Tracing an organometallic early—late transition element relationship

H. Berke and H. Jacobsen*

Institute of Inorganic Chemistry, University of Zurich,
*190 Winterthurer Strasse, CH-8057 Zurich, Switzerland.**
Fax: 41 (1) 364 0191. E-mail: hberke@aci.unizh.ch

This work explores M. E. Vol'pin's early notion that $TiCp_2$ possesses carbenoid character, and transfers this concept to the related dicarbonyl bis(phosphorus donor)iron fragment. Similarities and differences in electronic and molecular structure of the titanium and iron fragment are elucidated based on density functional calculations. Isolobal analogies to the carbene unit are presented to rationalize the computational results. Experimental verification of analogies between $TiCp_2$ and $Fe(CO)_2L_2$ chemistries is given.

Key words: titanocene, dicarbonylbis(phosphine)iron, carbenoids; isolobal analogy; density functional theory.

One of the early "bridge building" ideas of M. E. Vol'pin arose in the area of early transition metal metallocene chemistry.[1—20] In 1963 he published an article[21] together with the coauthors in which the following curious statements were put forward:

"It has previously been shown that derivatives of divalent silicon and germanium possess "carbenoid" properties, *i.e.*, the ability to enter into the same types of reactions as compounds of divalent carbon (the carbenes). We presumed that compounds of the transition elements might also possess analogous carbenoid properties, provided the following fundamental conditions were observed..." "From this point of view, a "carbenoid" character should be possessed by dicyclopentadienyititanium, in particular, since the electronic configuration of titanium in this compound satisfied all of the conditions enumerated above..." and "It would be expected that this compound, like carbenes, would be capable of reacting with unsaturated compounds with the formation of two or four new titanium-carbon bonds. On the basis of these considerations, we undertook a study of the reaction of dicyclopentadienyititanium (nascent) with diphenylacetylene..."[21]

Later on this thoughtful idea that titanocene $TiCp_2$ is in its chemical and electronic properties comparable to carbenes CR_2 was supported further by quantum mechanical EHT calculations by Brintzinger and Bartell in 1970 [22] and by Hoffmann and Lauher in 1976.[23]

Furthermore, in 1982 R. Hoffmann[24] announced in a unifying approach his concept of isolobal analogy, which provided a general base for Vol'pin's original thought. Meanwhile this model of the isolobal analogy is extensively used to especially build bridges between inorganic or organometallic and organic chemistry relating these different areas of chemistry mostly by a fragmental view of molecules. As a quite general model the isolobal analogy is bound to abstract only a piece of reality and, as R. Hoffmann stated in his article,[24] it has to be seen "how far the model can be pushed" and "where it breaks down."

Based on this analogy this personal review attempts to trace the relation of Vol'pin's and others' early transition metal metallocene chemistry with the carbenoid $Fe(CO)_2(PR_3)_2$ chemistry of our laboratory. Indeed, the group IV metallocenes are isolobal to carbenes and these in turn are isolobal to $Fe(CO)_2(PR_3)_2$ fragments:

$$\mathrm{MCp_2} \underset{\smile}{\longleftrightarrow} \mathrm{R_2C} \underset{\smile}{\longleftrightarrow} \mathrm{Fe(CO)_2(PR_3)_2},$$

$$\mathrm{M = Ti,\ Zr,\ Hf.}$$

When we apply this concept in the further context, it will be intriguing to see that many important aspects of the chemical behavior of these fragments are very similar. However, we will also have to discover discrepancies, which make clear that metallocene fragments still bear their own electronic character which is different from that of $Fe(CO)_2(PR_3)_2$ units.

A precise view of the electronic properties of $TiCp_2$ and $Fe(CO)_2(PR_3)_2$ fragments based on ab initio calculations

Our first idea was to quantify the isolobal relationship between the $TiCp_2$ and $Fe(CO)_2(PMe_3)_2$ fragment,

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* Anorganische-chemisches Institut, Universität Zurich-Irchel, Winterthurer Strasse 190, CH-8057, Zürich, Schweiz.

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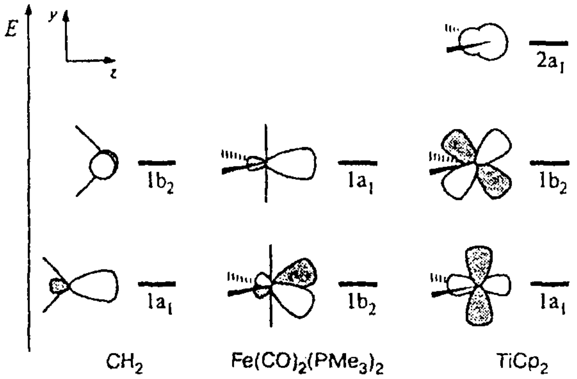
applying quantum chemical calculations[25] based on approximate density functional theory (DFT)[*].

The isolobal analogy, as formulated by Hoffmann, is designed to transfer the concepts in chemical bonding that have been justified for the first row and second row elements, to the area of transition metal chemistry. In particular, transition metal fragments are related to familiar building blocks from the field of organic chemistry. The notion implies that two fragments are called "isolobal" if the number, symmetry properties, relative energy, and shape of their frontier orbitals as well as the number of electrons occupying them are similar.[24] To establish the isolobal relationship between our transition metal fragments and the methylene unit, as stated above, we begin with a brief analysis of the frontier orbitals of the three moieties.

