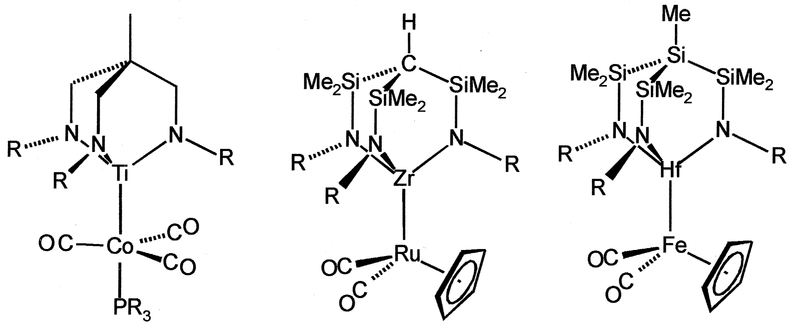
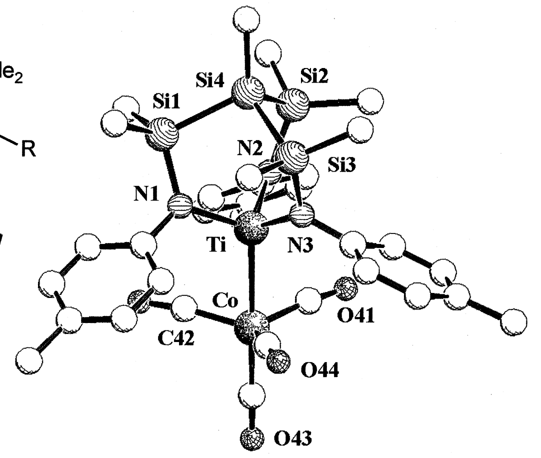


Ti—Fe	Zr—Fe	Hf—Fe
Ti—Ru	Zr—Ru	Hf—Ru
Ti—Co	Zr—Co	Hf—Co



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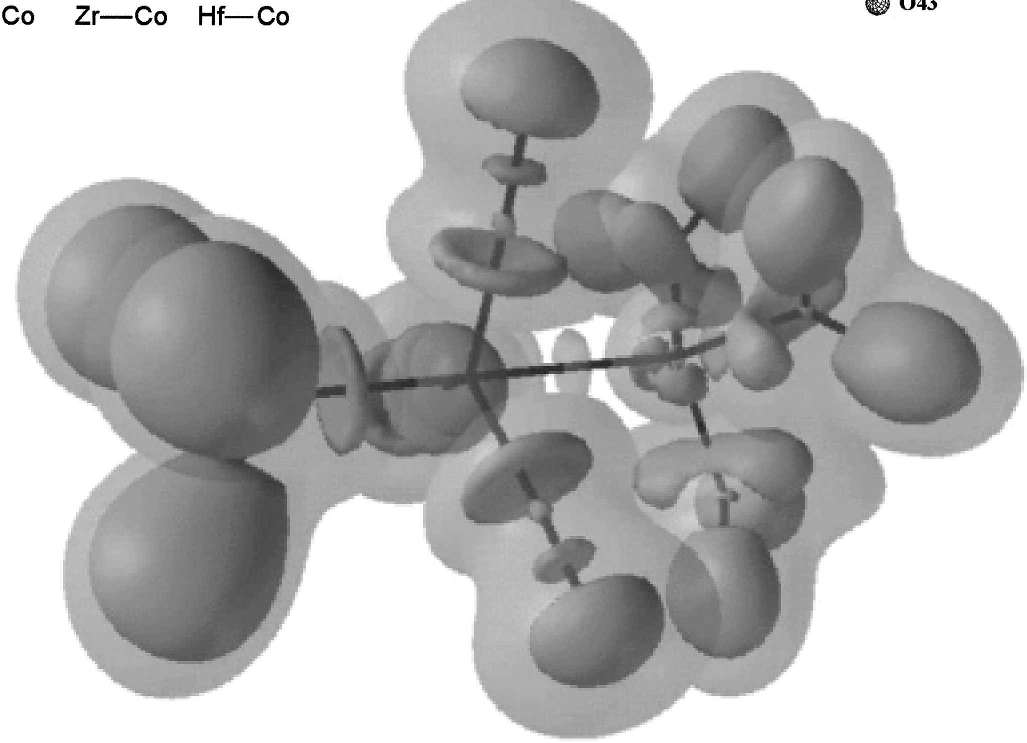

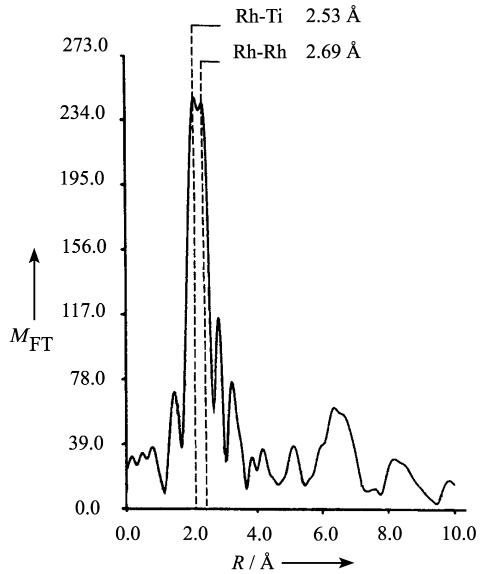

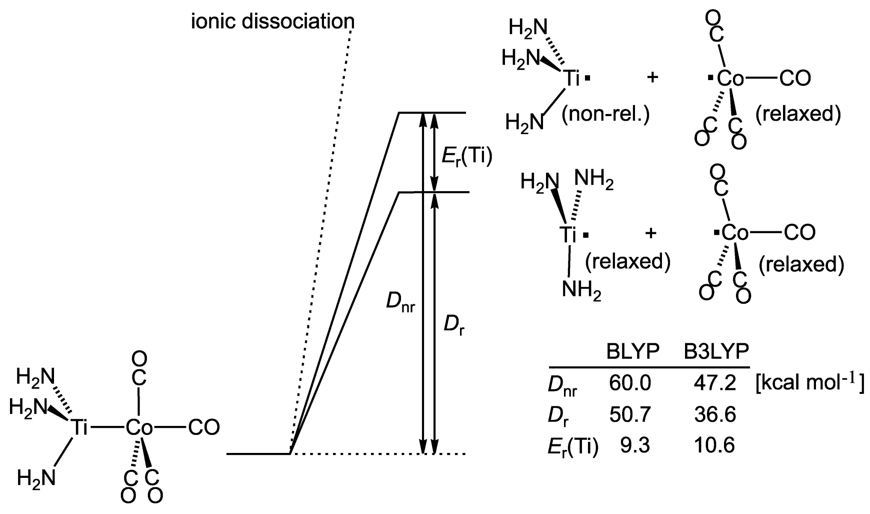

	BLYP	B3LYP	
D_{nr}	60.0	47.2	[kcal mol^{-1}]
D_r	50.7	36.6	
E_r(Ti)	9.3	10.6	

Highly Polar Metal – Metal Bonds in "Early – Late" Heterodimetallic Complexes

Lutz H. Gade*

Dedicated to Helmut Werner

Metal – metal bond polarity in its extreme form involving transition elements is found in di- or polynuclear complexes in which molecular fragments containing metal atoms from the two ends of the d block in the periodic table are combined. This linkage by direct metal – metal bonds of metal centers having very different oxidation states has been a challenge to the synthetic chemist. The suppression of degradative reaction channels caused by intramolecular single-electron transfer and the protection of the highly Lewis acidic early transition metal center by an appropriately designed ligand shell have opened up the systematic investigation of such systems. Concomitant with this development, advances in the conceptual framework for the quantitative description of bond polarity have led to a refined understanding of the nature of this type of metal – metal bonding. The greatest stimulus for the development of this field of research is the investigation of the cooperative reactivity of two or more coordination centers in their interaction with and transformation of organic substrates. This cooperativity, which is characterized by the different functions adopted by the metal centers in these conversions offers attractive perspectives in stoichiometric or even catalytic transformations.

Keywords: cluster compounds · metal – metal interactions · organometallic compounds · transition metals

Introduction

A metal – metal bond in a di- or polynuclear complex tends to be its most characteristic structural feature and at the same time bears a reactive potential which sets it apart from the other components of the molecule.[1–3] Its chemical characteristics are not only strongly influenced by the nature of the metals involved but equally so by the set of ligands coordinated to the metals. The latter reflects the formal oxidation states of the metal centers and thus—to some extent—the charge distribution between them.

Two metal centers adjacent to each other may in principle simultaneously interact with a molecule entering the ligand sphere. Upon introducing metal – metal bond polarity, as a consequence of different metal centers or sets of ancillary ligands, this interaction with an incoming ligand or substrate will become nonsymmetrical. The greater the disparity of the electronic properties of the linked complex fragments and thus the greater the polarity of the metal – metal bond, the more clearly cut are the differences in the roles assumed by the metals involved in this interaction and in the conversion of the substrate in question. Transformations which are enhanced by the interaction with two or more coordination centers adopting different functions are frequently referred to as *cooperative*, and it is this cooperativity which offers attractive perspectives in stoichiometric or even catalytic conversions involving "dimetallic activation".[4] This concept is realized in its extreme form in the chemistry of early – late heteronuclear complexes in which complex fragments in high oxidation states with no or few d-electrons are directly linked to those of the d-electron rich late transition metals in relatively low oxidation states.[5]

The vastly different redox properties of such metal fragments combined by direct bonding have thwarted many early attempts to synthesize such heteronuclear compounds of sufficient stability to allow systematic studies of their reactivity. This has only been achieved in a systematic way during the course of this past decade. The progress which has been achieved in the exploration of the reactive potential of significantly different metal centers linked directly to each other and thus located at very close proximity to each other

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will be highlighted in this article. Its principal focus, however, will be the properties of the highly polar metal–metal bonds themselves.

1.1. Direct Metal–Metal Bonding in Polynuclear Complexes: A Brief Historical Perspective

Few conceptual innovations in inorganic chemistry exemplify Thomas Kuhn's postulate of the change of paradigms[6] equally well as the formulation of covalent bonds between metal centers within polynuclear complexes which established metal–metal bonding as a structural principle in the late 1950s and early 1960s. It did not evolve as a natural extension of Alfred Werner's coordination theory[7] but rather developed in spite of it and in view of an ever growing amount of experimental data which apparently violated the accepted rules of molecular structure.[8]

The first steps in this development date back to the mid 1920s when the crystal structure analyses of the mercurous halides indicated Hg–Hg contacts of about 2.5 Å.[9] The possibility of direct metal–metal bonding in the dimercury dication was additionally supported by the report of a low-frequency band in the Raman spectrum of $Hg_2(NO_3)_2$ (171 cm^{-1}) by Woodward in 1934.[10] These early speculations, however, received little notice, and it was the report of the crystal structure of $[Fe_2(CO)_9]$ by Powell and Ewens in 1939, in which the authors invoked a metal–metal bond between the two Fe centers, which attracted greater interest.[11] This view was immediately endorsed by Pauling in the 1940 edition of his famous book "The Nature of the Chemical Bond"[12] but initially met with fierce opposition from other researchers.[13]

The importance of X-ray crystallography for the further development of the area is highlighted by the establishment of short metal–metal distances in the trianion $[W_2Cl_9]^{3-}$[14] and the metal octahedra in $[\{Mo_6Cl_8\}Cl_4(H_2O)_6]\cdot 6\,H_2O$ and $[Ta_6X_{14}]$ (X = Cl, Br) by C. Brosset[15] and L. Pauling[16] during the period between 1935 and 1950. In these compounds the metal–metal vectors are associated with bridging ligands thus leaving a certain degree of ambiguity as to their structural role. Metal–metal bonds between transition metal atoms which are unsupported by bridging ligands were first established for $[\{Cp(CO)_3Mo\}_2]$ and $[M_2(CO)_{10}]$ (M = Mn, Re) in 1956 and 1957, respectively.[17, 18]

From 1960 onwards there was a rapid succession of publications reporting various aspects of metal–metal bonding. The discovery of metal–metal multiple bonds by F. A. Cotton and his co-workers[19] ranks among the most important discoveries of this period and began with the report and theoretical analysis of the structure of the $[Re_3Cl_{12}]^{3-}$ cluster anion which was formulated as containing Re=Re double bonds.[20] A bond multiplicity of greater than three in the form of a Re–Re quadruple bond was established for the dinuclear complex $[Re_2Cl_8]^{2-}$ in 1964,[21] while the missing link in this series, a metal–metal triple bond, could be found for the first time in the neutral compound $[Re_2Cl_5(dth)]$ (dth = $CH_3SCH_2CH_2SCH_3$).[22]

The formulation of direct bonding between transition metal atoms is nowadays an integral part of the conceptual texture of inorganic chemistry.[23, 24] The structural characteristics and reactivity of di- and polynuclear complexes containing metal–metal bonds has been extensively reviewed and has uncovered a multitude of bonding combinations and reactive patterns.[1–3] The stabilization and unambiguous identification of complexes containing highly polar metal–metal bonds between transition metal atoms from the two ends of the d block in the periodic table has only been achieved since the late 1970s.[5] The first structural characterization of such an unsupported metal–metal bond was achieved by Schmid and co-workers for the rather complicated system $[Cp\{Co_3(CO)_9(\mu\text{-}CO)\}_2Ti\text{–}Co(CO)_4]$ which was isolated from the reaction of $[CpTiCl_3]$ with $Na[Co(CO)_4]$.[25] However, a systematic investigation of these "early–late" heteronuclear complexes was initially hampered by the apparent instablity of most compounds synthesized at that stage.

