower than the vertical excitation energy, but still be rather high.

C$_2$H$_4$ in the complex WCl$_4$(C$_2$H$_4$) is much higher (D_e 12.1 kcal mol^{-1} plus the excitation energy of C$_2$H$_4$) || than the bond dissociation energy, which explains the short W–C bond lengths. On the other hand, a completely different type of bonding is present in the W(CO)$_5$L series: the ligands and the metal interact only weakly in a donor–acceptor kind of way, but in order to form these bonds the fragments do not have to give up their closed-shell ground states and the resulting net bond energy is rather high. Thus, the somewhat surprising difference in bond energy between the two series can only be understood if one takes into account a different type of bonding.

Another surprising result can be found in Table 3: in the WCl$_4$L series the ethylene ligand is predicted to be significantly more weakly bonded to the metal (12.1 kcal mol^{-1}) than acetylene (36.6 kcal mol^{-1}), while the opposite trend holds for the W(CO)$_5$L series (41.4 and 35.3 kcal mol^{-1}, respectively). This observation can also be easily explained if one considers the difference in bonding: in the covalent compounds WCl$_4$L the acetylene ligand is more strongly bonded because the metallacyclopropene WCl$_4$(C$_2$H$_2$) has formally sp^2-hybridised carbon atoms, while the carbon atoms in the metallacyclopropane WCl$_4$(C$_2$H$_4$) are sp^3 hybridised. It is well known that a covalent bond of a given atom or group to C(sp^2) is much stronger than to C(sp^3). On the other hand, ethylene is known to be a better electron donor as compared to acetylene, leading to a higher bond energy of the donor–acceptor complex W(CO)$_5$(C$_2$H$_4$) than W(CO)$_5$(C$_2$H$_2$).

Case study two: low-valent (Fischer-type) and high-valent (Schrock-type) carbene complexes

The two series of complexes WCl$_4$L and W(CO)$_5$L are one example to illustrate that it is possible and useful to distinguish between covalent and donor–acceptor type of bonding to a transition metal. Another example is given by the carbene complexes of Schrock or Fischer type. Fischer carbenes are characterised by a metal atom in low oxidation state and π-donating substituents at the C atom, while Schrock carbenes can also be described as alkylidene complexes with a metal atom in a higher oxidation state and only alkyl substituents at the carbenic C atom. We investigated two series of carbene complexes: W(CO)$_5$L with L = CH$_2$, CF$_2$, CHF or CHOH, and WX$_4$(CH$_2$) with X = F, Cl, Br, I or OH.[24,25] Full geometry optimisations were performed at the MP2 level of theory using an effective core potential at tungsten and valence basis sets of double-ζ plus polarisation quality. Subsequent analyses of the electronic structures of the compounds revealed the main differences between Schrock- and Fischer-type carbene complexes.

The most important results in this investigation can be summarised using the two typical complexes WCl$_4$(CH$_2$) **3** and W(CO)$_5$(CHOH) **4** as an example. Their calculated structures are given in Fig. 4. A substantial difference in the W–C$_{carbene}$ distance is noticed at first glance: it amounts to 2.088 Å in W(CO)$_5$(CHOH), but to only 1.850 Å in WCl$_4$(CH$_2$). Obviously, the metal–carbene interactions are much stronger in the Schrock carbene than in the Fischer carbene. The corresponding H–C–H angle in **3** is 119.5° indicating that the carbenic C atom is sp^2 hybridised. The W–C bond is best described as a W=C double bond. On the other hand, the H–C–OH angle in W(CO)$_5$(CHOH) amounts to only 105.2°, as compared to 101.5° in free singlet CHOH and 120.4° in free triplet CHOH. A true rehybridisation has not taken place upon co-ordination of singlet CHOH to W(CO)$_5$, but it seems that electronic charge has been moved from the carbenic lone pair to the empty carbon orbital, leading to some mixing in of triplet character for the co-ordinated carbene. This kind of charge transfer is just what is expected according to the Dewar–Chatt–Duncanson model. Altogether, the structures shown in Fig. 4 suggest that the ligand in the Schrock carbene WCl$_4$(CH$_2$) is bonded in a
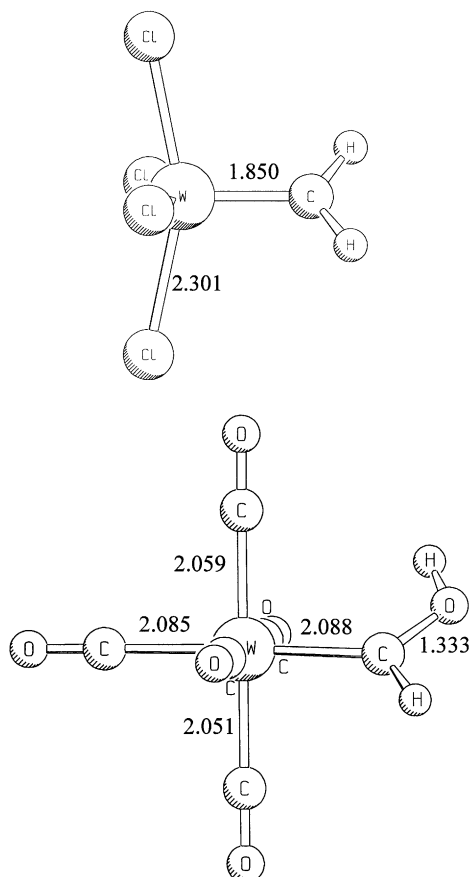
Fig. 4 Optimised geometries of WCl$_4$(CH$_2$) **3** and W(CO)$_5$(CHOH) **4**. Bond lengths in Å at the MP2/II level