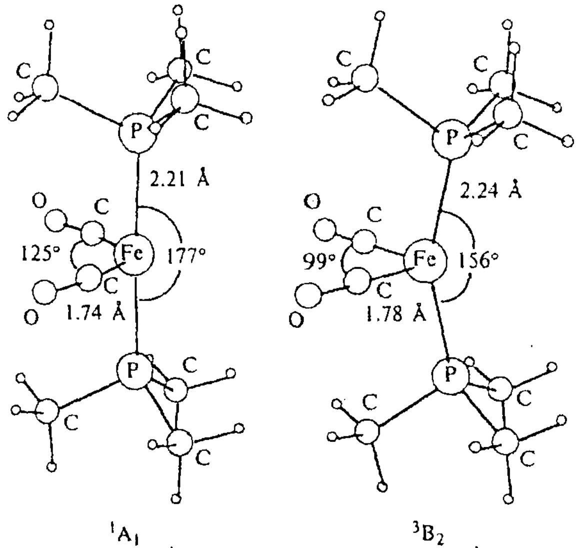
The frontier orbitals of the carbene prototype CH_2 are displayed on the left side in Scheme 1. We essentially have one orbital available for σ-bonding, as well as one orbital which can undergo π-interactions. According to C_{2v} symmetry, these orbitals are classified as $1a_1$ and $1b_2$, respectively. The frontier orbitals of $Fe(CO)_2(PMe_3)_2$ and $TiCp_2$ are well known;[26] they can be analyzed as representatives of the d^8-ML_4 [26a] and d^2-MCp_2 [26b] class, respectively. As indicated in Scheme 1, the frontier orbitals of $Fe(CO)_2(PR_3)_2$ are indeed similar, in shape and in symmetry, to that of CH_2; the $1a_1$ and $1b_2$ orbitals are dominated by contributions from metal based d-orbitals. One difference between the main group moiety and the d^8-ML_4 fragment is that for the latter the π-binding orbital $1b_2$ is at lower energies than the $1a_1$ σ-orbital. For d_2-$TiCp_2$, the set of frontier orbitals is usually considered to consists of three orbitals, namely two of a_1 and one of b_2 symmetry, as displayed on the right side of Scheme 1. For our further discussion, the orbital $2a_1$ will be of minor importance. Again, the set $TiCp_2\{1a_1, 1b_2\}$ is isolobal to the set $CH_2\{1a_1, 1b_2\}$. The frontier orbitals, as discussed above, mainly determine the kind of bonding interactions our transition metal fragments will undergo. It should be noted, however, that secondary orbital interactions involving occupied or unoccupied orbitals at lower or higher energies also play a role in the chemical bonding of these units. This is one important point in which the transition metal fragments differ from their related, isolobal main group counterparts.

Scheme 1



Two electrons have to be distributed among the $1a_1$ and $1b_2$ frontier orbitals. This may cause different electronic configurations. One can for example realize a singlet state, in which the $1a_1$ and $1b_2$ orbital form the HOMO/LUMO set, or one can think of a triplet state, in which $1a_1$ and $1b_2$ are both occupied by one electron of equal spin. Methylene is experimentally known[27] to have a $^3B_2(1a_1)^1(1b_2)^1$ ground state; the $^1A_1(1a_1)^2$ singlet state lies 38 kJ mol^{-1} above the triplet state.[*]

Scheme 2



$^1A_1$
(0 kJ mol^{-1})

$^3B_2$
(4 kJ mol^{-1})

For $Fe(CO)_2(PMe_3)_2$, optimized geometries corresponding to the $^1A_1(1b_2)^2$ singlet and the $^3B_2(1a_1)^1(1b_2)^1$ triplet are shown in Scheme 2. The singlet fragment adapts a typical C_{2v} butterfly arrangement, whereas the

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[*] The DFT calculations utilized the ADF program package, release 2.1.[25a] Nonlocal gradient corrections due to exchange[25b] and correlation[25c] were included self-consistently. Use was made of the frozen core approximation. For C and O, the valence shells were described using a double z-STO basis, augmented by one d-STO polarization function (ADF database III). For the *ns*, *np*, *nd*, (*n* + 1)s, and (*n* + 1)p shells on the transition metals, an uncontracted triple z-STO basis was employed (ADF database IV with three (*n* + 1)p functions). H was treated with a double z-STO basis and one additional p-STO polarization function (ADF database III). All calculations were performed in C_{2v} symmetry. For a more detailed description, as well as further references, see Ref. 25d.

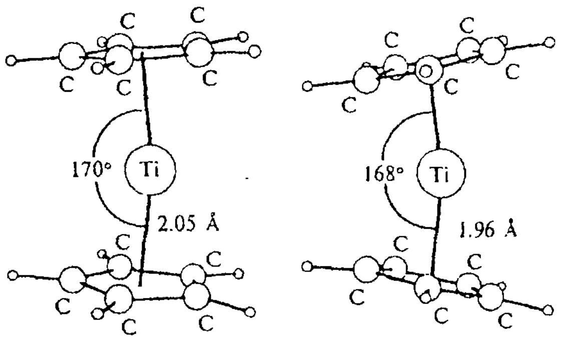
[*] For a discussion of DFT calculation of methylene, see, *e.g.*, Ref. 28.

triplet fragment is significantly distorted towards an idealized tetrahedral coordination. This trend can easily be rationalized by qualitative orbital arguments.[26a]

It is interesting to compare the $Fe(CO)_2(PMe_3)_2$ fragment with the d^8-ML_4 prototype $Fe(CO)_4$. Calculations[29] indicate that this molecule now has a $^3B_2$ triplet ground state, with a similar distorted tetrahedral geometry. This is also in agreement with experimental studies done on $Fe(CO)_4$.[30] However, the $^1A_1$ singlet state lies only about 10 kJ mol^{-1} higher in energy, and is still close to the ground state.