2. Metal–Metal Bond Polarity

Homodinuclear complexes containing metal–metal bonds are mostly symmetrical "dimers" in which the bond linking the two metal centers is consequently nonpolar. This pattern applies to a wide range of such species and M–M bonds of different multiplicity. A certain degree of polarity of the

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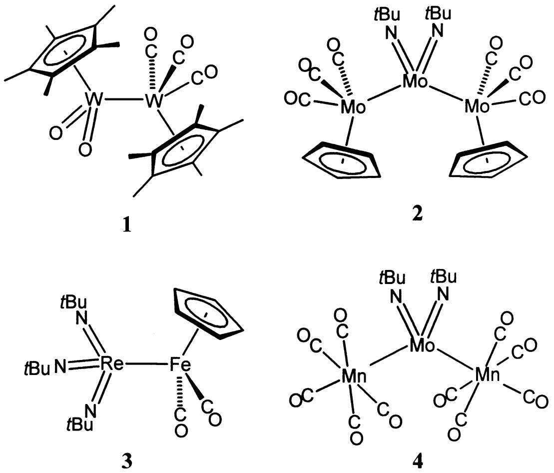
metal–metal bond may be achieved by ligand substitution at one metal center of a *homodinuclear* complex or by linking different transition metals, thus generating *heterodinuclear* complexes.

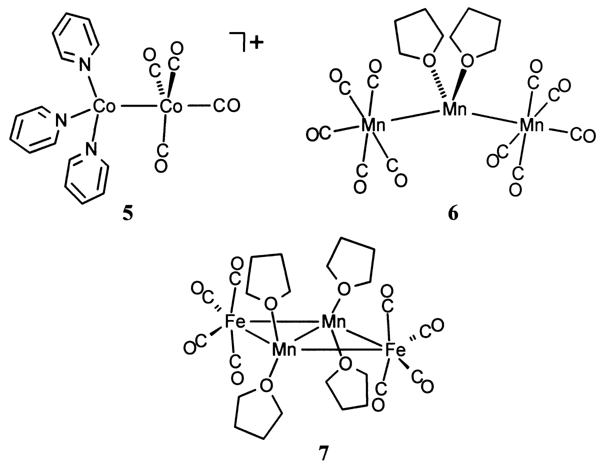
A high degree of metal–metal bond polarity is to be expected if the metal atoms in the two complex fragments have a significantly different partial atomic charges. This will be the case if their formal oxidation state differs substantially. Thus, even homodimetallic complexes may contain highly polar metal–metal bonds such as those in compounds **1** and **2** in Scheme 1.[26–28] The same applies to the high-valent–low-valent complexes **3** and **4** in which the metal atoms are fairly close to each other in the periodic table but in which the different ligand spheres—imido ligands stabilizing the formal high oxidation state, CO ligand the higher electron density at the low oxidation state fragment—define the different nature of the M–M′ linked complex fragments.



Scheme 1. Complexes with polar metal–metal bonds between metal centers in high and low formal oxidation states.

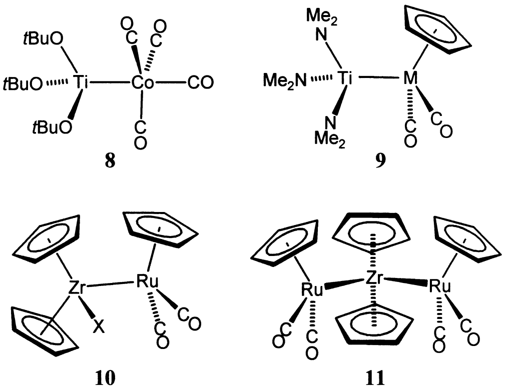
A second type of complexes in which metal–metal bond polarity is due to an extreme inequality of the ligand spheres was first isolated from redox disproportionations of metal carbonyls in the presence of relatively hard donor ligands. An example for such a system is the dicobalt complex **5** which was isolated by Fachinetti et al. from the reaction of [$Co_2(CO)_8$] with pyridine and which contains what the authors regarded as a contact ion pair between the complex ions [$Co(py)_3$]$^{2+}$ and [$Co(CO)_4$]$^-$ (Scheme 2).[29]

The polynuclear complexes **6** and **7**, in which "classical" Alfred Werner-type complex fragments are bonded to metal carbonyls are further examples of this class of compounds for which the term "xenophilic" ("stranger loving") has been proposed.[30–32] Their facile (though not decomposition-free) ionic dissociation in polar solvents supports the interpretation of the metal–metal bonding as being highly polar. However, a major factor in this tendency to dissociate may be the inherent weakness of the metal–metal bond between fragments with considerably divergent bonding capabilities. In the "classical" hard-donor/intermediate "oxidation state" compounds the d-orbital shell is thought to be highly contracted and barely participates in the metal–ligand bonding (which, incidently, is the reason for the applicability of Ligand Field Theory to such systems).[33] Overlap of the d orbitals with those of a neighboring metal carbonyl fragment is expected to be very weak and thus the covalent bond order fairly low. A recent theoretical study by Xu and Lin of such "xenophilic" complexes has established high partial charges on the linked complex fragments.[34] It also successfully explained the major aspects of the interesting magnetic properties of these compounds while not directly addressing the issue of metal–metal bond strength and polarity.



Scheme 2. "Xenophilic" clusters with polar metal–metal bonds.

The third and possibly most radical strategy to generate highly polar metal–metal bonds is based on the combination of complex fragments from the extreme ends of the d block in the periodic table (**8**–**11**, Scheme 3).[35–39, 41–44] The d-electron rich metal atoms in these "early–late" heterodimetallic complexes are directly bound to d-electron poor metal centers. The principle is thus closely related to that of the high-valent–low-valent complexes discussed above. In both types of compounds the frequencies of the ν(CO) infrared vibrations indicate that the negative charge at the late (low-valent) transition metal lies somewhere in the middle between those of the homonuclear dimers and the carbonyl metalate anion. An overview of the ν(CO) frequencies of the {FeCp-$(CO)_2$} fragment bonded to different metal centers is given in Table 1 and compared with those of [$CpFe(CO)_2$]$^-$.[40]



Scheme 3. Early–late heterodimetallic complexes containing unsupported metal–metal bonds.

Table 1. Infrared carbonyl stretching frequencies of Ti–Fe, Zr–Fe, and Hf–Fe complexes containing the $\{CpFe(CO)_2\}$ fragment.

Complex	$\tilde{\nu}_{sym}(CO)$, $\tilde{\nu}_{asym}(CO)$ [cm^{-1}]	Ref.
Ti–Fe		
$[\{MeSi[SiMe_2N(p\text{-}Tol)]_3\}Ti{-}FeCp(CO)_2]$	1978, 1931	[44]
$[\{HC[SiMe_2N(p\text{-}Tol)]_3\}Ti{-}FeCp(CO)_2]$	1975, 1928	[42]
$[\{MeC(CH_2NSiMe_3)_3\}Ti{-}FeCp(CO)_2]$	1968, 1916	[42]
$[(Me_2N)_3Ti\text{-}FeCp(CO)_2]$	1948, 1898	[35]
Zr–Fe		
$[\{MeSi[SiMe_2N(p\text{-}Tol)]_3\}Zr{-}FeCp(CO)_2]$	1961, 1910	[44]
$[\{CH_2(CH_2NSiMe_3)_2\}(Cp)Zr{-}FeCp(CO)_2]$	1947, 1895	[43a]
$[Cp_2(Me)Zr{-}FeCp(CO)_2]$	1937, 1872	[37]
Hf–Fe		
$[\{MeSi[SiMe_2N(p\text{-}Tol)]_3\}Hf{-}FeCp(CO)_2]$	1969, 1915	[44]
$K[FeCp(CO)_2]$	1866, 1772	[40]

2.1. Metal–Metal Bonding between Early and Late Transition Metals in Bare Cluster–Dimers and Intermetallic Solids

The bonding between the metals of the two ends of the d block in the periodic table was first considered and studied for solid intermetallic phases. More than 25 years ago Brewer and Wengert predicted the trends and stability of transition metal alloys.[45a] One result of their work was the postulate that particularly stable alloys were expected to be formed by the *combination of the early and late d-block elements.* The intermetallic bonding interaction determining this stability was proposed to be a type of Lewis acid/Lewis base interaction whereby paired d electrons of the late transition metal are donated to the empty acceptor orbitals of the early transition element. An optimization of this type of interaction would then result in highly negative heats of formation. The thermodynamic data reported by Topor and Kleppa for a series of binary intermetallic phases appear to support this early proposal.[45b]

The stability trends which emerged for the solids were further supported by theoretical studies reported for heterometallic transition metal dimers in the gas phase.[46] For the dimers containing iron and a second transition metal the calculated dissociation energies summarized in Table 2 indicate that an increase in the difference of the electronic structure of the atoms combined to give Fe–M leads to higher stability of the metal–metal bond with the homodimer Fe_2 being the least stable molecule.[47]

Enhanced metal–metal bonding in heterometallic solids has also been established in the bonding analysis of the large number of ternary systems, in particular in the early–late mixed metal halides and chalcogenides studied by Corbett, Hughbanks, Tremel, Harbrecht, and others.[48–52] A particularly instructive example is the ternary compound Hf_5FeTe_3 reported by Abdon and Hughbanks in which the iron atoms are situated in the center of hafnium tricapped trigonal-prismatic cages.[52] The Hf–Fe distances within the trigonal prism lie between 2.6 and 2.7 Å and indicate strong bonding interaction (Figure 1).

Table 2. Dissociation energies of the diatomic M–Fe molecules.

M–Fe	$D°$(M–Fe) [kcal mol^{-1}]	M–Fe	$D°$(M–Fe) [kcal mol^{-1}]
Sc-Fe	55	Fe_2	18
Ti-Fe	42	Co-Fe	30
V-Fe	44	Ni-Fe	39
Cr-Fe	32	Cu-Fe	30

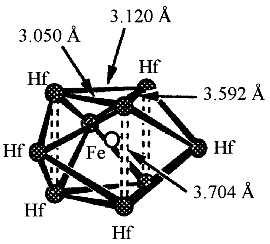


Figure 1. Arrangement of the iron atoms in the center of hafnium tricapped trigonal-prismatic cages in Hf_5FeTe_3 (from ref. [52]).

The nature of the metal–metal bonding was qualitatively established by extended Hückel (EH) band structure calculations. Crystal overlap populations were determined for the metal–metal bonded framework and the averaged curves for Hf–Fe and Hf–Hf interactions in Hf_5FeTe_3 are depicted in Figure 2. While the availability of Hf–Hf bonding levels above the Fermi level indicate that addition of electrons would enhance the homometallic Hf–Hf bonding, the intermetallic Hf–Fe bonding is evidently optimized in the given case and it is this optimization of the heterometallic bonding which appears to stabilize the metal–metal bonded framework. Moreover, Hf–Fe bonding is polar covalent with the metal–metal bonding levels being primarily Fe localized, while the antibonding levels are unoccupied and primarily Hf localized. This result appears to be consistent with the donor–acceptor model proposed for the metal–metal bonding in intermetallic phases.

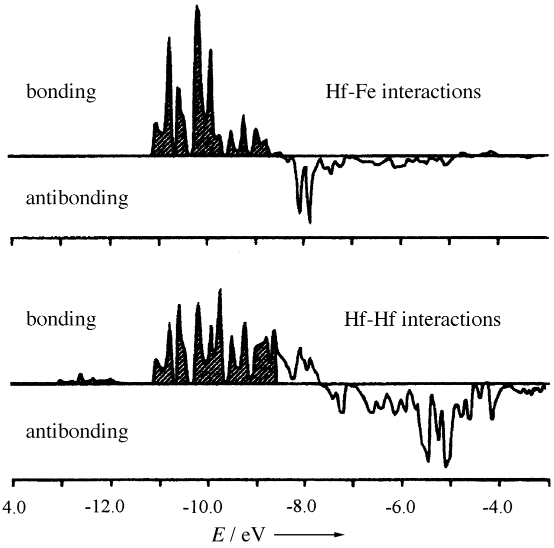


Figure 2. Average crystal orbital overlap population curves for Hf–Fe and Hf–Hf contacts in Hf_5FeTe_3 (from ref.[52]).

If early–late transition metal bonding appears to be particulartly favored in bare clusters and heterometallic ternary phases, why then were stable coordination compounds containing such metal–metal bonds extremely rare until recently? As high-level calculations performed for models of unsupported early–late heterodinuclear complexes have shown, their metal–metal bonds are by no means less stable than those of the homonuclear dimers.[53] However, the proximity of a high valent early transition metal and a low valent late transition metal opens up reaction channels caused by intramolecular single electron transfer which lead to a degradation of the dinuclar complex. In addition, unless the highly Lewis acidic early transition metal center is protected by an appropriately designed ligand shell, bimolecular interactions of the complexes or with the solvent may destabilize these systems.