(a)

(b)
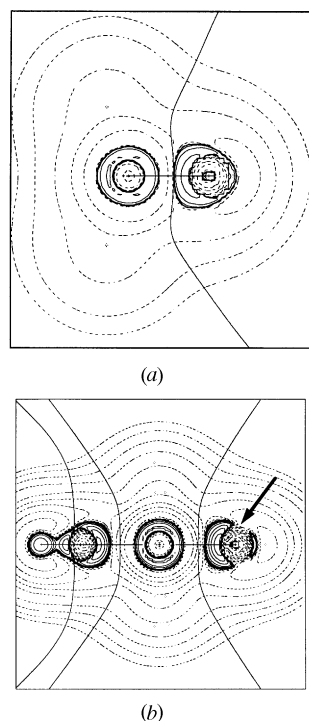
Fig. 5 Contour-line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ at the MP2/II level of (a) WCl$_4$(CH$_2$) and (b) W(CO)$_5$(CHOH) in the respective plane perpendicular to the carbene ligand. Details as in Fig. 3

covalent fashion, while the Fischer carbene W(CO)$_5$(CHOH) is a typical donor–acceptor complex.

Can these structural observations be confirmed by the Bader analysis of the electronic density distribution? Fig. 5 shows the contour-line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ of complexes **3** and **4** in the respective plane perpendicular to the

Table 4 Calculated energy density H_b (hartree Å^{-3}) at the bond critical point, Laplacian $\nabla^2\rho(r)$ (e Å^{-5}) at the bond critical point and bond order of the W–C$_{carbene}$ bonds

	3 WCl$_4$(CH$_2$)	**4** W(CO)$_5$(CHOH)
H_b	−0.973	−0.272
$\nabla^2\rho(r)$	0.576	7.646
Bond order	1.82	0.93

Table 5 Charge decomposition analysis of the complexes in their MP2 geometries

	3 WCl$_4$(CH$_2$)	**4** W(CO)$_5$(CHOH)
d	−0.031	0.417
b	−0.058	0.177
r	0.141	−0.285
Δ	0.416	−0.007

carbene ligand. There is a subtle but decisive difference in the two pictures: as indicated by an arrow, the Laplacian distribution of the Fischer carbene **4** has a hole at the carbenic C atom, where the region of negative $\nabla^2\rho(r)$ is interrupted by a spot of positive $\nabla^2\rho(r)$. Thus, the C atom of the Fischer carbene has a region of relative charge depletion where it should be easily attacked by a nucleophile. In the case of the Schrock carbene there is no such hole in the negative Laplacian surrounding the carbenic C atom. It is completely shielded by an area of relative charge concentration and attack by a nucleophile should be substantially more difficult. Indeed, chemical experience shows that Schrock carbenes easily react with electrophiles, while Fischer carbenes prefer nucleophilic reagents.

However, does the Bader analysis also provide us with some indications of a different bonding scheme in the two carbene complexes? Table 4 shows the characteristic data for the W–C$_{carbene}$ bond critical points, including covalent bond orders according to the definition of Cioslowski and Mixon.[21] The energy density H_b at the W–C bond critical point amounts to −0.973 hartree Å^{-3} for the Schrock carbene WCl$_4$(CH$_2$), while it is only −0.272 hartree Å^{-3} for the Fischer carbene W(CO)$_5$-(CHOH). As discussed above, this is a clear indication for a much higher covalency of the metal–carbene bond in Schrock carbenes. Another indication of a difference in bonding is given by the value of the Laplacian at the bond critical points. Applications of the Bader analysis to electronic structure problems have shown that a clearly positive value of $\nabla^2\rho(r)$ at the bond critical point is typical for interactions between two closed-shell fragments,[26] while shared covalent interactions between a metal and a ligand are characterised by rather small values of the Laplacian.[27] Thus, in the present case it appears that in W(CO)$_5$(CHOH) [$\nabla^2\rho(r)$ = 7.646 e Å^{-5}] the closed-shell fragments W(CO)$_5$ and CHOH form a donor–acceptor bond, while the bond in WCl$_4$(CH$_2$) [$\nabla^2\rho(r)$ = 0.576 e Å^{-5}] is of covalent character. This interpretation is supported by the calculated covalent bond orders: the W–C bond in WCl$_4$(CH$_2$) has an order of 1.82; it should thus be described as a true double bond comparable to the C=C bond in ethylene (bond order: 1.89). The W–C$_{carbene}$ bond order in W(CO)$_5$(CHOH) amounts to only 0.93. We should think of it as a single bond.