The calculations on the $TiCp_2$ imply that this fragment should have a $^3B_2(1a_1)^1(1b_2)^1$ triplet ground state. Very close in energy, and 2 kJ mol^{-1} above the ground state, there is a $^3A_1(1a_1)^1(2a_1)^1$ state. The lowest energy singlet state is $^1A_1(1a_1)^2$, and is 41 kJ mol^{-1} above the ground state. Also of importance is the $^1A_1(1b_2)^2$ singlet state, which is 5 kJ mol^{-1} higher in energy. In contrast to $Fe(CO)_2(PMe_3)_2$, the $TiCp_2$ fragment shows a sizable singlet-triplet splitting, comparable to that of methylene. The geometries for the lowest energy singlet and triplet states are displayed in Scheme 3. One notes that the cyclopentadienyl rings are only slightly bent away from a linear C_c—Ti—C_c arrangement by 10° and 12°, C_c being the centroid of the Cp rings.

Scheme 3

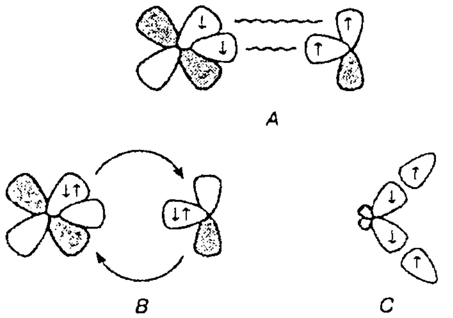


$^3B_2$
(0 kJ mol^{-1})

$^1A_1$
(41 kJ mol^{-1})

Having evaluated the electronic configuration of our two transition metal fragments, we now carry the isolobal analogy one step further. The CR_2 unit is usually regarded as the main building block for formation of double bonds. According to the isolobal analogy, the $Fe(CO)_2(PMe_3)_2$ and the $TiCp_2$ units should be able to undergo similar bonding interactions. Depending on the choice of our electronic valence state, we either can describe the resulting double bonds as singlet coupling of two triplet fragments, leading to genuine double bonds with nearly covalent σ and π contributions (Scheme 4, *A*), or as donor-acceptor bonds between two singlet fragments, resulting in polarized σ- and π-bonds (Scheme 4, *B*). Another important bonding interaction for d^8-ML_4 and d^2-MCp_2 fragments is the formation of two single bonds with two additional ligands both having one unpaired electron. Here, the valence state of the transition metal fragment is again the triplet state (Scheme 4, *C*). We will not discuss this situation in detail, but rather focus on the different modes of double bonding for CH_2-isolobal fragments.

Scheme 4



We optimized the geometries for four [M]=L systems ([M] = $Fe(CO)_2(PMe_3)_2$, $TiCp_2$; L = CH_2, CO), Here, CH_2 is chosen as a model ligand for the formation of a genuine double bond, whereas CO serves as prototype for a donor-acceptor ligand. Selected structural parameters of this molecules are collected in Table 1.

We see that during the process of bond formation the transition metal fragment undergoes a geometry distortion, in order to reduce repulsive steric interaction with the incoming ligand. The major changes are observed in the soft vibrational modes, that is, in the C_c—Ti—C_c or

Table 1. Calculated structural parameters for [M]=L complexes

Complex	Bond length/Å				Bond angle/deg	
	Ti—L [a]	Ti—C_c	C_c—TiC_c	Fe—L [a]	P—Fe—P	C—Fe—C [b]
[Ti]=CH_2 [c]	195	205	145			
[Ti]=CO [c]	199	201	151			
[Fe]=CH_2 [d]				182	173	102
[Fe]=CO [d]				177	180	120

[a] L = CH_2, CO. [b] C = CO_{eq}. [c] [Ti] = $TiCp_2$. [d] [Fe] = $Fe(CO)_2(PMe_3)_2$.

P—Fe—P angle bents.* The angle CO_{eq}—Fe—CO_{eq} in [Fe]=CH_2 resembles that of the corresponding triplet fragment. We also note that the titanium fragment forms a shorter bond with CH_2 than with CO, but that for the iron fragment this situation is reversed. This might suggest that the [Ti] fragment favors the genuine double bond over the donor-acceptor bond.

To get a deeper understanding of the particular bonding situations, we perform a bond analysis for the reaction

$$[M] + L \rightarrow [M]{=}L, \qquad (1)$$

$[M] = Fe(CO)_2(PMe_3)_2$, $TiCp_2$; $L = CH_2$, CO.

The energy BE, which is related to the reaction in Eq. (1), can be interpreted as the [M]=L bonding energy, and can be written as

$$BE = BE_{snap} - \Delta E_{prep}. \qquad (2)$$

In Eq. (2), the so-called preparation energy, ΔE_{prep}, represents the energy required to make the ligands ready for the formation of the bond. It involves deformation of the ligand framework to the geometry in the final molecule, and, if required, electronic preparation from the ground state of the free fragment to its valence configuration. The electronic contribution is strongly determined by the singlet-triplet gap of the corresponding fragment. The term BE_{snap} in Eq. (2), the so-called bond snapping energy**,[31] then describes the energy of bond formation of the two fragments. We write the bond snapping energy as***

$$BE_{snap} = -(\Delta E_{\sigma}{}^{A_1} + \Delta E_{\pi}{}^{B_2} + \Delta E_{res}), \qquad (3)$$

where $\Delta E_{\sigma}{}^{A_1}$ is the orbital interaction energy due to formation of the σ-bond, whereas $\Delta E_{\pi}{}^{B_2}$ is related to π-bonding (*cf.* Scheme 4). The residual energy ΔE_{res} covers all remaining energy terms. It is dominated by steric repulsion, but also contains secondary orbital interactions. The results of our analysis are presented in Table 2.