2.2. Metal – Metal Bonds between Complex Fragments of Significantly Different Electronic Properties: Single Bonds and Formal Multiple Bonds

The complexes **8** – **11** are formally derived from tetravalent Group 4 complexes in which one anionic ligand has been replaced by a carbonyl metalate derivative. The late transition metal fragment therefore plays the role of a pseudo halide, a notion which was also put forward by Bursten and co-workers in their analysis of this type of metal – metal bonding (see Section 2.3).[54] The metal – metal bond in **1** – **4** or complexes such as **8** – **11** may therefore be interpreted as a polar single bond even though the actual covalent bond order may be well below unity as will be discussed below. However, the high-valence state of the early transition metal and the metal – metal bond polarity render these bonds remarkably short in comparison to homometallic single bonds which normally range between 2.7 and 3.0 Å. This is shown for various Ti–M complexes in Table 3.

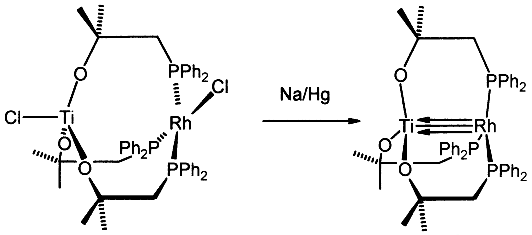
The early transition metal fragment in **8** and **9** possesses unoccupied d orbitals which would have the correct symmetry for further donor – acceptor interactions with a d-electron rich, late transition metal fragment. This additional donor – acceptor interaction would then reinforce the metal – metal bond and lead to an increased bond order, manifested in a short interatomic distance.

Table 3. Metal – metal bond lengths in Ti–M heterodinuclear complexes containing unsupported Ti–M bonds.

Complex	*d*(Ti–M)	Ref.
Ti–Mn		
$[(t\text{BuO})_3\text{Ti–Mn(CO)}_5]$	2.684(1)	[59]
Ti-Fe		
$[\{\text{MeC(CH}_2\text{NSiMe}_3)_3\}\text{Ti–FeCp(CO)}_2]$	2.433[a]	[41]
$[\{\text{MeSi[SiMe}_2\text{N(2-FC}_6\text{H}_4)]_3\}\text{Ti–FeCp(CO)}_2]$	2.433(4)	[82]
$[\{\text{MeSi[SiMe}_2\text{N(}p\text{-Tol)]}_3\}\text{Ti–FeCp(CO)}_2]$	2.460(1)	[44]
$[(\text{Me}_2\text{N})_3\text{Ti–FeCp(CO)}_2]$	2.568[a]	[35]
Ti–Ru		
$[\{\text{MeC(CH}_2\text{NSiMe}_3)_3\}\text{Ti–RuCp(CO)}_2]$	2.527(1)	[41]
$[\{\text{HC[SiMe}_2\text{N(}p\text{-Tol)]}_3\}\text{Ti–RuCp(CO)}_2]$	2.503(4)	[41]
$[\{\text{MeSi[SiMe}_2\text{N(}p\text{-Tol)]}_3\}\text{Ti–RuCp(CO)}_2]$	2.5609(8)	[82]
$[(\text{Me}_2\text{N})_3\text{Ti–RuCp(CO)}_2]$	2.663(1)	[35]
$[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{O})_2(\text{Me}_2\text{N})\text{Ti–RuCp(CO)}_2]$	2.573(1)	[36]
Ti–Co		
$[\{\text{MeSi[SiMe}_2\text{N(}p\text{-Tol)]}_3\}\text{Ti–Co(CO)}_3(\text{PTol}_3)]$	2.471(4)	[53]
$[\{\text{MeSi[SiMe}_2\text{N(}p\text{-Tol)]}_3\}\text{Ti–Co(CO)}_4]$	2.5542(10)	[53]
$[(t\text{BuO})_3\text{Ti-Co(CO)}_4]$	2.565(2)	[39]
$[\text{Cp\{Co}_3(\text{CO})_9(\mu\text{-CO})\}_2\text{Ti–Co(CO)}_4]$	2.614	[25]

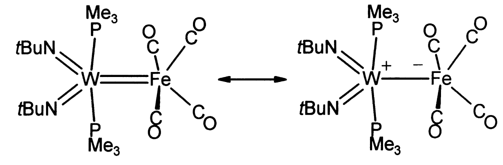
[a] Average value of two independent molecules in the asymmetric unit.

A complex containing a metal – metal bond bearing these characteristics has been reported by Slaughter and Wolczanski.[55] Reduction of the heterodinuclear complex **12** with sodium amalgam yielded the Ti–Rh bonded complex **13**. Its most characteristic structural element is the extremely short Ti–Rh distance of 2.2142(11) Å which is 0.362 less than the sum of the covalent metal radii. Since the bridging ligands are fairly flexible and undistorted in complex **13**, this short metal – metal distance was interpreted as arising from additional Ti–Rh donor – acceptor interaction and thus increased metal – metal bond order.



12 **13**

Highly polar formal metal – metal double bonds were expected to result from the salt metathesis of an early transition metal *dihalide* with a *carbonyl metalate dianion*. A well-characterized example of this type of metal – metal bond formation is known for a high-valent – low-valent heterodinuclear complex. Reaction of the bis(imido)tungsten complex $[\text{W(=N}t\text{Bu)}_2\text{Cl}_2]$ with $\text{K}_2[\text{Fe(CO)}_4]$ in the presence of trimethylphosphane yielded the W–Fe complex **14**.[56] Although the structure of complex **14** is well established, the question of the W–Fe bond multiplicity is not trivial. In species of high bond polarity such as this a zwitterionic formulation leaving the covalent bond order at about unity is equally conceivable. A detailed theoretical study of this compound is clearly warranted.



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2.3. Metal – Metal Bond Polarity: A Theoretical Approach

The concept of bond polarity, which is used in main group chemistry with reference to the electronegativities of the atoms involved, is less readily applied in a quantitative way to bonds between transition metals. Their nature may be more significantly influenced by the coordination spheres of the two or more metal centers involved rather than intrinsic properties of the metal itself. This increased level of sophistication required in a meaningful discussion of bond polarity in M–M′ bonds necessitates elaborate quantum-chemical methods to be used. However, this may render it difficult to extract information from the results of such calculations which are interpretable within the established paradigms of structure and bonding familiar to the chemist.

First attempts to tackle the problem of metal–metal bond polarity in early–late heterodinuclear complexes were reported by Bursten and Novo-Gradac who applied $X\alpha$-SW molecular orbital methods to Casey's system $[Cp_2(X)Zr{-}Ru(CO)_2Cp]$ (**10**) as well as the analogous Th–Ru complex $[Cp_3(X)Th{-}Ru(CO)_2Cp]$.[54, 57] Based on an analysis of the frontier orbitals it was concluded that the nature of the M–Ru bonding is essentially the same in the two systems and that it may be described as the donation from the filled $4d_{z^2}$ orbital of ruthenium into the empty d_{z^2} orbital of Th or Zr. This results in a slightly bent M–Ru σ-bonding orbital to which the frontier orbitals of the two metal centers contribute 15% (Zr) and 72% (Ru) (Figure 3). This highly unequal contribution of the two metal centers to the metal–metal bonding orbital may be interpreted as qualitatively representing a highly polar bond.

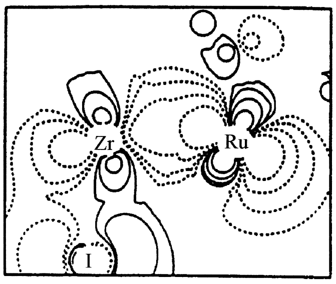
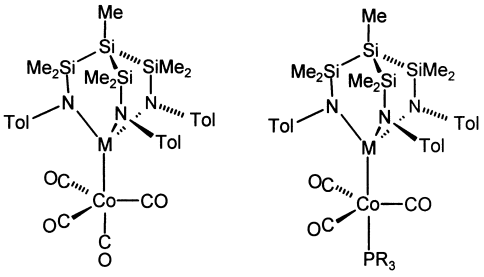


Figure 3. Contour diagram of the metal–metal bonding orbital in **10** (X = I) in the I-Zr-Ru plane.

Shortly thereafter, Wolczanski and coworkers published extended Hückel MO calculations on various early–late heterobimetallic complexes[58] and, more recently, Selent et al. reported the results of an EHMO study of $[(tBuO)_3Ti{-}M(CO)_n]$ (M = Co/Mn, $n = 4/5$).[59] All of these studies offered a qualitative analysis of the principal bonding interactions between the early and the late metal centers. However, the published theoretical analyses of the M–M′ bonds, based on the metric parameters derived from various crystal structures, although providing some valuable insight into the nature of this class of compounds, are unsuitable for addressing such questions as metal–metal bond polarity in even a semiquantitative way. An approach which addresses the principal difficulties of determining metal–metal bond polarity and offers a state-of-the-art theoretical analysis of the electronic structure of a suitable model complex has been reported recently and will therefore be reviewed in more detail.[53]

An important aspect governing the choice of an appropriate system of study was the molecular symmetry of the heterodinuclear complex. In order to facilitate the interpretation of the results obtained in calculations and in the experimental structural studies, both complex fragments, joined through the direct metal–metal (M–M′) bond, were required to have the same symmetry with respect to this bonding axis. Early–late heterodinuclear complexes meeting this requirement do indeed exist, such as the complexes **15** and **16** in which the *trans*-axial position at the cobalt atom is occupied either by a CO or a triarylphosphane ligand (Scheme 4).



15 **16**

Scheme 4. The Ti–Co and Zr–Co heterodinuclear complexes **15** and **16** (M = Ti, Zr, Hf; R = aryl). Tol = p-MeC_6H_4.

An X-ray crystallographic study of four compounds containing Ti–Co and Zr–Co bonds, with and without *trans*-axial phosphane substitution, provided the experimental "point of reference" for the metric parameters which characterize these complexes (Figure 4). The optimized structural parameters obtained by density functional theory (DFT) methods for the heterobimetallic model complexes $[(H_2N)_3Ti{-}Co(CO)_4]$ and $[(H_2N)_3Ti{-}Co(CO)_3(PH_3)]$ were compared to those obtained experimentally and good general agreement was found (Scheme 5).

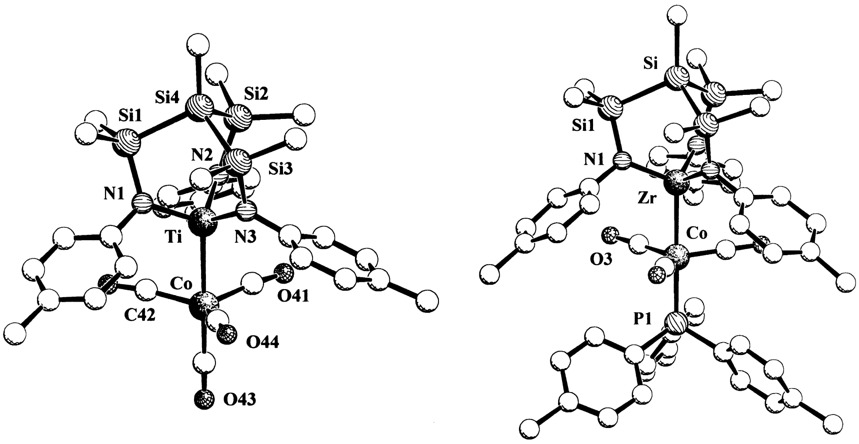
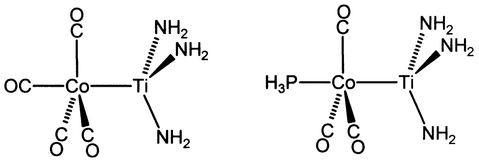


Figure 4. Molecular structures of the two M–Co heterodinuclear complexes $[\{MeSi[SiMe_2N(4\text{-}CH_3C_6H_4)]_3\}M{-}Co(CO)_3(L)]$ (M = Ti, Zr).



Scheme 5. Model compounds investigated in the theoretical study.[53]

To establish the degree of metal–metal bond polarity several independent theoretical approaches were employed. These included, on the one hand, orbital based population analysis schemes such as natural population analysis (NPA)[60] in combination with Wiberg bond indices[61] and charge decomposition analysis (CDA).[62] On the other hand, essentially orbital independent methods such as Bader's AIM ("atoms in molecules") approach[63–65] in combination with Becke's, Edgecombe's and Savin's ELF ("electron localization function")[66, 67] were employed.