According to the results for the π complexes, we should expect the charge decomposition analysis to clearly tell us whether our classification of the bonding in the two types of carbene complexes can also be deduced from the *ab initio* wavefunctions. Table 5 shows that this is indeed the case: W(CO)$_5$-(CHOH) is characterised as a typical donor–acceptor complex with C→W donation being markedly more important than W→C back donation. On the other hand, the CDA results for WCl$_4$(CH$_2$) show clearly that the bonding situation cannot be discussed in terms of donor–acceptor interactions; slightly

negative values for donation and back donation, a positive repulsive term and, most importantly, a huge residual term of 0.416 make such an interpretation meaningless. It follows that for the Schrock carbene a description in the framework of the Dewar–Chatt–Duncanson model is not appropriate and that the metal–carbene bond has to be understood as a covalent one. The term 'carbene complex' is not adequate for Schrock-type compounds, which should rather be considered as hetero(metalla)olefins.

In summary, the structural and electronic analyses have shown unambiguously that the metal–carbene bond in the Fischer carbene $W(CO)_5(CHOH)$ is of the donor–acceptor type, while it should be classified as covalent in $WCl_4(CH_2)$. The charge decomposition analysis confirms this interpretation, and, once again, it has proved to be a valuable theoretical indicator for the distinction between covalent and donor–acceptor bonds to a transition metal. The usefulness of this classification is immediately clear: Fischer and Schrock carbenes are two distinct classes of compounds with largely different chemical properties that should be explicable by bond theory. Even their characteristic difference in reactivity can be deduced from their electronic structure, as shown in the Laplacian distributions in Fig. 5.

The Bonding in Donor–Acceptor Complexes: Classification of Donor–Acceptor Ligands according to the CDA

Now that we have shown that a classification of bonds between a transition metal and a ligand into covalent and donor–acceptor ones is not only possible but also useful, we want to concentrate on donor–acceptor ligands and try to classify them in a theoretically unequivocal way, i.e. to quantify the relative donor and acceptor strength of the ligands. To this end, we carried out ab initio calculations on two series of complexes:[28] $M(CO)_3L$ (M = Ni, Pd or Pt) and $M(CO)_5L$ (M = Cr, Mo or W), with L = CO, SiO, CS, N_2, NO^+, CN^-, NC^-, HCCH, CCH_2, CH_2, CF_2 or H_2.

We optimised the geometries at the MP2/II level (double-ζ basis plus polarisation functions, see ref. 1), calculated improved bond dissociation energies at CCSD(T)/II for the MP2 structures and performed charge decomposition analyses at MP2/II using natural orbitals. The computational level chosen is well suited for a theoretical description of these complexes: the calculated geometries are in good agreement with the experimental data available; differences in bond lengths are generally smaller than 0.05 Å, in most cases even smaller than 0.02 Å, which is predominantly below the uncertainty caused by the experimental error range and solid-state effects. For the bond dissociation energies the agreement is also very good, with differences of consistently less than 5 kcal mol^{-1} and rather large uncertainty in the experimental data.

From a chemist's point of view, most of the complexes under investigation are typical donor–acceptor complexes with characteristic ligands known from textbooks on co-ordination chemistry. The results of the charge decomposition analysis confirm this appraisal: for all complexes, the calculations yield positive values for donation and back donation, negative values for the repulsion and nearly vanishing residual terms, indicating that a description according to the Dewar–Chatt–Duncanson model is appropriate. However, the CDA also allows a certain classification of the ligands, as we want to show by example using the results for the $W(CO)_5L$ series (Table 6). The same conclusions can be drawn for the remaining $M(CO)_5L$ complexes and for the series of $M(CO)_3L$ complexes.[28]

For the parent compound $W(CO)_6$ the CDA gives a donation of 0.315 and a back donation of 0.233. This must not be used as evidence that electron donation contributes more to the metal–carbonyl bond energy than back donation. There is no inform-