For the formation of a genuine double bond with CH_2, one finds that both the [Fe] and the [Ti] fragment form rather strong σ-bonds and much weaker π-bonds. [Fe]=CH_2 shows a higher bond snapping energy, but also needs a higher preparation energy, so that the bond energies, BE, for [Ti]=CH_2 and [Fe]=CH_2 are nearly identical. For the donor-acceptor bond, one finds for both metal fragments σ- and π-interaction of comparable size. However, for [Ti]=CO the π component represents the major bonding interaction, whereas for [Fe]=CO the σ contribution is dominant. The bond energies for [Ti]=CO and [Fe]=CO now differ by almost 100 kJ mol^{-1}. One reason is the higher BE_{snap} values for the iron system, but the main cause is the high preparation energy for the titanium system, which in turn is dominated by the large singlet-triplet splitting of the $TiCp_2$ fragment. Whereas the donor-acceptor bond seems to be a favorable bonding scheme for the d^8-ML_4 fragment, it is not a good bonding situation for the d^2-MCp_2 moiety.

Table 2. Energy decomposition (kJ mol^{-1}) for the reaction [M] + L [M] + L → [M]=L

Complex	$\Delta E_{\sigma}{}^{A_1}$	$\Delta E_{\pi}{}^{B_2}$	ΔE_{res}	BE_{snap}	$\Delta E_{prep}{}^{a}$		BE
					[M]	L	
[Ti]=CH_2 [b]	−453	−159	191	421	10	27	384
[Fe]=CH_2 [b]	−512	−144	209	447	30	35	382
[Ti]=CO [b]	−138	−179	103	214	62	7	145
[Fe]=CO [b]	−179	−166	82	263	23	7	233

[a] The preparation energy is divided into contributions due to the metal fragment [M] and the ligand L.
[b] For designations, see Notes "c, *d*" in Table 1.

Table 3. Electron polarization (au) of [M]=L bonds

Complex	$A_1(\sigma)$		$B_2(\pi)$	
	[M]	L	[M]	L
[Ti]=CH_2 [a]	0.53	−0.52	0.01	0
[Fe]=CH_2 [a]	0.51	−0.50	0.07	−0.06
[Ti]=CO [a]	0.21	−0.22	−0.48	0.49
[Fe]=CO [a]	0.27	−0.29	−0.37	0.39

[a] See Notes "c, *d*" in Table 1.

Analyzing the double bond in terms of electron polarization, as listed in Table 3, shows that chemical bonding for both the [Fe] and the [Ti] is essentially the same. For the genuine double bond, we find in both cases a polarized σ-bond with electron depletion at the metal center, and an almost covalent π component. For the donor-acceptor bond, we find that now both components of the double bond are polarized, as was to be expected. The subtle differences in the electron polarization terms for the Fe and Ti fragments are reflected in the differences in $\Delta E_{\sigma}{}^{A_1}$ and in $\Delta E_{\pi}{}^{B_2}$, and finally in the different values for BE_{snap}.

We conclude our comparison of the $TiCp_2$ and $Fe(CO)_2(PMe_3)_2$ fragments by extending our calculations from the interaction of the metal fragments with the 2ē donors CH_2 and CO, to that of halides as potentially 3ē donors. The model compounds we choose are complexes of the type [M]—Cl, which in both cases exhibit an odd electron count. Optimized geometries for the two complexes are displayed in Scheme 5. The structural parameters compare fairly well with the X-ray data for the related compounds $TiCp'_2Cl$[32] (Cp′ is

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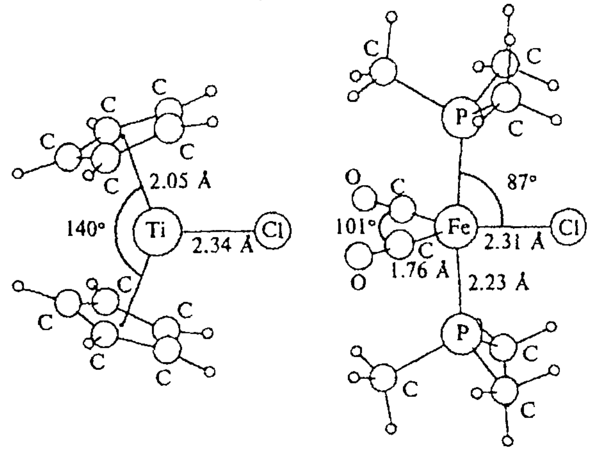
* The geometry of $(CO)Fe(CO)_2(PMe_3)_2$ is determined by symmetry.

** The terms BE and BE_{snap} are strongly related to dissociation enthalpies and bond enthalpy terms (*e.g.*, as defined in Ref. 31). Whereas dissociation enthalpies are accessible in the experiment, bond enthalpy terms often better describe the actual bond strength.

*** For detailed description and subsequent references, see, *e.g.*, Ref. 28.

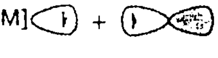
Scheme 5



pentamethylcyclopentadienyl)* and $Fe(CO)_2L_2X$ (L = $P(OPr)_3$, X = Br; L = PEt_3, X = I).** Again, the geometric arrangements of the carbonyl ligands in $Fe(CO)_2(PMe_3)_2Cl$ resemble that of the triplet $Fe(CO)_2(PMe_3)_2$ fragment.