Based on these methods, in particular the combination of Bader's partitioning of the molecules into atomic domains and the localization of electron pairs using the ELF formalism, a consistent picture of the nature of the Ti–Co bonds in the dinuclear complexes was obtained: First, the covalent metal – metal bond order is less than 0.5 and influenced (b.o. ca. 0.1) by the nature of the transaxial ligand coordinated to cobalt. Second, high partial charges assigned to the complex fragments of greater than 0.5 e were established which emphasize the highly polar character of the Ti–Co bonds. A depiction of an electron density isosurface of $[(H_2N)_3\text{-}Ti\text{–}Co(CO)_3(PH_3)]$ given in Figure 5 clearly shows the low level of electron density between the metal centers if compared to the situation for the metal – ligand bonds. This is to be seen as reflecting the high Ti–Co bond polarity.[53]

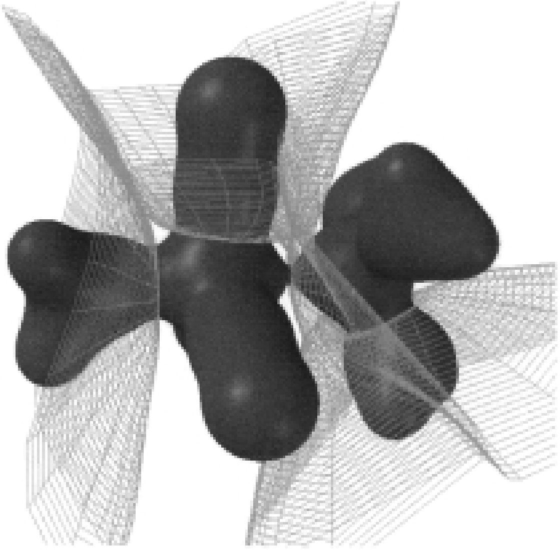


Figure 5. The isosurface of $[(H_2N)_3Ti\text{–}Co(CO)_3(PH_3)]$ ($\lg(\rho) = -1.3$) along with several of the Bader surfaces around the metal atoms. The molecule is depicted with the $(H_3P)(CO)_3Co$ unit pointing left and the $Ti(NH_2)_3$ unit pointing right. Note the area of low-electron density between the metal atoms.

Visualization of the nature of the Ti–Co bonds was most persuasively achieved by the representation of the ELF isosurface in relation to the AIM boundary surface between the two complex fragments bound to each other. The electron localization function (ELF) was originally introduced within the framework of Hartree – Fock theory by Becke and Edgecombe[66] as a function of the spherically averaged probability of finding an electron with a given spin in the neighborhood of another electron with the same spin which represents an indirect measure for the location of an electron pair with two electrons of opposite spin. ELF is then constructed in such a way that it assumes values of close to unity when there is a high probability of finding paired electrons (or single, unpaired electrons), and it assumes values close to zero in those regions of space where no electron pairing occurs. Figure 6 shows a superposition of a part of the ELF isosurface with some of the atom-separating surfaces around the metal atoms.[53] The metal – metal bond electron pair localization domain—being disk-shaped—and very close to the separating surface between the metal atoms is essentially concentrated on the side of the Co atom and thus is mainly in the atomic domain of that metal atom towards which the bond is polarized.[67]

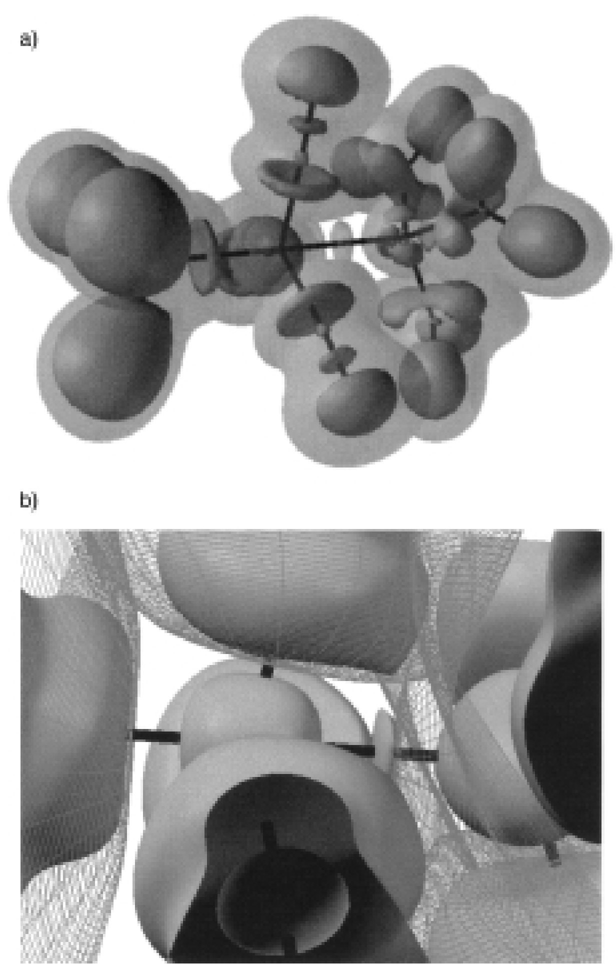
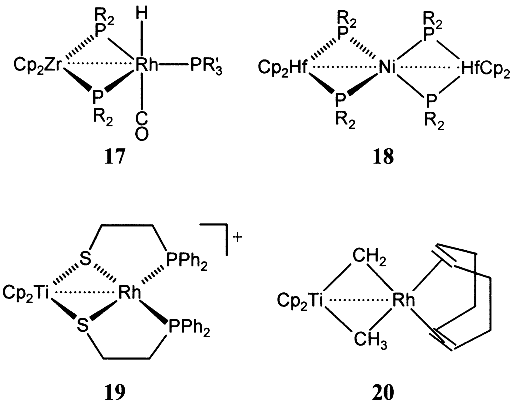


Figure 6. a) Isosurfaces of $[(H_2N)_3Ti\text{–}Co(CO)_3(PH_3)]$(ELF = 0.42: translucent, ELF = 0.83: solid) superimposed. The molecule is oriented in the same way as in Figure 5. b) A zoom into the Co–Ti bond region for ELF = 0.43, along with some of the Bader surfaces. This very clearly illustrates the localization of the bond electron pair close to the Co–Ti separating surface.

In summary, while molecular orbital based population analyses may provide a reliable measure of the polarity of a bond, it is only the direct analysis of electron distributions as achieved by the combination of Bader's AIM approach and the electron localization function (ELF) which achieves this independent from an MO basis set and enables us to visualize the polarization of the bonding electron pairs in real space. This theoretical approach is expected to find more widespread use in future studies of metal – metal bond polarity.

3. Directly Metal–Metal Bonded Early–Late Heterodinuclear Complexes with and without Bridging Ligands

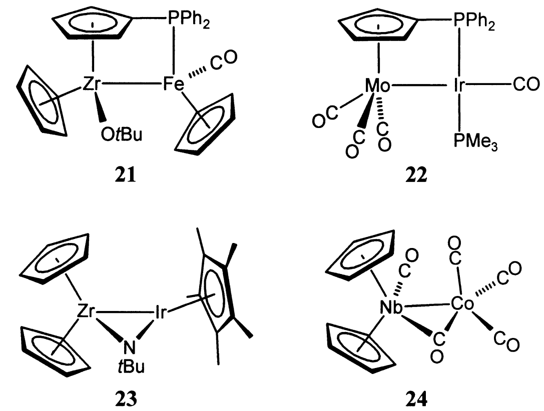
The focus of this article is the polar metal–metal bond in early–late heterodimetallic complexes. Its importance and structural function is beyond doubt in the systems without bridging ligands and many examples of these have been introduced in the previous sections. However, by far the majority of heterodinuclear complexes synthesized and studied to date contain bridging ligands. The chemistry of these species has been reviewed first by Stephan about a decade ago[5a] and, subsequently, by Chetcuti.[68] A very recent general overview of the area has been published by Wheatley and Kalck.[5b] Typical examples for heterodimetallic complexes (**17**–**20**) stabilized by bridging ligands are summarized in Scheme 6. In all of them, the presence or absence of direct metal–metal bonding is not unambiguously clarified but all would be conceivable without there being a metal–metal bond.[69–71]



Scheme 6. Early–late heterodimetallic complexes containing bridging ligands for which direct metal–metal bonding is not unambiguously clarified but which would be conceivable without a metal–metal bond. Cp = C_5H_5; R, R′ = alkyl, aryl.

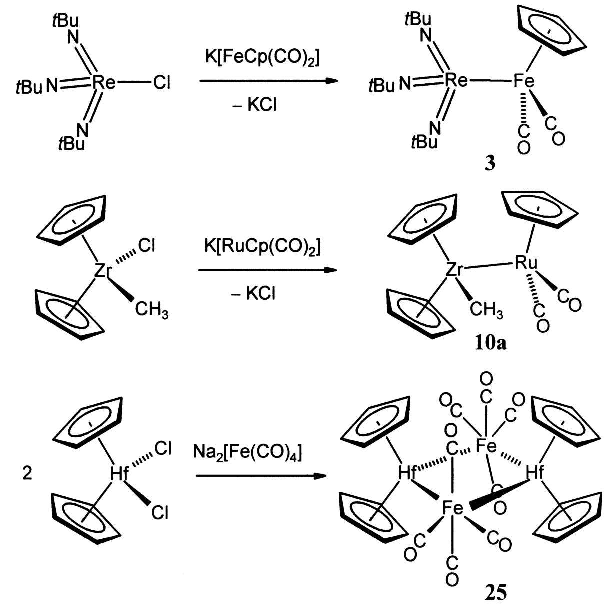
Significant metal–metal bonding between an early and a late transition metal may be assumed even in the presence of bridging ligands if the electron count and physical properties, the metal–metal distance established by X-ray crystallography and the patterns of chemical reactivity are in accord with such a bond. This is clearly the case for the complexes **21**–**24** (Scheme 7) and systems of this type will therefore be included in the following discussion of the generation and the reactivity of highly polar metal–metal bonds.[72, 73]

4. Synthetic Strategies for the Generation of Highly Polar Metal–Metal Bonds



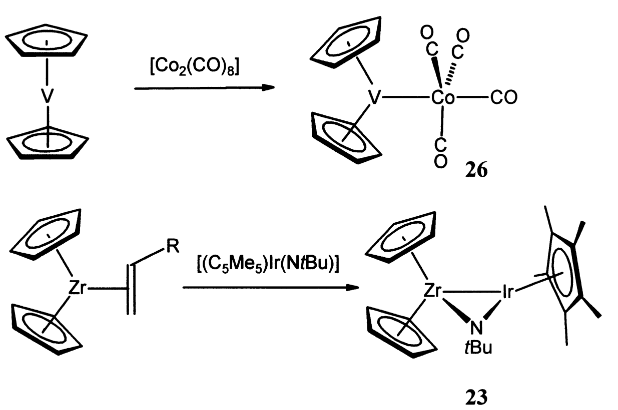
Scheme 7. Early–late heterodimetallic complexes containing bridging ligands in which the metal–metal bond is a significant structural feature.

The linking of the two electronically different transition metal centers to give a dinuclear complex containing a highly polar metal–metal bond may be achieved by several basic synthetic strategies. The most widely employed method is the simple salt metathesis which for early–late or high-valent–low-valent heterodinuclear complexes involves the reaction of an early (high-valent) transition metal halide with a alkali metal salt of an anionic late (low-valent) transition metal complex (mostly carbonyl metalates). Several examples of this method, which include the reaction of a dihalide with a dianionic metal carbonylate, are summarized in Scheme 8.[27, 37, 75]



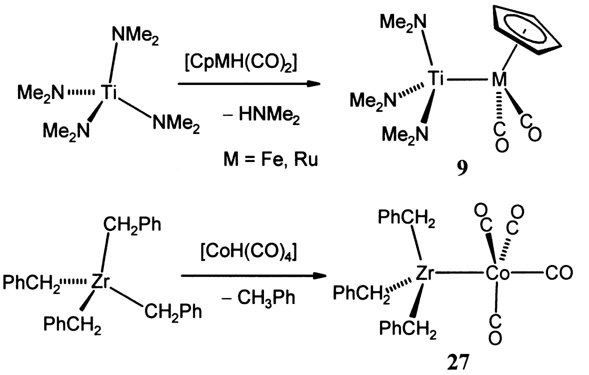
Scheme 8. Synthesis of heterodinuclear complexes by salt metathesis using alkali metal salts of the carbonyl metalates.

A severe limitation of this approach is the possibility of a single-electron transfer competing with the salt elimination and formation of the metal–metal bond. The high-valent, early transition metal complex fragments are almost always potential oxidizing agents and the carbonyl metalates reducing agents. An alternative M–M′ coupling strategy thus involves the reaction of neutral complexes and the elimination of a less polar molecule upon formation of the dinuclear complex. Examples of the former strategy are the synthesis of the unstable and thus incompletely characterized complex **26**[74] as well as the imido ligand bridged Zr–Ir complex **23** (Scheme 9).[73]



Scheme 9. Synthesis of heterodinuclear complexes by combination of neutral complex fragments.

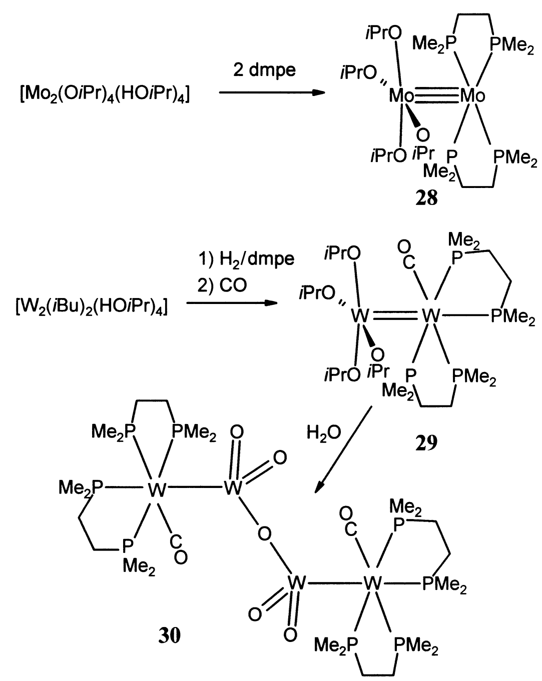
Dimetallic elimination reactions leading to metal – metal bond formation are the amine or alkane eliminations which result from the "condensation" of a late transition metal hydrido complex with an early transition metal amido or alkyl complex, respectively. Examples of this method are Selegue's synthesis of the first Ti–Fe and Ti–Ru complexes **9**[35, 36] and the reaction of $[Zr(CH_2Ph)_4]$ with $[CoH(CO)_4]$ (Scheme 10).[76]



Scheme 10. Metal – metal bond formation by bimolecular amine or alkane elimination.