Table 6 Charge decomposition analysis of the complexes $W(CO)_5L$ in their MP2 geometries*

Ligand L	d	b	r
CO	0.315	0.233	−0.278
SiO	0.214	0.213	−0.239
CS	0.259	0.308	−0.387
N_2	0.027	0.107	−0.252
NO^+	0.119	0.378	−0.318
CN^-	0.488	0.024	−0.241
NC^-	0.361	0.002	−0.252
HCCH	0.315	0.213	−0.419
CCH_2	0.404	0.324	−0.348
CH_2	0.314	0.282	−0.370
CF_2	0.369	0.219	−0.289
H_2	0.349	0.129	−0.105

* The residual term Δ was in all cases virtually zero (absolute values <0.010).

ation from the CDA about the importance of the charge contribution for the bond energy; in particular, the energetic effect of the repulsive term is not clear. The CDA results are a measurement of the change of the electronic structure in terms of donation and back donation. Even though the absolute values should not be taken too seriously, relative values are of great use for a comparison of different ligands. In this way, we can see from Table 6 that SiO is a weaker donor and a slightly weaker acceptor compared to CO. In contrast, CS has a clearly larger back donation than CO, in agreement with textbooks[29] which describe CS as a stronger π-acceptor ligand. As expected, N_2 is calculated to be a rather weak donor–acceptor ligand, but back donation clearly dominates. The same conclusion about the nature of the N_2 ligand was drawn using an analysis of the Mössbauer spectra of several dinitrogen complexes.[30] The charged ligands also follow the expectations: NO^+ is mainly characterised by back donation, while CN^- and also NC^- are virtually pure donor ligands. The observation that CF_2 is a stronger donor but a weaker acceptor as compared to CH_2 may easily be explained by π stabilisation of the difluoro-carbene ligand through the lone pairs at fluorine.[31] For the H_2 ligand a significant amount of back donation is expected as an explanation for the experimentally observed M–H_2 rotation barrier.[32] Indeed, the CDA for $W(CO)_5(H_2)$ yields some back donation, but overall H_2 is a stronger donor than acceptor.

To summarise, the charge decomposition analysis of the series of $W(CO)_5L$ complexes with various ligands L confirms a number of textbook ideas about classical ligands in co-ordination chemistry. The remarkable aspect of this result is that we have achieved the characterisation of the ligands in a well defined way from the ab initio wavefunctions of the complexes. It is important to note, however, that this characterisation only holds for complexes of the Dewar–Chatt–Duncanson type. We have shown above that there is a second class of transition-metal compounds that should be described in a different way.

Covalent Metal–Ligand Bonds: the Question of Hybridisation

As stated in the introduction, the question of valence-orbital hybridisation in covalent transition-metal bonds has received little attention by modern theoretical chemistry. The correlation between sp hybridisation and geometrical variables such as bond lengths and angles for main-group compounds is found in standard textbooks of chemistry. The question whether a similar correlation exists for transition-metal compounds, which have sd-hybridised bonds, is not trivial. Dobbs and Hehre[33] postulated in 1986 that the Ti–Cl bond length *increases* when the hybridisation at Ti changes from sd^3 to sd^2 and sd, which is opposite to the well known trend for sp^x-hybridised bonds of

Table 7 Calculated bond angles (°) of $(CH_3)_2XCl_2$ molecules at the MP2/II level; experimental values in parentheses

Molecule	C–X–C	Cl–X–Cl
$(CH_3)_2CCl_2$ [a]	113.1 (113.0 ± 0.4)	108.7 (108.3 ± 0.3)
$(CH_3)_2SiCl_2$ [b]	114.2 (114.7 ± 0.3)	108.2 (107.2 ± 0.3)
$(CH_3)_2GeCl_2$ [c]	118.3 (121.7 ± 1.4)	106.6 (106.1 ± 0.6)
$(CH_3)_2SnCl_2$ [d]	122.0 (110.1 ± 9.1)	105.9 (107.5 ± 3.9)
$(CH_3)_2PbCl_2$	128.9	105.1
$(CH_3)_2TiCl_2$ [e]	102.7 (102.8 ± 0.9)	120.1 (117.3 ± 0.3)
$(CH_3)_2ZrCl_2$	105.0	117.6
$(CH_3)_2HfCl_2$	104.9	116.5

[a] Ref. 35. [b] Ref. 37. [c] Ref. 38. [d] Ref. 39. [e] Ref. 40.