When performing the bond analysis, the electronic state of the Cl atom was chosen in such a way that the p_z orbital was singly occupied. Thus, σ-bond formation of the a_1 type becomes the main bonding interaction, as outlined in Scheme 6. In addition, the doubly occupied p_x and p_y orbitals give rise to π contributions of the b_1 and b_2 type, respectively.

Scheme 6



Considering the valence state of the metal fragments, the second a_1 orbital at the Ti fragment will be of special importance. The electronic state for the interacting fragment is now $^3A_1$ rather than $^3B_2$. As we have mentioned above, the preparation energy for this state only amounts to 2 kJ mol^{-1}. Consequently, the b_2 orbital is now empty and available for possible donation from the p_y orbital, and the single electron remains in an a_1 orbital, which is exclusively metal based (the contribution from Cl based fragment orbitals to the singly occupied molecular orbital in [Ti]—Cl is less than 1%). On the other hand, for the iron fragment, there is no possibility of extending the valence configuration. When forming the [Fe]—Cl bond, it comes to a 2-orbital 3ē-interaction of B_2 type, and the single electron resides in a b_2 orbital with antibonding character between Fe and Cl (the contribution from Cl based fragment orbitals to the singly occupied molecular orbital in [Fe]—Cl amounts to 10%). This is reflected in the fact that the bond snapping energy for $TiCp_2Cl$ is 39 kJ mol^{-1} higher compared to $Fe(CO)_2(PMe_3)_2Cl$ ([Ti]—Cl: BE_{snap} = 430 kJ mol^{-1}; [Fe]—Cl: BE_{snap} = 391 kJ mol^{-1}). Our analysis shows further that the contribution of b_2—π-interactions is in general small, but stabilizing for the Ti—Cl bond, and destabilizing for the Fe—Cl bond ([Ti]—Cl: $\Delta E_\sigma^{A_1} = -587$ kJ mol^{-1}, $\Delta E_\pi^{B_2} = -26$ kJ mol^{-1}; [Fe]=Cl: $\Delta E_\sigma^{A_1} = -562$ kJ mol^{-1}, $\Delta E_\pi^{B_2} = 15$ kJ mol^{-1}).

At this point, we will summarize the results of our theoretical investigations. As predicted by the isolobal analogy, both the $TiCp_2$ and the $Fe(CO)_2(PMe_3)_2$ show similar bonding behavior toward CO and CH_2. The important difference in the electronic configuration of these fragments is the difference in singlet-triplet splitting. For $Fe(CO)_2(PMe_3)_2$, both a singlet and a triplet valence state are energetically easily accessible, so that this fragment should be able to form donor-acceptor bonds, as well as genuine double bonds. The higher lying singlet state of the $TiCp_2$ fragment is the main reason why this moiety prefers bonding interaction out of its triplet valence state. The difference in bonding behavior toward Cl lies in the possibility of the $TiCp_2$ fragment to extend is triplet valence coordination. Possible π-interactions stabilize the Ti—Cl bond, but destabilize the Fe—Cl bond, leading to the calculated differences in the bond snapping energies.

As we mentioned above, the formation of the two single bonds with two radical ligands is another possible bonding situation for the triplet fragment. The formation of $[\mathrm{M}]\!<^{\mathrm{L}}_{\mathrm{L}}$ molecules is known for both $Fe(CO)_2(PMe_3)_2$ and $TiCp_2$, but is for the latter by far the most common coordination mode. Other arguments come into play, which are not covered by the isolobal analogy. First, one has to note that the [Ti] fragment is more unsaturated than the [Fe] fragment, both coordinatively and electronically. This might favor $[\mathrm{Ti}]\!<^{\mathrm{L}}_{\mathrm{L}}$ coordination over [Ti]=L interaction. Also, secondary orbital interactions may become of crucial importance. For the $TiCp_2$ system, it has been suggested that the $1b_1$ orbital, which is perpendicular to the plane of the $1b_2$ orbital (see Scheme 1), might play an important role in chemical bonding.[34] Nevertheless, the results of our analysis are in complete accord with the intuitive descriptions brought forward by Vol'pin almost 35 years ago.

Experimental verification of analogies between $TiCp_2$ and $Fe(CO)_2L_2$ chemistries

Following the spirit of Vol'pin's early statement, this article is meant to emphasize generalities. Our analysis of real chemistry will try to establish a compari-

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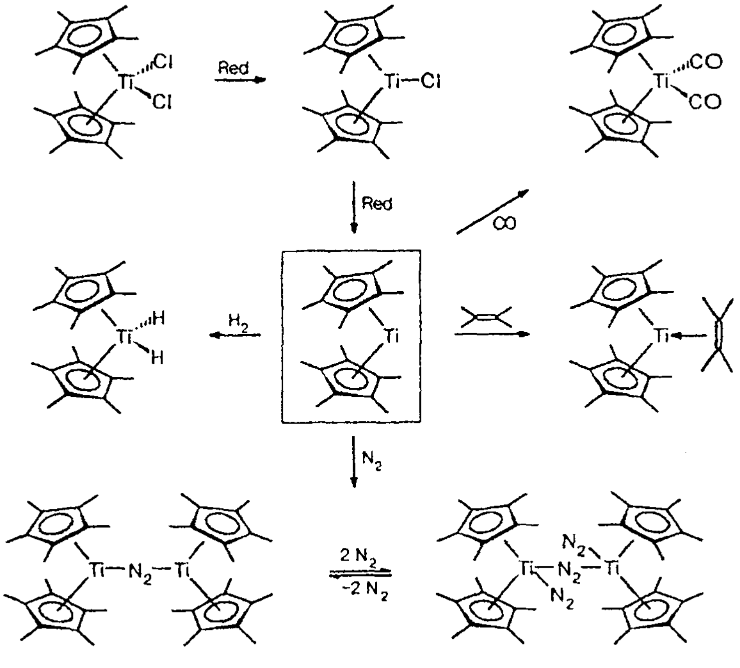
* Selected geometric parameters of $TiCp'_2Cl$: Ti—Cl, 2.363(1) Å; Ti—C_c, 2.01(1) Å; C_c—Ti—C_c angle, 143.6(2)°; C_c being the centroid of the Cp rings (for details, see Ref. 32).