A method frequently employed in the synthesis of homodinuclear complexes is the elimination of halide ligands by reduction. This strategy is applicable in the synthesis of heterodinuclear complexes if bridging ligands effect the prearrangement of the two metal centers, as is exemplified by the synthesis of the Ti–Rh complex **13** already discussed in Section 2.2 which was obtained by Na/Hg reduction of the halide precursor **12**.[55]

A remarkable synthetic strategy for homodinuclear complexes of the high-valent – low-valent type of the Group 6 metals involves the reaction of a symmetrical precursor complex containing metal centers in an intermediate oxidation state with a soft ligand such as a phosphane. Chisholm and co-workers have reported several examples of this reactive pattern. These include the reaction of the dimolybdenum complex $[Mo_2(OiPr)_4(HOiPr)_4]$ with dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) to give the unsymmetrical Mo^0 – Mo^{IV} complex $[Mo_2(OiPr)_4(dmpe)_2]$ (**28**), and the hydrogenation of $[W_2(iBu)_2(OiPr)_4]$ in the presence of dmpe and subsequent carbonylation to give $[W_2(OiPr)_4(dmpe)_2(CO)]$ (**29**) (Scheme 11).[77] The latter could be hydrolyzed to give the remarkable tetranuclear complex $[W_2O_4(\mu\text{-}O)\{W(CO)(dmpe)_2\}_2]$ (**30**) with a formal W^0 – W^V oxidation state pattern.



Scheme 11. Ligand rearrangement and formal redox disproportionation of the metal centers upon reaction of a symmetrical precursor complex containing metal centers in an intermediate oxidation state with a soft ligand.

This pattern of reactivity may be understood in view of the ambivalent character of the Group 6 metal with respect to their chemical hardness. Depending on the oxidation state they act as hard or soft Lewis acids and thus—at the extremes of the partial charge scale—preferentially ligate only hard or soft ligands.

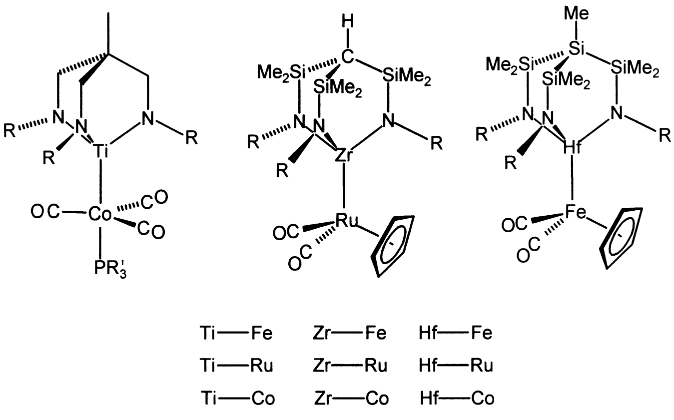
4.1. Factors Influencing the Stability of "Unsupported" Metal – Metal Bonds in "Early – Late" Heterodimetallic Complexes

As is the case for most metal-bound molecular fragments in coordination compounds, the stabilization of the metal – metal bonds in early – late heterodimetallic complexes may be achieved by the appropriate choice of the ancillary ligands. This, in particular, applies to the early transition metal fragment which is generally highly Lewis acidic and chemically hard and thus requires an appropriate set of hard σ and π donor ligands. It is therefore not surprising that by far most of the metal – metal-bonded complexes of the early – late or high-valent – low-valent type have sets of ligands coordinated to the high-valent transition metal center which comprise alkoxy, amido, imido, and oxo ligands.[78] These chemically hard ligands not only meet the electronic demands of the Lewis acidic metal center to which they are bound but at the same time stabilize the oxidation state of this coordination center and thus suppress degradation by single-electron transfer processes. Among other potential factors, this characterisic property of the ligands in question explains the relative stability of Selegue's Ti–Fe and Ti–Ru complexes $[(Me_2N)_3Ti{-}MCp(CO)_2]$ in comparison with the inaccessible Ti–M derivatives containing the Cp_2Ti unit. Titanocene derivatives are generally more readily reduced than the amido and alkoxy complexes of the same element.

Whereas the discussion so far has centered around the correct choice of the donor functions to stabilize the early transition metal, their integration into a polydentate ligand system and thus the design of the chemical environment of the donor atom may be of equal importance for the successful stabilization of the dinuclear complex. Amido functions (R_2N^-), which possess two substituents at the donor atom, may be readily incorporated into polydentate ligand systems which are designed to shield most of the coordination sphere of the metal center and, additionally, enforce a particular coordination geometry.[79, 80] Both aspects effect, respectively, the kinetic and an additional thermodynamic stabilization of the highly polar metal–metal bond and an example of the practical implementation of this concept is discussed in the following section.

4.2. Stabilization of Early–Late Heterodinuclear Complexes by Use of Tripodal Amido Ligands

The remarkable development which early transition metal chemistry has experienced during the past decade as a consequence of the development of many new types of polydentate amido ligands has also had its effect on the synthesis of stable early–late heterodimetallic complexes containing unsupported metal–metal bonds. The tripodal amido ligands displayed in Scheme 12[81] have provided the key to, a systematic program of complex synthesis.[41–44, 53, 82]

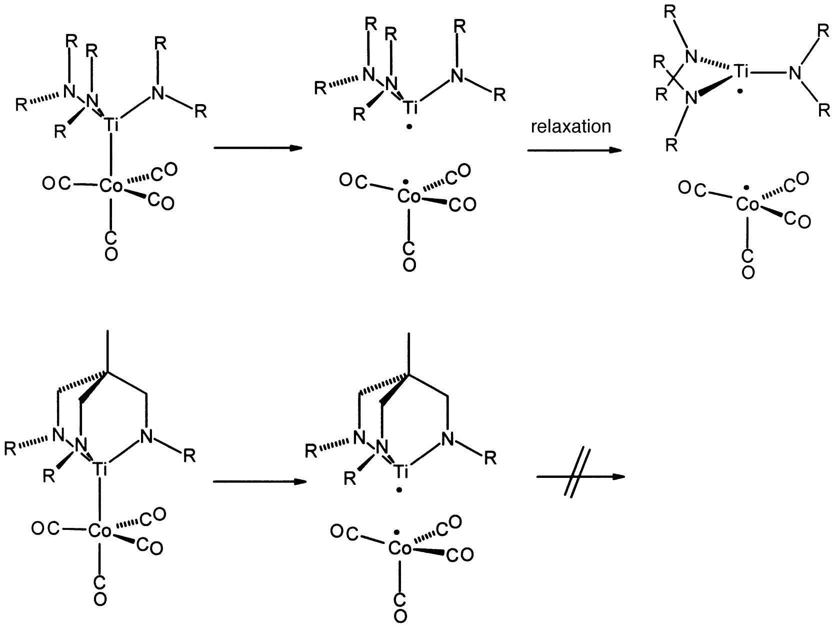


Scheme 12. Unsupported early–late heterodinuclear complexes stabilized by tripodal amido ligands. R = aryl, silyl; R′ = aryl. The metal–metal bonds displayed above were stabilized by using this approach.

While the ligand framework effectively shields the part of the coordination sphere opposite to the metal–metal bond, the latter is kinetically protected by the peripheral (silyl or aryl) substituents at the nitrogen donor functions.

At least as important as this kinetic stabilization of the dinuclear complexes is a significant thermodynamic contribution to their stability which is the result of the incorporation of the early transition metal into the rigid bicyclo[2.2.2]octane-like cage structure of the tripod–amide unit.[81, 82] This geometric fixation destabilizes the potential fragmentation product, the triamidometal fragment. In the analogous systems containing monodentate anionic ligands at the early transition metal center the $\{ML_3\}$ fragment undergoes planarization upon cleavage of the metal–metal bond, a process which stabilizes the fragment. This planarization is suppressed in the tripod cage (Scheme 13).

In order to have an estimate of the energetic contribution of this geometric relaxation of the early transition metal complex fragment, a theoretical study was carried out on the Ti–Co model complex $[(H_2N)_3Ti{-}Co(CO)_4]$ which was already discussed in Section 2.3.[53] Figure 7 schematically represents the overall energetics for the dissociation into two neutral fragments. D_r and D_{nr} are the dissociation energies for the dissociation into, respectively, completely relaxed and partially nonrelaxed complex fragments. In the nonrelaxed case the geometry of the Ti fragment was fixed to that of $[(H_2N)_3Ti{-}Co(CO)_4]$, while in both cases the Co fragment was energetically minimized.[53]



Scheme 13. Thermodynamic stabilization of dinuclear complexes with tripodal–aminde ligands by suppression of the possible relaxation into a planar structure in systems with monodentate ligands.

As indicated in Figure 7 the planarization energy E_r(Ti) of the Ti fragment is about 10 kcal mol^{-1}. This represents an upper boundary of the hypothetical relaxation energy of the Ti fragment containing the tripod ligand, which is unable to achieve the planar geometry of the free $[Ti(NH_2)_3]$ complex.

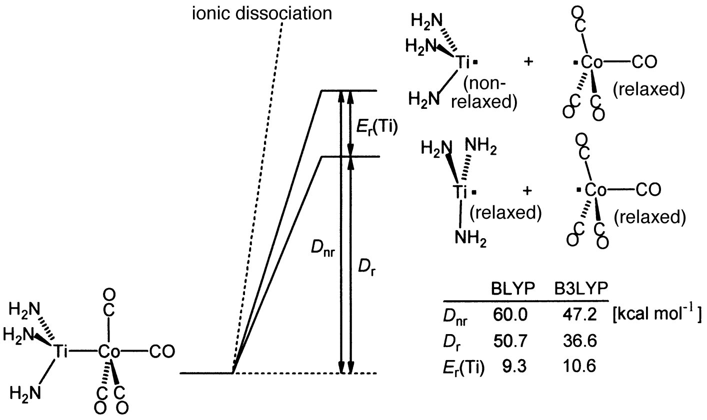


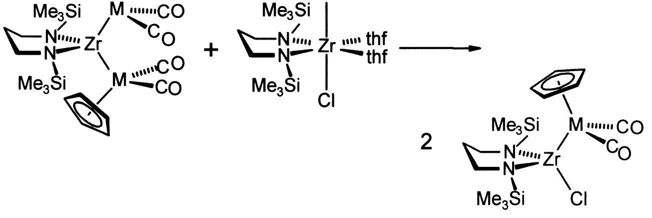
Figure 7. Energy diagram for the homolytic dissociation of the metal–metal bond in $[(H_2N)_3Ti{-}Co(CO)_4]$.

Therefore, one can estimate that the tripod ligand thermodynamically stabilizes the Co–Ti complex by about 10 kcal mol^{-1} with respect to fragmentation of the metal–metal bond. Since the early transition metal fragment is the same in the whole range of heterodinuclear complexes coordinated by tripodal amido ligands, this figure can be regarded as a general estimate of the thermodynamic stabilization of the complexes with respect to their mononuclear fragments.

5. Basic Patterns of Reactivity Observed for Metal–Metal Bonded Early–Late Heterodinuclear Complexes

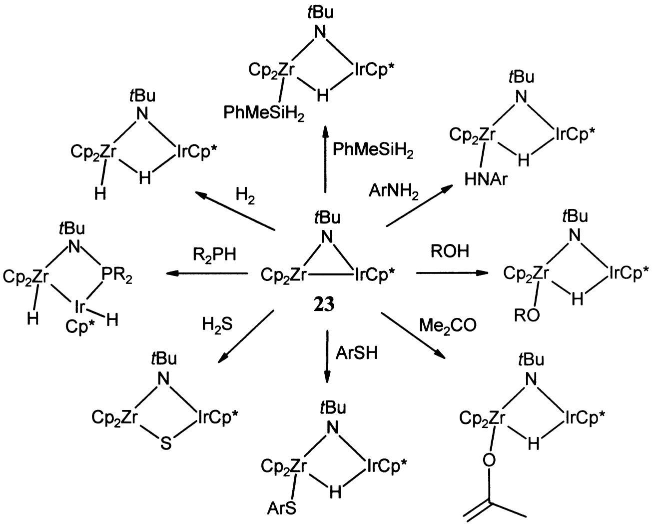
Generally, the discussion of the reactivity of metal–metal bonded polynuclear complexes may focus either on metal–ligand, that is metal–substrate interactions or the redistribution of metal complex fragments which implies cleavage and re-formation of metal–metal bonds. Most of molecular cluster complex reactivity may be described within the framework of this partitioning or by a combination of the two. Early–late heterodimetallic complexes were found to undergo redistribution reactions of their metal fragments, such as the "conproportionation" of $[Cp_2Zr\{RuCp(CO)_2\}_2]$ with $[Cp_2ZrCl_2]$ to give the dinuclear complex $[Cp_2(Cl)Zr{-}RuCp(CO)_2]$ or similar reactions involving the amido-stabilized complexes (Scheme 14).[37, 38, 83]

The scope of this complex fragment redistribution is limited. It was, for instance, not possible to obtain the heterotrimetallic complex $[\{CH_2(CH_2NSiMe_3)_2Zr\{FeCp(CO)_2\}\{RuCp(CO)_2\}]$ by reaction of the $ZrFe_2$ with the $ZrRu_2$ complex.