Table 8 Results of the NBO analysis of the compounds $(CH_3)_2XCl_2$ at the MP2/II level*

	X–C			X–Cl		
Molecule	% s(X)	% p(X)	% d(X)	% s(X)	% p(X)	% d(X)
$(CH_3)_2CCl_2$	31.4	68.5	0.1	18.6	81.1	0.2
$(CH_3)_2SiCl_2$	29.3	69.2	1.5	20.7	76.8	2.6
$(CH_3)_2GeCl_2$	30.7	68.8	0.5	19.3	79.4	1.3
$(CH_3)_2SnCl_2$	30.6	69.3	0.2	19.4	79.8	0.8
$(CH_3)_2PbCl_2$	31.8	68.2	0.0	18.2	81.6	0.2
$(CH_3)_2TiCl_2$	22.7	0.1	77.2	27.1	0.3	72.6
$(CH_3)_2ZrCl_2$	24.2	0.2	75.7	25.7	0.5	73.8
$(CH_3)_2HfCl_2$	25.5	5.4	69.1	24.4	11.0	64.6

* % s(X), % p(X) and % d(X) gives the hybridisation of the X–C and X–Cl bonds at the central atom X.

main-group elements. In the following we will show that the correlation between sp[x] hybridisation and bond angles for compounds of main-group elements, which is known as Bent's rule,[34] is also opposite to the correlation between sd[x] hybridisation and bond angles in transition-metal compounds.

Bent's rule states that 'atomic s-character concentrates in orbitals directed toward electropositive substituents'.[34] The rule was derived from a systematic comparison of the physical properties of molecules and a correlation with qualitative models such as valence-bond structures and hybridisation. It was very successful in predicting the changes of a structure upon exchange of two atoms or groups of different electronegativity.[35] However, does it also hold for transition-metal compounds with covalent metal–ligand bonds? In order to address this question we studied the equilibrium geometries of the main-group compounds $(CH_3)_2XCl_2$ (X = C, Si, Ge, Sn or Pb) and the isostructural transition-metal compounds $(CH_3)_2XCl_2$ (X = Ti, Zr or Hf).[36] The calculated C–X–C and Cl–X–Cl angles (MP2/II) are given in Table 7. The agreement with experimental data is very good. The experimental value for the C–Sn–C angle has a large error bar, which makes the reported value questionable.

For the main-group compounds the calculated as well as experimental C–X–C angles are always larger than the corresponding Cl–X–Cl angles. This is in agreement with Bent's rule: the chlorine atom has a much higher electronegativity than the methyl group and consequently the X–Cl bonds have a higher p character at the central atom than do the X–C bonds. The calculations predict also that the Cl–X–Cl angle decreases and the C–X–C angle increases continuously from X = C to Pb. The opposite order of the Cl–X–Cl and C–X–C bond angles is calculated for the transition-metal compounds. The Cl–X–Cl angle is always clearly larger than the C–X–C angle for X = Ti, Zr or Hf. This result seems to be in opposition to the predictions of Bent's rule. It cannot simply be explained by the size or the electronegativity of the central atom. The trend of the bond angles of the transition-metal compounds is also in contradiction to the original valence shell electron pair repulsion (VSEPR) model,[41] which predicts that higher ligand electronegativity should lead to smaller bond angles.** It is obvious that the calculated and experimentally observed change of the bond angles has to be traced back to a fundamental difference in the covalent X–Cl and X–C bonds for X = C to Pb and Ti to Hf.

In order to elucidate this difference in bonding, we carried out a natural bond orbital (NBO) analysis[43] of the compounds (Table 8). For the main-group molecules the argumentation leading to Bent's rule is fully confirmed: the central atom is sp[x] hybridised in the bonds to chlorine as well as in the bonds to the methyl groups, but the s contribution is always clearly smaller in the X–Cl bonds. For the transition-metal compounds we get a completely different picture. All the bonds are essentially sd[3]

** A more recent version of the VSEPR model, which takes into account the effect of Pauli repulsion and core polarisation, gives an explanation why the original VSEPR model fails for these molecules.[42]

hybridised at the central atom with negligible contributions by the metal p orbitals. This is in agreement with photoelectron spectroscopic studies of $(CH_3)TiCl_3$ which clearly demonstrate that Ti is sd[3] hybridised.[44] However, the s character at X = Ti and Zr is *lower* for the X–C than for the X–Cl bonds, in contrast to the results for the main-group molecules and to the predictions of Bent's rule. In the case of $(CH_3)_2HfCl_2$ we find a significant amount of p character in the Hf–C and particularly in the Hf–Cl bonds. The s character at Hf for the Hf–C bonds is higher than for the Hf–Cl bonds, but the amount of the (energetically higher-lying) metal p contribution is clearly larger in Hf–Cl than in Hf–C.