** Selected geometric parameters of $Fe(CO)_2(PEt_3)_2I$: Fe—P, 2.250(2) Å and 2.245(2) Å; Fe—C, 1.774(7) Å and 1.777(7) Å; C—Fe—C angle, 97.5(5)° (for details, see Ref. 33).

Scheme 7



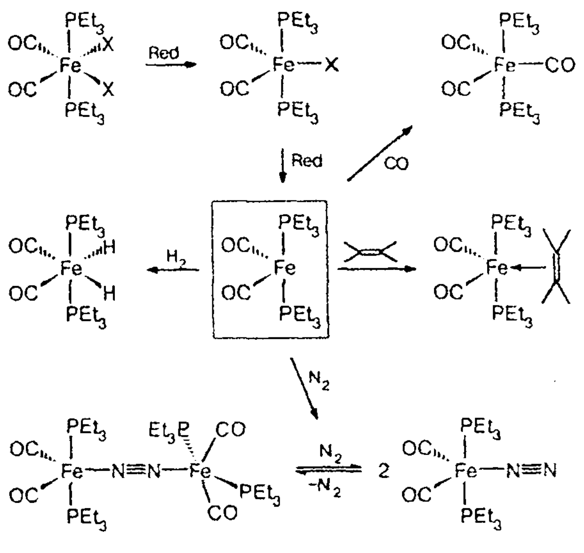
Red is a reducing agent

son of MCp_2 (M = Ti, Zr, and Hf) chemistry, which in part is indeed work from the Vol'pin group, and of $Fe(CO)_2L_2$ (L is a phosphorus donor) chemistry from our group. It will be interesting to see that the majority of general features of this "early—late" relationship really consists of similarities as indicated by the foregoing theoretical considerations. Seeking similarities without losing a critical view for those phenomena, which tend to indicate limitations of the analogies, we have chosen to start with a glance at very basic decamethyltitanocene chemistry (Scheme 7) developed by groups of Brintzinger and Bercaw[35] and our dicarbonylbis(phosphorus donor)iron chemistry[36] (Scheme 8).

Not going into too much detail, it is really amazing to recognize immediately that both schemes show great similarities in the two reduction steps and most substitution reactions. Dissimilarities arise in the two cases of the reactions with N_2 and CO, where titanocene takes up more than just one equivalent of ligand per Ti center. This reflects an enhanced capability of this fragment for ligand binding, which has also been clearly analyzed in the foregoing theoretical study. A closer look at the electronics of the related $TiCp_2Cl$ and $Fe(CO)_2(PMe_3)_2I$ radical species disclosed significant differences in their electronic structure, where the Ti system showed an almost purely metal centered SOMO, while that of the iron molecule possessed a considerable halogen contribution, but this apparently has no obvious structural consequence.

A more comprehensive survey of the early transition metal metallocene chemistry would then, however, reveal that a $TiCp_2Cl$ molecule has a dimeric structure[37] demonstrating again the higher potential of the $TiCp_2$ fragment for additional ligand uptake. In the permethylated system of Scheme 7 this tendency seems to be partly suppressed by the higher steric congestion of the C_5Me_5 group.

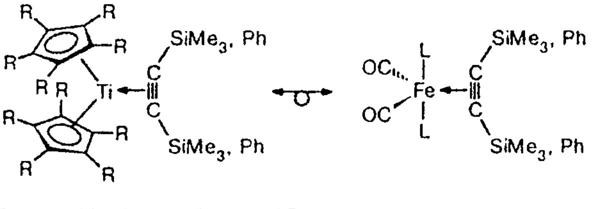
Scheme 8



Red is a reducing agent

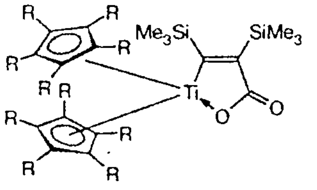
Let us now turn to the acetylene chemistry of the titanocene[1,2,4–12,14–17,19,21] and $Fe(CO)_2L_2$ fragments.[38,39] Both can take up one equivalent of tolan and bis(trimethylsilyl)acetylene to form isolobal complexes (Scheme 9). The respective titanocene, as well as the decamethyltitanocene chemistry, was even to a major extent explored in the Vol'pin group.