Scheme 14. Complex fragment redistribution in the reaction of $[\{CH_2(CH_2NSiMe_3)_2\}Zr\{MCp(CO)_2\}]$ with the dichloro complex $[\{CH_2(CH_2NSiMe_3)_2\}ZrCl_2(thf)_2]$ resulting in the formation of the corresponding dinuclear species. M = Fe, Ru.

The reactivity of the polar metal–metal bonds towards organic substrates is of more general interest. As for many other types of heterodinuclear complexes extensive reactivity studies were carried out with the aim of establishing cooperative reactivity between the electronically very different reactive sites which may interact with the substrate. Essentially two types of reaction were possible. The first involves the interaction of the metal–metal bond with substrates of no or low polarity which are fragmented and transformed to a "polarized" form at the two metal centers. For example, this is the general pattern of the addition of H_2 or a silane to the Zr–Ir bond in Bergman's heterodinuclear complex **23** (Scheme 15).[84]



Scheme 15. Cooperative reactivity of the heterodinuclear complex **23** with nonpolar and polar substrates. Cp* = C_5Me_5.

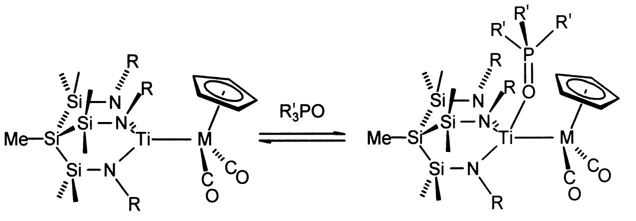
Reactivity towards substrates which match the polarity of the metal–metal bonds is far more common. Examples in Scheme 15 are the reactions of alcohols, amines, thiols, ketones, and H_2S with the Zr–Ir complex.

In the simplest case heterodinuclear complexes will react as pairs of metal electrophiles and nucleophiles. Cooperative reactivity is particularly likely with polar substrates. In this case the electropositive early transition metal center may react with the more Lewis basic part of the substrate, while the nucleophilic late transition metal complex fragment will attack the more Lewis acidic part of the substrate molecule. For metal–metal single bonds between the two metal centers this interaction will go along with the cleavage of the metal–metal bond. In many cases it is difficult to establish whether the cission of the metal–metal bond precedes the transformation of the substrate or whether it occurs at a later stage.

5.1. The Principle of the "Masked" Pairs of Metal Nucleophiles and Electrophiles

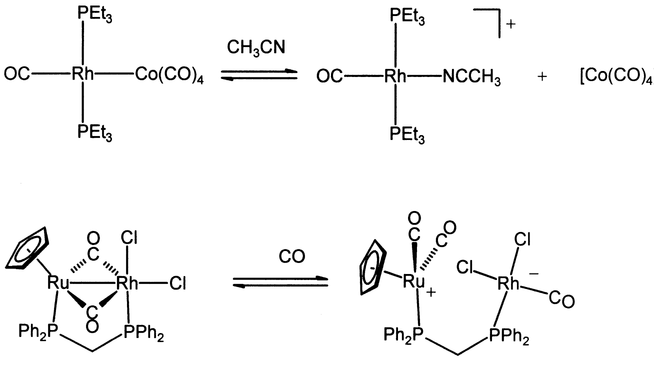
A systematic study of the reactive behavior of Ti–M and Zr–M heterodinuclear complexes (M = Fe, Ru, Co) has elucidated the early stages of the interaction of polar substrates with the two metal centers and allowed the notion of the pair of metal electrophiles and nucleophiles to be put to a test. The initial interaction of a polar substrate with the heterodinuclear complex is the formation of a Lewis acid base adduct at the early transition metal center. In most cases this adduct formation is thought to be reversible and such intermediates of Ti–M complexes with phosphane oxides could be detected spectroscopically (Scheme 16).[85]

This adduct formation may be viewed as the first step in a solvation process of the early transition metal center which leads to the ionic dissociation of the metal–metal bond giving the solvent-stabilized early transition metal cation and the late transition metal complex anion.[86] The cleavage of metal–metal bonds yielding ionic complex fragments was already discussed in Section 2.2 in connection with the solution properties of the "xenophilic" cluster complexes.



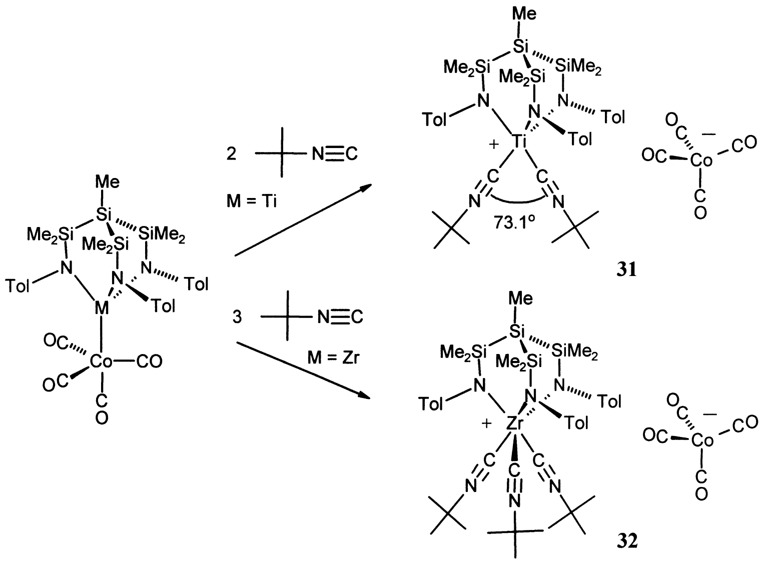
Scheme 16. Reversible formation of a Lewis acid base adduct at an early transition metal as exemplified by the reaction of Ti–M complexes with phosphane oxides. R = aryl; R′ = alkyl, aryl.

Although ionic dissociation of metal–metal bonds has been known for some time, there are only a few well characterized examples of this behaviour in which no concomitant redox reaction is involved. (Scheme 17).[87, 88]



Scheme 17. Heterolytic dissociation of heterodinuclear complexes.

This reactive behavior is also observed for early–late heterodinuclear complexes, provided the late transition metal fragment is essentially nonnucleophilic, as is the case for $[Co(CO)_4]^-$.[89] Reaction of $[\{MeSi[SiMe_2N(4\text{-}CH_3C_6H_4)]_3\}\text{-}M\text{–}Co(CO)_4]$ (M = Ti, Zr) with *t*BuNC leads to immediate dissociation of the metal–metal bonds and formation of the salts **31** and **32** (Scheme 18) both of which could be isolated and structurally characterized by X-ray crystallography (Figure 8).



Scheme 18. Ionic cleavage of the Ti–Co and Zr–Co bonds in $[\{MeSi[SiMe_2N(4\text{-}MeC_6H_4)]_3\}M\text{–}Co(CO)_4]$ (M = Ti, Zr).

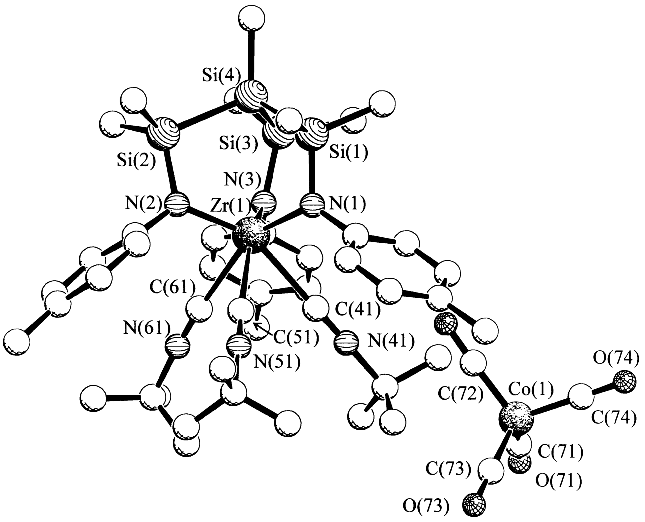


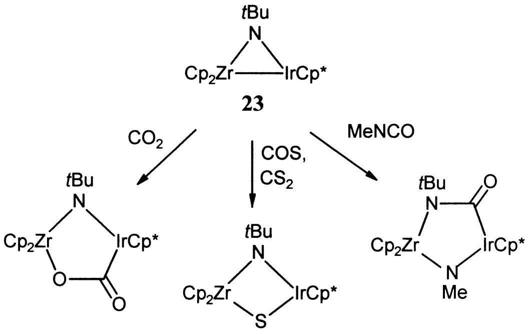
Figure 8. Molecular structure of **32** as determined by X-ray crystallography

The importance of the nucleophilicity of the complex anion could be established by the reaction of **31** with $K[RuCp(CO)_2]$, the alkali metal salt of a strongly nucleophilic metal carbonylate. Initially, immediate displacement of the isonitrile ligands at the Ti center takes place and the Ti–Ru complex thus formed is subsequently slowly converted to the product of an insertion of the isonitrile into the polar metal–metal bond. The latter reaction is reversible and the equilibrium constant was found to be 0.91 $L\,mol^{-1}$ at 298 K in benzene.[89]

The insertion of an isonitrile into a polar metal–metal bond is the analogue of the polar α-addition to isonitriles, the nucleophile and electrophile being metal complexes. Insertions of substrate molecules into the metal–metal bonds are the first step in most of the reactions of polar organic molecules with the heterodinuclear complexes and thus deserved closer attention.

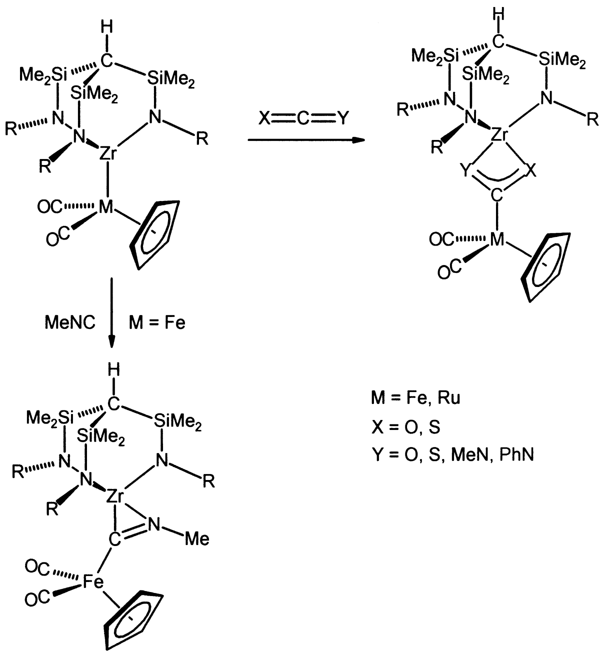
5.2. Insertions into Polar Metal–Metal Bonds

The simplest pattern of reactivity observed for early–late hereodimetallic compounds is the insertion of an unsaturated polar organic substrate into the metal–metal bond. The first such reaction was reported by Culter and co-workers who showed that Casey's Zr–M complexes insert CO_2 into their metal–metal bond[90] while Bergman et al. studied the reactions of the imido-bridged Ir–Zr complex **23** with CO_2, COS, CS_2, and MeNCS (Scheme 19).[91] While the insertion of CO_2 occurs in the expected fashion with the CO unit bridging the two metal centers remain still linked by the imido ligand, the other heteroallenes undergo fragmentation.



Scheme 19. Insertion and fragmentation of heteroallenes upon reaction with the Zr–Ir complex **23**.

The insertion of isonitriles discussed in the previous section provides yet another example of this reactive behavior. Insertion reactions of isonitriles and heteroallenes carried out with the tripod-stabilized early–late heterodinuclear complexes which led to stable products are summarized in Scheme 20. The molecular structure of $[\{HC[SiMe_2N(2\text{-}FC_6H_4)]_3\}Zr(\mu\text{-}CS_2)\text{-}FeCp(CO)_2]$, the product derived from the insertion of CS_2 into a Zr–Fe bond is depicted in Figure 9.[92]



Scheme 20. Insertion of isonitriles and heteroallenes into the unsupported metal–metal bond of Zr–M heterodinuclear complexes. R = $2\text{-}FC_6H_4$.