How can we explain the apparent contradiction between the calculated s character of the transition-metal bonds and the predictions of Bent's rule? To this end, it is useful to work out the theoretical foundation of the rule which was originally suggested only for main-group elements. Covalent σ bonds of main-group elements are mainly sp[x] hybridised. The valence p orbitals of a main-group element are always higher in energy than the valence s orbitals. Atomic p character concentrates in orbitals directed toward electronegative substituents, because the electron density can more easily be withdrawn from higher-lying orbitals than from the more tightly bound low-lying orbitals. For transition metals we face a somewhat different situation: covalent σ bonds of transition metals are mainly sd[x] hybridised. The most important aspect to consider is that the energy levels of the valence d orbitals are generally below the energy level of the valence s orbital.[45] It follows that covalent bonds of transition metals with electropositive substituents should have a higher d character than transition-metal bonds with electronegative elements. This is exactly what is calculated for $(CH_3)_2XCl_2$ (Table 8). Bent's rule should therefore be formulated in a more general way: 'The energetically lower-lying valence orbital concentrates in bonds directed toward electropositive substituents'.

Unfortunately, the correlation between sd[x] hybridisation and bond angle is not as straightforward as for sp[x]-hybridised bonds. For example, a pair of sd[3] functions has two energy minima at angles of 71 and 109°.[46] The calculated results presented in Tables 7 and 8 indicate that for the studied transition-metal compounds a higher d character leads to a smaller bond angle, but further investigations are necessary in order to generalise these findings.

Borderline Cases

In the previous sections we showed that a classification of the bonds of a ligand to a transition metal into covalent and donor–acceptor types is possible in a theoretically well defined way and that it is also very useful. Like all bonding models which are helpful for a classification of the observed phenomena, there are examples that make it difficult to decide to which type they belong. For instance, strongly polar bonds can be
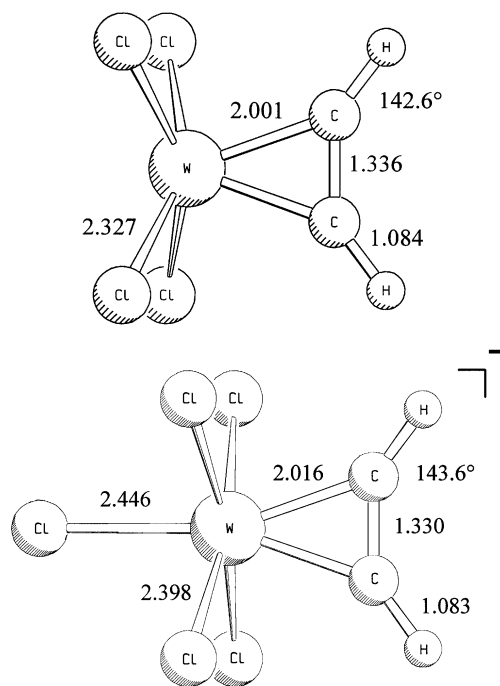
Fig. 6 Optimised geometries of WCl$_4$(C$_2$H$_2$) **5** and WCl$_5$(C$_2$H$_2$)$^-$ **6**. Bond lengths in Å at the MP2/II level
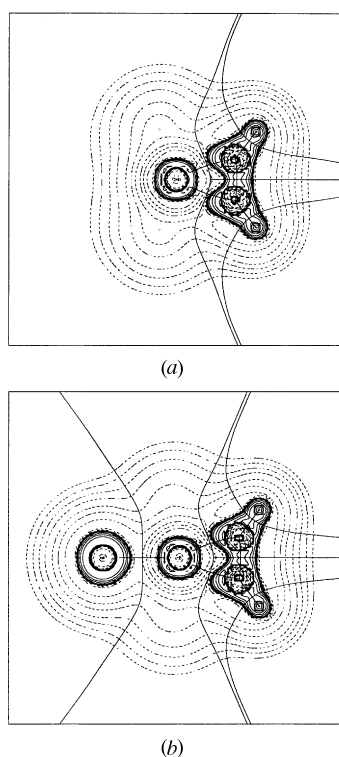
Fig. 7 Contour-line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ at the MP2/II level of (*a*) WCl$_4$(C$_2$H$_2$) and (*b*) WCl$_5$(C$_2$H$_2$)$^-$ in the respective molecular plane. Details as in Fig. 3

considered as mainly ionic or as still being covalent. In the case of the distinction between covalent and donor–acceptor types of bonds to a transition metal, there are a number of borderline cases, for which a classification into either type is possible and leads to a reasonable description of the compounds. The result of the bonding analysis using the CDA method depends on the fragments chosen. For example, the W–Cl bond in WCl$_6$ is clearly covalent, if the molecule is regarded as being built from a chlorine atom and the WCl$_5$ fragment. Nevertheless, the bonding can as well be understood as the interaction between

Table 9 Calculated bond orders and energy densities H_b (hartree Å^{-3}) at the bond critical points