Scheme 9



R = H, Me; L = P(OMe)$_3$, PEt$_3$

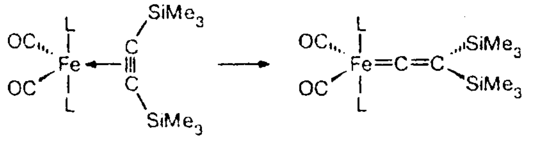
While the structural relationship of both types of acetylene species is obvious, their reactivity patterns show characteristic differences. In the case of the titanocene complexes further reactivity can be noticed, which again is dominated by the presence of a second low-lying empty orbital. This for instance enables the TiCp$_2$(Me$_3$SiC≡CSiMe$_3$) molecule to add CO$_2$ and further transform into a metallacylic species.[12,15]



R = H, Me

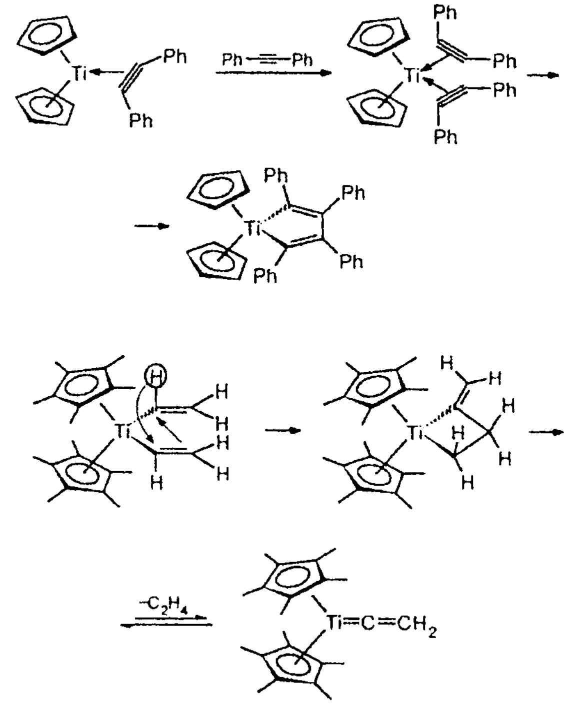
A similar reaction mode has been demonstrated for the TiCp$_2$(tolan) molecule,[7] which can take up another equivalent of tolan to finally undergo an oxidative cyclization[4,16,21] (Scheme 10). This reaction behavior is again in contrast to that of a Fe(CO)$_2$L$_2$(tolan) complex,[38] which is inert in this respect. Once again, this behavior may be attributed to the coordinative unsaturation caused by the additional low-lying LUMO of TiCp$_2$.

Although the bissilylacetylene iron compounds cannot be converted in this manor, they are not unreactive. They turned out to be susceptible to an acetylene/vinylidene rearrangement producing vinylidene complexes as thermodynamic products.



L = P(OMe)$_3$, PEt$_3$

Scheme 10



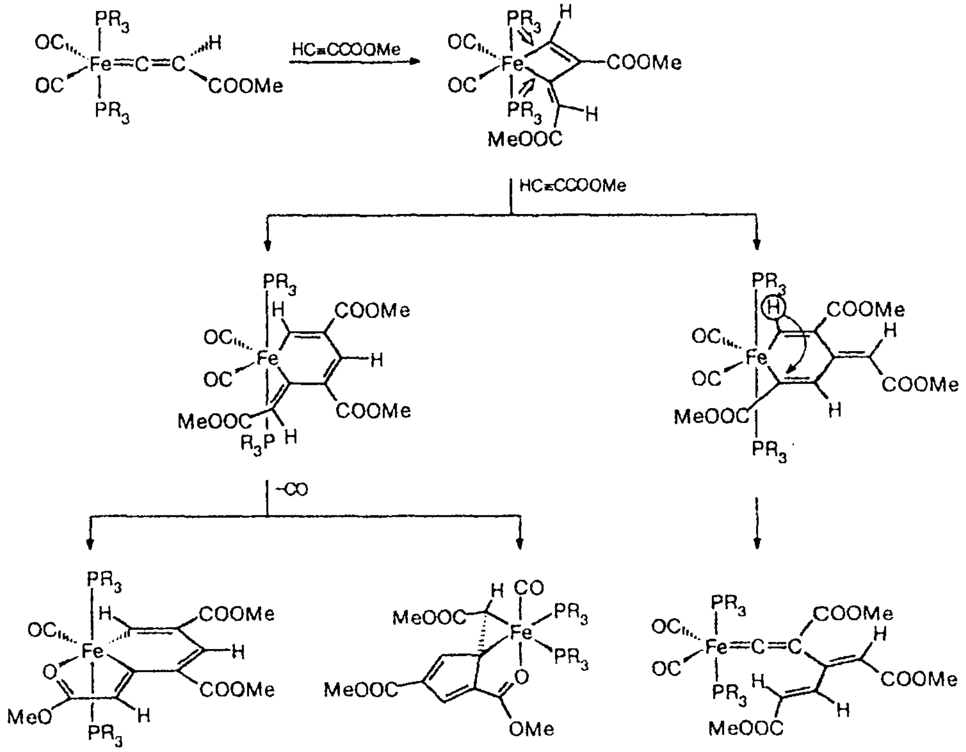
We note that there is apparent absence of an acetylene/vinylidene rearrangement for the TiCp$_2$(Me$_3$SiC≡CSiMe$_3$) species, which may be interpreted in terms of a thermodynamic preference of the acetylene complex. However, this statement must be taken with caution, since it is even very likely that considerable kinetic barries prevent this reaction in the more sterically crowded MCp$_2$ environment.