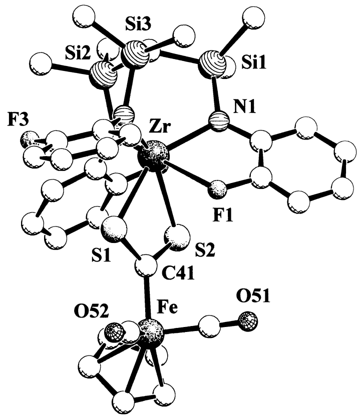
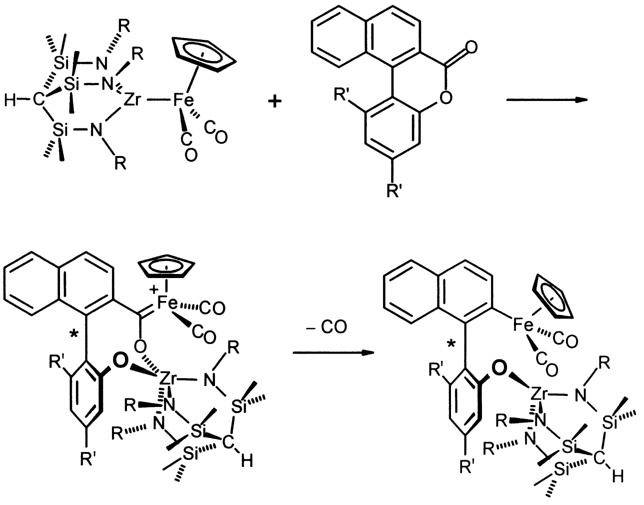


Figure 9. Molecular structure of the insertion product $[\{HC[SiMe_2N(2\text{-}FC_6H_4)]_3\}Zr(\mu\text{-}CS_2)FeCp(CO)_2]$ as determined by X-ray crystallography.

5.3. Transformations of Carbonyl Compounds in the Coordination Sphere of Zr–M Complexes

The products of the simple insertion of an organic molecule (or a functional group in it) into the polar metal–metal bond are rarely isolable and, most often, further transformations follow this initial step. In the simplest case, these subsequent transformations closely mimic those which the organic molecules undergo with "classical" nucleophiles and electrophiles. An example is the cleavage of esters RC(O)OR′ giving the early transition metal alkoxide and the acyl–metal derivative of the late transition metal complex fragment. This reaction was extended to include lactones, in particular configurationally labile prochiral biaryllactones which were readily cleaved and subsequently decarbonylated to give the ring-opened products (Scheme 21). The chiral biaryl axis in



Scheme 21. Ring opening and decarbonylation of biaryllactones. R = $2\text{-}FC_6H_4$; R′ = Me, OMe.

the reaction product is evident in the view of the molecular structure of one of the product complexes shown in Figure 10.[93]

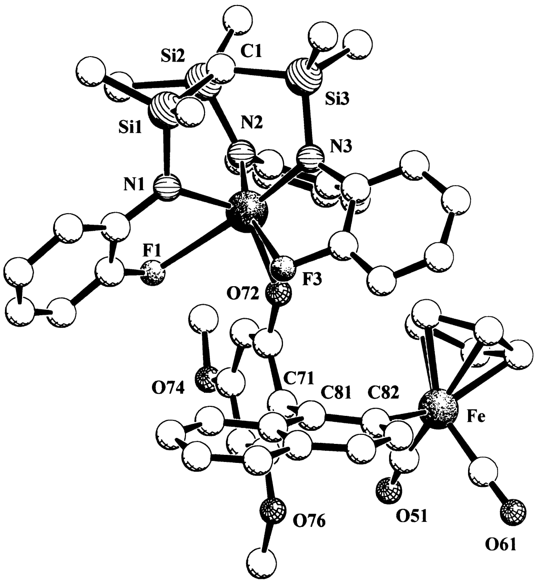
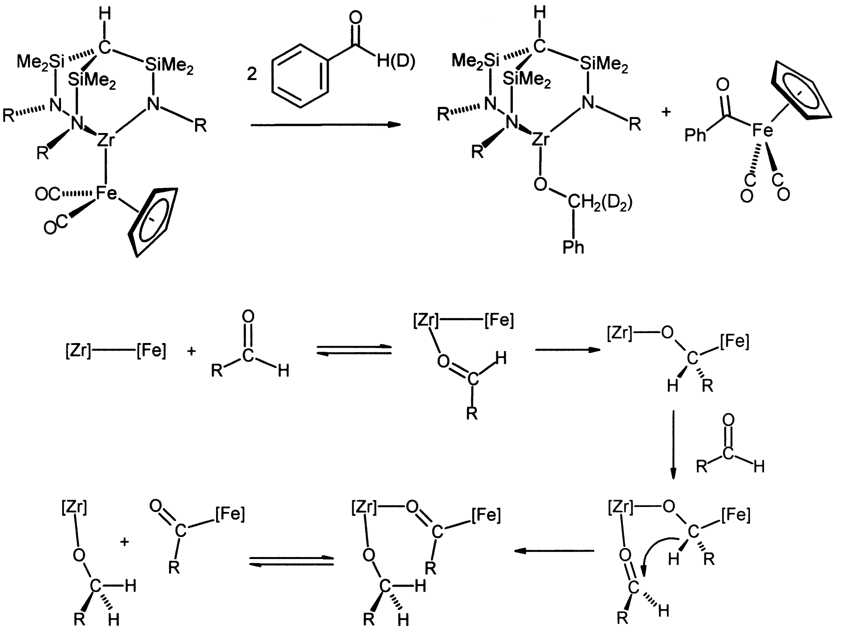


Figure 10. Molecular structure of the ring-opening product of [{HC[SiMe$_2$N(2-FC$_6$H$_4$)]$_3$}Zr–FeCp(CO)$_2$] with a biaryl lactone showing the chiral biaryl axis.

Aryl aldehydes react with Zr–M heterodinuclear complexes according to the pattern of a Cannizzaro or Tishchenkov reaction yielding the aroyl–M complex and the benzoxyzirconium derivative (Scheme 22).[94] The first step in the reaction sequence is thought to be the addition of an aldehyde molecule to the Lewis acidic early transition metal center which is followed by its insertion into the metal–metal bond. The cleavage of the Zr–Fe bond reduces the coordination number at the zirconium center which in turn facilitates the addition of the second molecule of the aldehyde. The crucial reaction step is the hydride transfer which follows and involves an analogous intermediate as proposed for the Cannizzaro disproportionation. Support for this intramolecular mechanism was obtained from the results of an isotope-labeling experiment employing C$_6$H$_5$CDO.



Scheme 22. Top: Cannizzaro-type disproportionation of aryl aldehydes upon reaction with a Zr–Fe heterodinuclear complex. Bottom: Proposed mechanism of the “hydride transfer”.

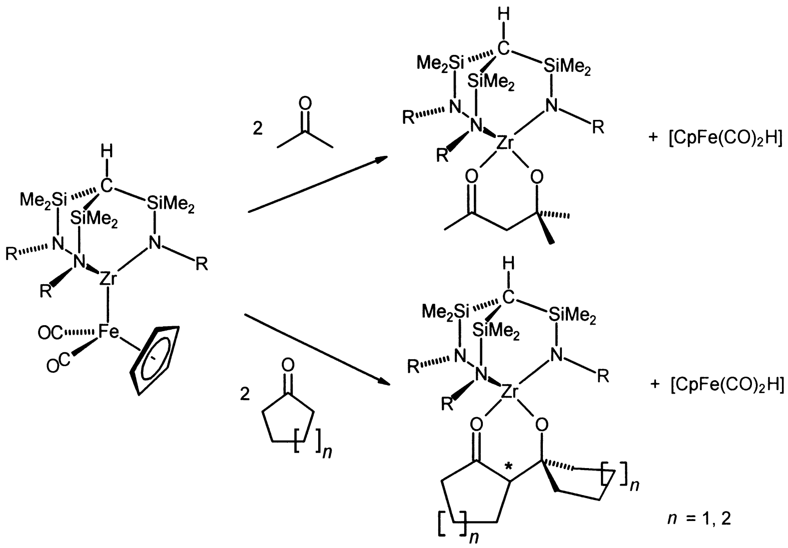
Finally, reaction of [{HC[SiMe$_2$N(2,3,4-F$_3$C$_6$H$_2$)]$_3$}-Zr–FeCp(CO)$_2$] with ketones gave the aldol coupling products ligated to the Zr center and equivalent amounts of the hydridoiron complex [CpFeH(CO)$_2$] (Scheme 23). The hydrido complex is thought to be formed in a first reaction step following the insertion of the carbonyl group into the metal–metal bond; the latter yields an extremely reactive enolate which in turn rapidly undergoes aldol coupling with a second molecule of ketone.[94]

5.4. Oxygen Atom Transfer within the Coordination Sphere of Zr–M Complexes

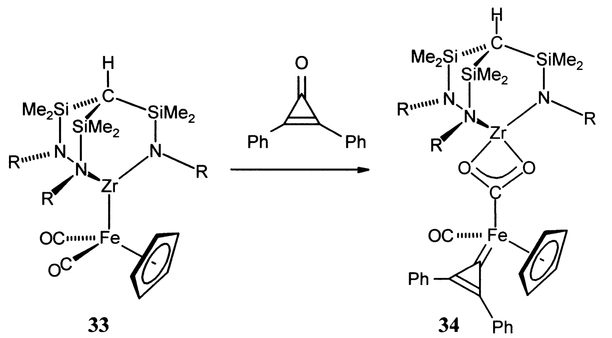
The transformations discussed so far in this section leave the ligand already present in the starting materials unchanged. The carbonyls coordinated to the late transition metal may, however, participate directly in the conversion of a substrate. The late transition metal fragment is thus not only the nucleophile in the primary reaction step with the substrate but at the same time the binding site (or source) of the second reactant. This type of cooperativity has been found in a series of oxygen-transfer reactions. The most remarkable of these is the reaction of the Zr–Fe complex **33** with 1,2-diphenylcyclopropenone giving the carbeneiron complex **34** in which the oxidized carbonyl ligand links the two metal centers as a μ-CO$_2$ unit (Scheme 24).[94] The result is thus formally a reduction of a ketone by CO yielding a carbene and CO$_2$, a reaction which is thermodynamically driven by the formation of two Zr–O bonds and the stable CO$_2$ unit in the product.

Similar oxygen-transfer reactions have been observed with sulfoxides and other element oxides, which yielded the late transition metal bound thioethers or the corresponding reduced ligands.[95] The pattern of the oxygen transfer has been established by ^{17}O- and ^{13}C-labeling studies in all these cases.[82] That both metal centers participate in the conversion of the element oxide is evident from the inability of either of the metal complex fragments linked by the Zr–M bond to effect these tranformations on their own. These considerations led to the proposal of a reaction mechanism for the deoxygenation of the cyclopropenone given in Scheme 25 as well as analogous reaction pathways for the other oxygen transfers.[94]

That the interaction of these substrates with only one of the mononuclear units may lead to quite different results was shown inter alia by reaction of 1,2-diphenylcyclopropenone with [CpMCO)$_2$]$^-$ (M = Fe, Ru),

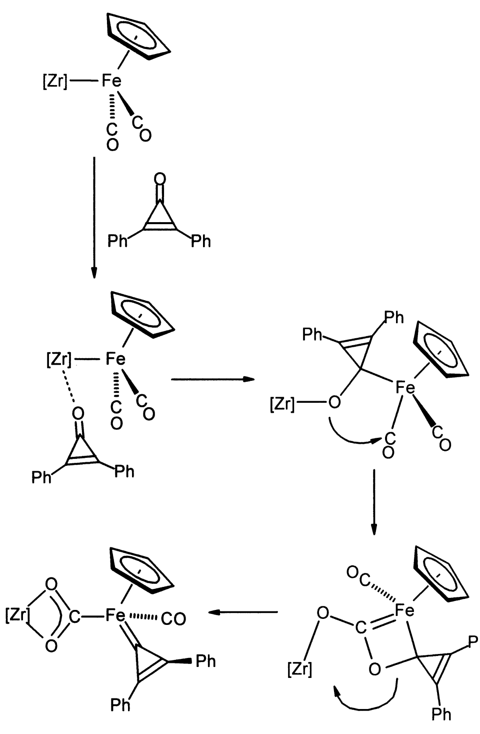


Scheme 23. Aldol coupling products obtained from the reaction of [{HC[SiMe$_2$N(2,3,4-F$_3$C$_6$H$_2$)]$_3$}Zr–FeCp(CO)$_2$] with ketones. R = 2,3,4-F$_3$C$_6$H$_2$.



33 **34**

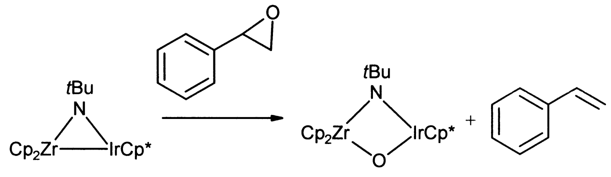
Scheme 24. Deoxygenation of 1,2-diphenylcyclopropenone giving the carbeneiron complex **34**. R = 2,3,4-F$_3$C$_6$H$_2$.



Scheme 25. Proposed reaction mechanism of the oxygen transfer in the conversion of 1,2-diphenylcyclopropenone to give the carbeneiron complex **34**.

which gave a metallacyclopentenedione instead of a carbene complex.

Rapid transfer of oxygen has been observed in reactions of **23** with pyridine *N*-oxide, nitrous oxide, and styrene oxide.[96] However, the result of these reactions is the formation of oxo-bridged heterobimetallic complexes such as **35**. Similar transfer reactions with sulfur have also been observed.