	Molecule	Bond	Order	H_b
5	WCl$_4$(C$_2$H$_2$)	W–C	1.09	−0.486
		C–C	1.64	−2.605
6	WCl$_5$(C$_2$H$_2$)$^-$	W–C	1.04	−0.452
		C–C	1.66	−2.618

Table 10 Charge decomposition analysis of the complexes in their MP2 geometries

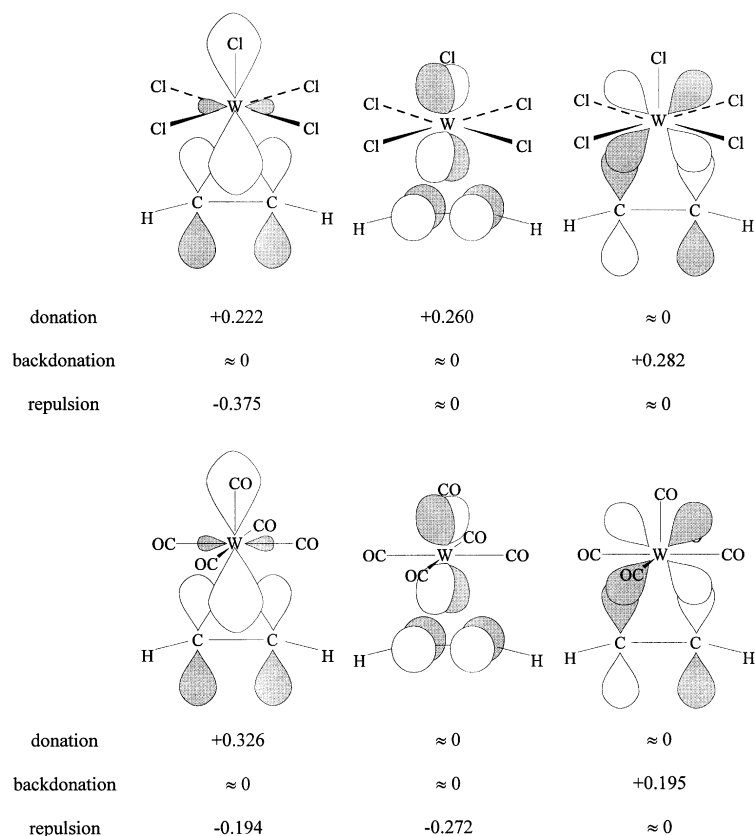|	**5** WCl$_4$(C$_2$H$_2$)	**6** WCl$_5$(C$_2$H$_2$)$^-$
d	0.057	0.308
b	−0.140	0.234
r	−0.189	−0.760
Δ	0.382	−0.048

a chloride anion and WCl$_5^+$. In this way, we can also apply the charge decomposition analysis which yields reasonable results and characterises the Cl$^-$ ligand as purely donative ($d = 0.767$, $b = -0.044$, $r = -0.408$, $\Delta = -0.019$). The value of such an interpretation depends on the questions one wants to address. It should be noted, however, that even the ethane molecule can be interpreted as a donor–acceptor complex, if it is divided heterolytically into methyl anion and methyl cation.

However, there are also borderline cases of the classification for which the division of the molecule into a metal fragment and ligand is rather unambiguous. One such example is the WCl$_5$(C$_2$H$_2$)$^-$ anion, which can be thought of as being derived from WCl$_4$(C$_2$H$_2$) by addition of a chloride ion. As discussed above, WCl$_4$(C$_2$H$_2$) **5** is a typical transition-metal compound with a covalently bonded ligand. The calculated W–C bond is very short (2.001 Å) and the C–C bond of the co-ordinated acetylene is as long as in free ethylene (1.336 Å),[47] in excellent agreement with experimental data (Fig. 6).[48] The analysis of the electron-density distribution confirms that WCl$_4$(C$_2$H$_2$) is a metallacyclopropene: the Laplacian distribution shows a strong distortion of the co-ordinated acetylene (Fig. 7) and the energy density at the W–C bond critical point is clearly negative ($H_b = -0.486$ hartree Å^{-3}, Table 9). Furthermore, the covalent bond order is 1.09 for the W–C bond and 1.64 for the C=C bond, which is comparable to the value of 1.89 for the C=C double bond in free ethylene. Last but not least, the charge decomposition analysis supports the picture of a covalent metal–ligand bond: a negative value for the back donation and a large residual term (Table 10) clearly indicate that the interpretation of the bonding within the Dewar–Chatt–Duncanson model is not appropriate.