It is no surprise that the quite ubiquitous acetylene/vinylidene rearrangement of terminal acetylenes can easily be accomplished at Fe(CO)$_2$L$_2$ centers.[40—45] For group IV metallocenes this type of elementary step has been postulated in the context of acetylene polymerization, but it is still waiting for a definite proof. Nevertheless, the TiCp$_2$(C=CH$_2$) can be prepared, however, only *in situ* and not by an acetylene/vinylidene rearrangement route. According to Scheme 10 a TiCp$_2$Vinyl$_2$ derivative is a suitable starting material.[46]

Our DFT calculations have shown that a carbene moiety can tightly bind to both titanocene and Fe(CO)$_2$(PMe$_3$)$_2$ units with about equal strength. These findings should also hold for the carbenoid vinylidene fragment. Despite this bond strength biscyclopentadienyl vinylidene and alkylidene titanium[47] are quite reactive species, which can only be stabilized in [2+2] addition reactions involving an extra olefin molecule.

Alkyl- or aryl-substituted vinylidene complexes with the Fe(CO)$_2$L$_2$ fragments do not show particularly enhanced reactivity.[39—41,43,44] However, we recently showed that ester-substituted vinylidene units do un-

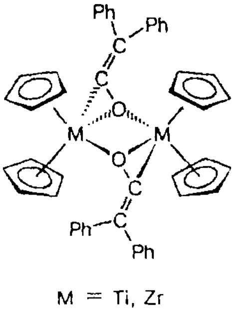
Scheme 11



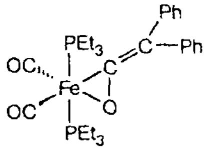
dergo further transformations at iron centers,[38,42,45] which are even related to the titanocene chemistry of Scheme 10. The general electron deficiency of such acetylenes and their vinylidene congeners now promotes the [2+2] addition of another propiolate molecule to form a ferracyclobutene moiety[45] (Scheme 11).

In a further acetylene addition step two regioisomeric bisvinyl iron complexes are formed, which stabilize themselves in different ways depending somewhat on the type of the phosphorus donor. It is interesting to see that the ultimate vinylvinylidene product of one such stabilization pathway can only be explained by the assumption of a 1,5-hydrogen transfer at the bisvinyl system quite analogous to the described transformation of the bisvinyl titanocene derivative (see Scheme 10). It is really amazing how similar such chemistries can be!

Finally we would like to turn our attention to ketene complexes of both fragments as further instructive examples of how far the analogy of both fragments would go. Group IV metallocene ketene complexes were prepared first in the late 1970s.[48] They showed a dimeric structure emphasizing the character of valence unsaturation for a MCp_2(ketene) unit. According to the discussed chemical behavior of MCp_2 fragments, this is no surprise.



M = Ti, Zr



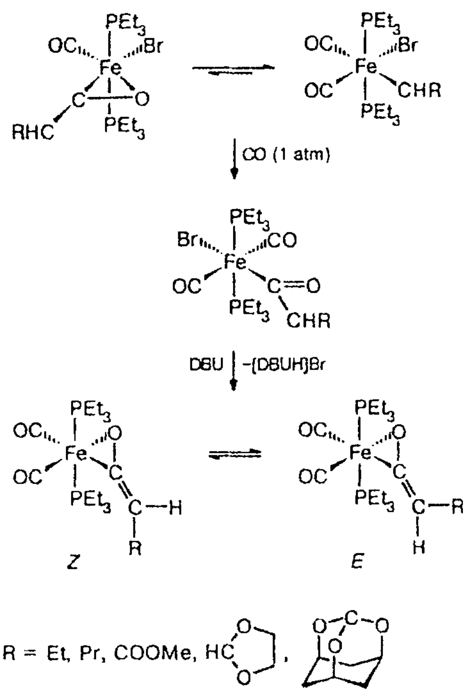
Their synthesis was achieved by a substitutional process starting from $MCp_2(CO)_2$ (M= Ti, Zr) and $Ph_2C=C=O$. Some time ago we could synthesize a $Fe(CO)_2L_2(Ph_2C=C=O)$ complex, also by a substitution route.[49]

The relationship of both types of complexes is obvious and needs no further comment. Recently we were able to extend the iron ketene chemistry in a synthetically very useful way.[50] A new route to iron ketene complexes was discovered, which allows the build-up of the ketene moiety at the iron center from simple starting materials (Scheme 12).

Thus, even such ketene complexes can be accessed, which contain ketene units unstable in the free state. By analogy, a pathway to comparable group IV metallocene complexes, which involves the formal coupling of a carbene and CO, presumably has a great chance to be realized, but yet remains to be done.

In conclusion it can be stated that the carbene analogs, the group IV transition metal metallocenes and the $Fe(CO)_2L_2$ fragments, in general showed striking relationships, despite their differences in chemical nature. However, at some points of our excursion through the chemistries of both fragments we saw diverging chemical pictures evolving, which mainly originated from the fact that the group IV metallocenes have two low lying unoccupied orbitals and in certain instances both of them come into play.

Scheme 12



Both chemistries are very similar, but they are not the same.

* * *

M. E. Vol'pin was a chemist of genius and one of Russia's leading scientists. If one were to further characterize M. E. Vol'pin's leading edge scientific achievements, there would be not much doubt that one had to denominate his outstanding capability of intuition which governed all his chemical endeavours. M. E. Vol'pin was always paces ahead of his time by generating marvelous ideas which he then further substantiated in striking experiments. M. E. Vol'pin with his outstanding capability of imagination was able to foresee the essential chemical aspects of group IV metallocenes by stating the titanocene/carbene analogy for the first time. He thus initiated building bridges in the area of organometallic chemistry and he intuitively took the right direction. In this article we have tried to establish that such bridges might even span a much larger bow and connect seemingly unrelated areas, and still the major impacts of the analogies are kept valid.

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