23 **35**

6. Strong Metal Support Interaction and the Possibility of Metal–Metal Bonding at the Surfaces of Supported Heterogeneous Catalysts

Our discussion has focussed on metal–metal bonding between early and late transition metals and its implications for the reactivity at the interface between two complex fragments of very different chemical properties. The interface character of such metal–metal interactions is thought to be important in an area of heterogeneous catalysis which superficially has little in common with the systems discussed so far. For the past two decades the interaction of late transition metals deposited on oxidic early transition metal supports, such as TiO$_2$, has received much attention. The phenomenon that the adsorption of H$_2$ and CO on the surface of Group 8–10 metals deposited on partially reduced early transiton metal oxides is partially or completely suppressed has been dubbed *strong metal-support interaction (SMSI)*.[98, 99] This suppression of the chemisorption and the decrease in the catalytic activity of such supported materials is due to a remarkable restructuring of the catalyst surface upon treatment of the early transition metal oxide carrying the late transition metal crystallites with H$_2$ at high temperatures. This leads to a partial reduction of the metal oxide supports, of which TiO$_2$ has received most attention. As a consequence of this reduced oxide surface two processes affect the deposited metal: on the one hand the oxidic material rapidly encapsulates the metal particles with a sheath of titanium oxide and thus passivates them in subsequent catalytic studies. On the other hand, the deposited metal particles may reorganize themselves to form flat, raftlike structures. Both processes lead to a maximized interface between the partially reduced early transition metal support material and the deposited late transition metal. These processes are thought to be thermodynamically driven by strong bonding forces between the two phases.[97]

The question of potential metal–metal interactions in such supported catalysts has received much attention. Whereas nowadays the concept of SMSI is referred to mostly in the phenomenologigal way, relating to the difference in adsorption properties and catalytic activity believed to arise from an interaction of deposit and support, some researchers use the term in the more specific relation to structural reorganization of the interface and thus the possibility of bonding interactions.[97]

A system which was studied in particular detail is that of rhodium deposited on TiO_2 which displays all the characteristics mentioned above. There is clearly no evidence for any kind of metal–metal bonding in the system before treatment with H_2 at high temperatures as was, for example, established by X-ray photoelectron spectroscopy and UV photoelectron spectroscopy of Rh on the fully oxidized support.[100] The deposition of metallic rhodium on a reduced TiO_2 surface, for which Auger electron spectroscopy showed the presence of Ti^{3+}, led to a partial electron transfer from the trivalent titanium to the deposited rhodium, a possible indication of a polar bonding interaction.[101] This was additionally supported by an EXAFS study, by Haller and co-workers, of a Rh/TiO_2 catalyst after reduction with hydrogen at 500 °C which not only indicated Rh–Rh bonding (2.69 Å) within the deposited metal but, additionally, a metal–metal distance of 2.53–2.56 Å which was attributed to Ti–Rh bonding (Figure 11).[102] Remarkably this Rh–Ti distance is significantly shorter than the metal–metal bond found in the monoclinic alloy TiRh (2.68 Å).[103]

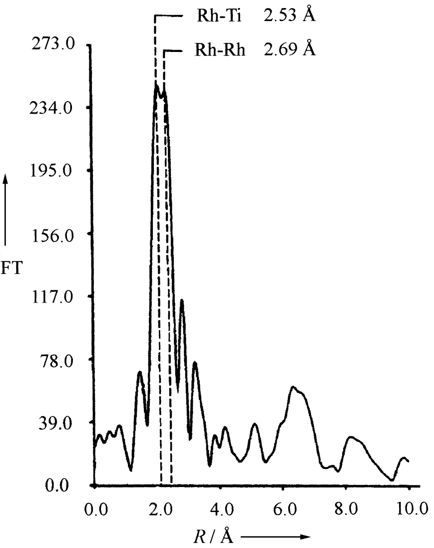


Figure 11. The k^3-weighted Fourier transform (M_{FT}) of the EXAFS spectra for a Rh/TiO_2 catalyst after in situ reduction with H_2 at 500 °C for 90 min.

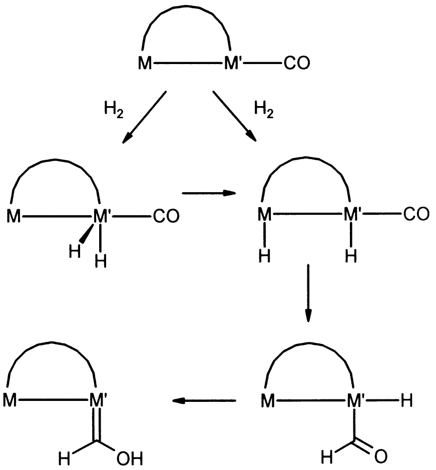
Strong metal-support interactions might have found much less attention if the interaction of TiO_x or NbO_x with deposited Ni, Pd, or Pt would not lead to a markedly increased Fischer–Tropsch activity of such supported catalysts.[104] In this industrial process synthesis gas (CO/H_2 1/3) is converted to a mixture of hydrocarbons. The rate of the hydrogenation of CO to form methane or other hydrocarbons is found to be increased by 1–2 orders of magnitude and the product distribution significatly changed. While the mechanistic details of this effect have not been established beyond doubt, it has been proposed that the activation of CO happens at the interface between the deposited late transtion metal and the reduced oxide. The CO molecule possibly "straddles" this interface with the oxygen atom coordinated to the titanium center and the carbon atom coordinated to the late transition metal in the same way as observed in early–late heterodimetallic complexes containing a bridging "isocarbonyl ligand". In addition, the presence of "spillover" hydrogen is thought to be important for the Fischer–Tropsch activity. This is H_2 which dissociates on the late transition metal surface and then "spills" into the partially reduced surrounding support to provide highly reactive reducing sites, possibly hydridic species.

6.1. Zr–M Heterodinuclear Complexes: The Quest for Homogeneous Fischer–Tropsch Catalysts

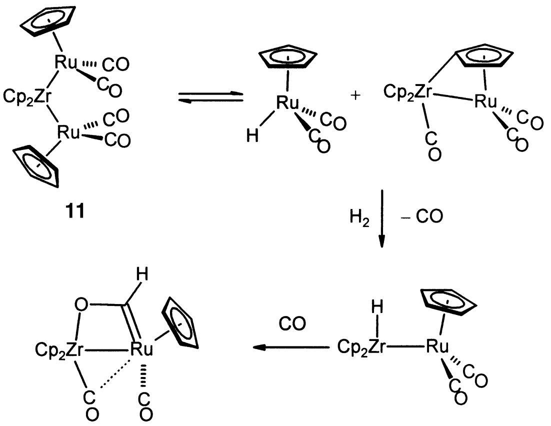
As discussed above, a direct bonding interaction between the late transition metal component in a heterogeneous catalyst and the early transition metal support material has been proposed especially for TiO_2 supported contacts. The relationship with an important industrial heterogeneous catalytic process inspired the first systematic study into the reactivity of directly metal–metal bonded early–late heterodimetallic compounds. This was carried out by Casey and coworkers in connection with the renewed interest in the chemistry of the Fischer–Tropsch process which emerged in the wake of the oil crisis in the 1970s.[105] The development of a homogeneous catalyst effecting this transformation under milder and more controlled conditions was regarded as a desirable goal and inspired a detailed investigation of the conversion of CO ligands to hydrocarbon fragments at the metal centers of organometallic complexes. Several such reactions could indeed be established although none of the systems studies showed promise for the developement of a catalyst.

A concept for a potential catalytic system was formulated in Casey's group and based on the accessibility of a heterometallic dihydrido complex containing one "hydridic" M–H bond to a high oxidation state early transition metal along with an acidic hydride at the late transition metal center. Ideally, the two metal centers were to be linked by a bridging ligand which would ensure their proximity even after the metal–metal bond was cleaved. The combination of the two differently polarized metal hydrides, generated by activation of H_2, would then provide the appropriate "reagent" for the hydrogenation of a metal-bound CO molecule, possibly along the route proposed by Casey which is outlined in Scheme 26.

The experimental study carried out throughout the 1980s mainly focussed on the unsupported Zr–Ru heterodimetallic complexes **10** and **11**. While the original objective of H_2 splitting generating a pair of hydridic and acidic hydrides and the subsequent reduction of CO was not achieved with these, the work carried out by the Madison group led to the discovery of some fascinating organometallic chemistry which has been reviewed previously in detail.[105] One example of a reaction sequence involving the conversion of CO in compound **11** is given in Scheme 27.[106]



Scheme 26. Mechanism of the nonsymmetrical activation of H_2 across a polar metal–metal bond in an early–late heterodinuclear complex (containing a bridging ligand) and the subsequent hydrogenation of coordinated CO.



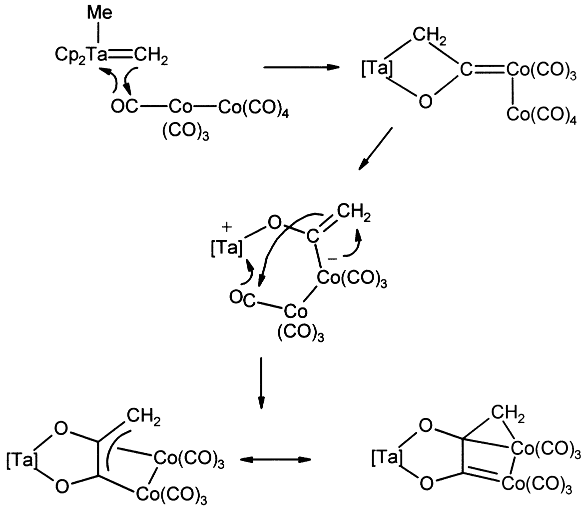
Scheme 27. Reaction of the trinuclear complex **11** with H_2 and CO resulting in the transfer of a hydride to a carbonyl ligand.

Recently, Fandos et al. reported the Ti–Rh heterometallic complex $[(C_5Me_5)Ti(\mu\text{-}O)_3\{Rh(cod)\}_3]$ (cod = 1,5-cyclooctadiene) which they regard as a molecular model for SMSI in TiO_2-supported Fischer–Tropsch catalysts. In the presence of this material, CO was indeed reduced at 250 °C and 20 bar (H_2/CO 3/1) to give, inter alia, methane and short chain alcohols. However, neither the structure of the catalytically active species nor the importance of a possible bonding interaction between the metal centers has been established.[107]

That the combination of early and late transition metal centers and the different sets of ligands they bear may induce interesting patterns of C–C bond fomation was also shown by Proulx and Bergman who reacted neutral metal carbonyls with Schrock's tantalum methylidene complex $[Cp_2(CH_3)Ta{=}CH_2]$ (Scheme 28). It seems though that metal–metal bonding between the early and late transition metal fragments does not play a role in any of these cases.[108]

7. Conclusion and Outlook

When the chemistry of early–late heterodimetallic complexes was first reviewed comprehensively a decade ago[5] there were only a few examples for which metal–metal bonds were unambiguously established. Moreover, the nature of this type of heterometallic bonding and its implications for the chemical reactivity of such systems was barely explored. The broadening of the preparative strategies available for the generation of compounds containing highly polar metal–metal bonds and in particular the availability of new types of complex fragments which may be combined to this end have significantly advanced the field.



Scheme 28. C–C bond formation by reaction of $[Cp_2(CH_3)Ta{=}CH_2]$ with $[Co_2(CO)_8]$.

A conceptual framework is now available for a quantitative description of metal–metal bond polarity and is accompanied by a wealth of structural data derived from several systematic studies. It is the specific use of ligand design in order to stabilize the coordination geometry and environment required for high metal–metal bond polarity which has demonstrated a strategy which has potential beyond the currently known types of structures. The quest for stable early–late heterodimetallic complexes has entailed the chemical "taming" of the early transition metal and at the same time opened up other applications of this approach in organometallic chemistry.

Early–late heterodimetallic complexes have been shown to act as homogeneous catalysts.[109] However, in none of the examples studied to date is the presence of the two *complementary* metal centers an *indispensible prerequisite* for the conversion which is effected. The usefulness of the combination of the two very different metal centers at close proximity in catalytic reactions remains to be demonstrated and it is this aspect, in particular, which will provide the challenge in future studies. This is also related to the question whether bond breaking and re-formation between early and late transition metals may be productively incorporated in a catalytic cycle.

I would like to thank my students and postdoctoral researchers who worked in the area reviewed in this article: They were, in rough chronological order, Stefan Friedrich, Harald Memmler, Martin Schubart, Bernd Findeis, Christina Platzek, Uta Kauper, Andreas Schneider, Dominique Trösch, Santiago Garcia-Yuste, Sylvie Fabre, Izoldi Bezougli, and Matthias Lutz. Our work relied heavily upon structure determinations by X-ray crystallography, and I am particularly grateful to Mary McPartlin (London) and her co-workers who not only carried out most of the X-ray diffraction studies but contributed significantly to the conceptual development. Georg Jansen (Düsseldorf/Nancy) and Catherine Housecroft (Basel) performed theoretical calculations on heterodimetallic complexes and corrected some naïve views of mine concerning metal–metal bond polarity. Georg explained the fundamentals of density functional theory to me and introduced me to Bader's AIM theory. Our research was generously supported by the Deutsche Forschungsgemeinschaft, the European Union (TMR Program MECATSYN), the Fonds der Chemischen Industrie, the British Council, and the DAAD. Most important for the author has been the unlimited support he received from Helmut Werner during his time at Würzburg.

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