Fig. 6 shows that the addition of Cl$^-$ to the neutral WCl$_4$(C$_2$H$_2$) leads to only minor geometrical changes. As expected, the W–Cl distances are somewhat elongated. More importantly, the acetylene ligand is more weakly bonded in the charged complex WCl$_5$(C$_2$H$_2$)$^-$ ($D_e = 22.3$ kcal mol^{-1}) than in WCl$_4$(C$_2$H$_2$) ($D_e = 36.6$ kcal mol^{-1}). The lower dissociation energy correlates with the changes in the calculated bond lengths: the W–C distance increases from 2.001 to 2.016 Å, while the C–C distance slightly decreases from 1.336 to 1.330 Å. The overall geometry changes in favour of a donor–acceptor description, with the acetylene ligand occupying just one co-ordination site in the pseudo-octahedral complex **6**. However, can the addition of a single chloride ion lead to a fundamental change in the type of bonding?

The Bader analysis of WCl$_5$(C$_2$H$_2$)$^-$ shows that there is no substantial change in the electron-density distribution as compared to the neutral molecule **5**. In the Laplacian distribution (Fig. 7) we can still see the strong distortion of the co-ordinated acetylene and again calculate a clearly negative energy density

donation	+0.222	+0.260	≈ 0
backdonation	≈ 0	≈ 0	+0.282
repulsion	-0.375	≈ 0	≈ 0

donation	+0.326	≈ 0	≈ 0
backdonation	≈ 0	≈ 0	+0.195
repulsion	-0.194	-0.272	≈ 0

Fig. 8 Schematic representation of the most important complex orbitals for the metal–acetylene interactions in $WCl_5(C_2H_2)^-$ and in $W(CO)_5(C_2H_2)$ as revealed by the charge decomposition analysis

at the W–C bond critical point (Table 9). The covalent bond orders (W–C, 1.04; C–C, 1.66) also suggest that the metal–ligand bond in $WCl_5(C_2H_2)^-$ is just as covalent as in $WCl_4(C_2H_2)$. However, and this is why we should think of it as of a borderline case, the charge decomposition analysis tells us that we can describe $WCl_5(C_2H_2)^-$ as a donor–acceptor complex (Table 10). The acetylene ligand is a somewhat stronger donor than acceptor and, as a result of the total negative charge of the complex, the repulsive term is unusually large (−0.760). This explains the rather low bond dissociation energy of the acetylene ligand. The breakdown of the CDA data into orbital contributions yields a further remarkable result:[47] in $WCl_5(C_2H_2)^-$ the C_2H_2 ligand acts as a four-electron donor; there are contributions to the donation from the in-plane and from the out-of-plane π orbital. This is only possible because the WCl_5^- fragment has a d^2 electronic configuration at tungsten with unoccupied orbitals of the correct symmetry to interact with both filled π orbitals of acetylene. In contrast, the $W(CO)_5$ fragment has a d^6 electronic configuration and there is no empty orbital at tungsten to receive electrons in the perpendicular plane. Consequently, the CDA shows that acetylene acts as only a two-electron donor in $W(CO)_5(C_2H_2)$.[47] This is schematically shown in Fig. 8, which displays the most important orbital interactions of $WCl_5(C_2H_2)^-$ and $W(CO)_5(C_2H_2)$ as revealed by the charge decomposition analysis.

Conclusion

In this Perspective we wanted to demonstrate that the results of state-of-the-art quantum-mechanical calculations of transition-metal compounds do not only give highly accurate geometries, bond dissociation energies and other molecular properties that are helpful for the experimental chemist. In addition, the calculations can also be employed to extract useful chemical models which lead to a better understanding of the bonding situation of the molecules. Modern theoretical methods have been

developed in order to analyse the calculated numbers and to transform the complex numerical expression of the electronic structure into a chemical model. It is suggested that the bonding interactions in transition-metal compounds should be classified into donor–acceptor bonds between the metal and the ligand, which are characteristic for true complexes, and covalent bonds where each bonding partner contributes one electron. It is shown that the puzzling structural and chemical properties of molecules belonging to two exemplary classes of transition-metal compounds, *i.e.* compounds with π-bonded ligands and metal–carbene compounds, can be understood when the bonding is interpreted either in the covalent or in the donor–acceptor bonding model. The charge decomposition analysis renders it possible to decide if a given transition-metal compound can reasonably be discussed as a complex between a ligand L and the metal fragment. The calculated L→M donation and M→L back donation for a complex can be used as a quantitative expression of the Dewar–Chatt–Duncanson model, with the additional information of the calculated L↔M repulsive polarisation. It is pointed out that the effect of metal sd hybridisation on the molecular structure of transition-metal compounds needs further theoretical studies. The main message of this Perspective is that quantum chemistry has now been developed not only as a quantitative tool for calculating transition-metal (and other heavier atom) compounds, but that it also provides the basis for giving *insight besides the numbers*.

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